Heliyon 10 (2024) e37736

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Optimization of the removal efficiency of three biodegradable chelating agents for soil cadmium

Jiajia He [a,1], Ruidong Mi [b,1], Zilin He [a], Jiyuan Jin [b], Jie Liu [b], Jian Lang [b],
Gang Yang [a,*]

[a] *Institute of Ecological and Environmental Sciences, Sichuan Agricultural University, Sichuan, 611130, China*
[b] *Chengdu Engineering Corporation Limited (Power China), No. 1 North Huanhua Road, Qingyang District, Chengdu, 610072, China*

ARTICLE INFO

Keywords:
Soil Cd pollution
Biodegradable chelating agent
Response surface method
Chemical soil leaching

ABSTRACT

In recent years, there has been a significant increase in the release of cadmium-containing pollutants into the environment from mining, industrial emissions, wastewater irrigation and the use of chemical fertilizers and pesticides. This leads to the degradation of soil quality and poses a threat to human health. Chemical leaching remediation technology is an effective method for controlling Cd contamination in soil. However, the leaching agent has a low removal efficiency of heavy metals. In order to find more suitable environmentally friendly new leaching agents, this study investigates the effects of three biodegradable chelating agents PMAS, EDTMPS and GLDA on the removal of heavy metal Cd in soil in the single factor soil leaching experiment. The concentration of the chelating agents, the leaching time and the pH of the leaching solution were varied to study their effects. The Box-Behnken (BBD) effect based on RSM was used to design the experimental conditions to optimize the leaching process of three biodegradable chelating agents. The optimum conditions for Cd removal by PMAS, EDTMPS and GLDA were obtained as follows: concentration 7 %, pH = 3.61, reaction time 180 min; concentration 4.94 %, pH = 3.0, reaction time 180 min; and concentration 4.96 %, pH = 3.0, reaction time 180 min. The validation test results showed that the deviation from the experimental value is less than 3 % under the theoretically optimal washing conditions, confirming the reliability and accuracy of the response surface methodology optimization process, which provides a reference for the development of efficient, environmentally friendly and low-cost leaching agents.

1. Introduction

The accumulation of toxic metals in soils has become a significant environmental problem due to the excessive use of mining, industrial emissions, wastewater irrigation and chemical fertilizers and pesticides [1]. It is important to note that this is an objective assessment, not a subjective one. The 2014 National Soil Pollution Survey Bulletin of China reveals an alarming soil pollution situation [2]. The report shows that heavy metal pollution accounts for 82.8 % of total soil pollution, with cadmium representing the primary pollutant, exhibiting an exceedance rate of 7 %. Cadmium is a highly toxic heavy metal that inhibits plant growth and development when present in the environment. It can also accumulate in plants and enter the human body through the food chain, causing disease

---

[*] Corresponding author.
E-mail address: yg8813@sicau.edu.cn (G. Yang).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.heliyon.2024.e37736
Received 25 June 2024; Received in revised form 9 September 2024; Accepted 9 September 2024

and even death in areas such as the nerves, skin, bones and heart [3–5]. At present, heavy metal pollution in soil has a significant negative impact on human health and ecological security [6]. Therefore, there is an urgent need to address and remediate cadmium-contaminated soils.

Chemical leaching remediation represents a widely used method for the remediation of heavy metal contaminated soils, which has the advantages of high efficiency, short cycle time, simple operation and thorough removal of heavy metals. It is also suitable for remediating soils with high concentrations of contaminants compared to traditional physical remediation technology. However, the efficacy of chemical leaching in removing heavy metals from soil depends not only on the physical and chemical properties of the soil, but also on the factors that affect the removal rate of heavy metals in the soil, such as the type and concentration of the leaching agent, the concentration, the leaching time and the pH [7]. Therefore, leaching remediation can be highly efficient. The efficiency of leaching remediation depends largely on the leaching agent used. Commonly used leaching agents include chelating agents, inorganic detergents and surfactants [8,9]. Chelating agents have gained attention due to their ability to form soluble and stable complexes with heavy metals, thus effectively removing heavy metals from the soil surface [10,11]. Synthetic chelating agents, such as ethylenediaminetetraacetic acid (EDTA), are commonly used due to their easy combination with metals, but they lead to secondary contamination [12]. In contrast, although natural chelating agents are degradable in soil, they are not as effective in removal as synthetic chelating agents [13]. Therefore, there is an urgent need to develop efficient, environmentally friendly and cost-effective chelating agents. Poly Maleic anhydride-acrylic acid sodium salt (PMAS), a carboxylic acid polymer, is biodegradable and bioabsorbable and has good chelating and adsorption properties [14]. Ethylenediamine tetramethylene phosphonic acid (EDTMPS) is widely used for scale inhibition in water treatment and bone tumour treatment [15], and has biocompatibility and easy photodegradation [16]. Glutamate diacetate tetrasodium (GLDA) has excellent biodegradability and its CO_2 emission during processing is extremely low. The CO content of GLDA is also very low [17,18].

The single factor control experiment only considers the effect of each factor on the removal efficiency of heavy metals. They do not consider the effect of the interaction between the factors on the removal efficiency of heavy metals, and the obtained optimum value is unreliable. Therefore, it is necessary to find more effective methods for designing soil chemical leaching experiments.

Response surface methodology has become a popular approach to experimental design optimization in recent years. It combines experimental design and mathematical modelling to fit the quadratic regression equation conform to the functional relationship between multiple factors and response values [19]. This allows the optimal value to be found within a certain level range [20]. This method is more economical and time-saving than the traditional single factor variable optimization method. Response surface methodology has been widely used in various fields such as domestic wastewater optimization [21], mechanical engineering [22] and edible fungi research. However, there is little research on the efficiency of heavy metals removal from contaminated soils by leaching. It is important to explore this area further. Therefore, the Box-Behnken (BBD) effect design based on RSM is an efficient technique to optimize the removal of heavy metals by leaching with biodegradable chelating agents.

This research investigates the effects of three chelating agents PMAS, EDTMPS, and GLDA on the removal of Cd from soil. The concentration of the chelating agents, the leaching time, and the pH of the leaching solution were varied to study their effects. The response surface methodology (RSM) of Box-Behnken design was used to analyse the interactions between the factors based on the equilibrium points of concentration, pH and time in the single factor experiment to optimize the leaching process of three biodegradable chelating agents.

2. Materials and methods

2.1. Soil sampling

Soil was sampled from the surface layer (0–20 cm) of farmland located near a mining area in Huidong County, Liangshan Prefecture, Sichuan Province, China. To remove plant and animal residues, stones and other debris, the soil was allowed to dry naturally and then passed through a 2 mm nylon sieve. The screened soil was mixed and stored in a sealed bag for future use.

The pH of the soil tested was 8.45, and the total amount of Cd in the soil was 9.60 ± 0.02 mg kg^{-1}. The content of heavy metal Cd is obviously exceeded. The basic physical and chemical properties of the tested soil are shown in Table 1.

2.2. Leaching reagent

The leaching reagent used in this experiment is Poly Maleic anhydride-acrylic acid sodium salt (PMAS), Ethylenediamine tetramethylene phosphonic acid (EDTMPS), Glutamate diacetate tetrasodium (GLDA). The three chelating agents were purchased from Shandong Yusuo Chemical Technology Co., Ltd. and Xuzhou Yuxin Chemical Technology Co., LTD.

Table 1
Physical-chemical characteristics of contaminated soils.

Sample	pH	Organic content (g kg^{-1})	CEC (cmol kg^{-1})	Total nitrogen content (g kg^{-1})	Cd content (mg kg^{-1})
Experimental soil	8.45	13.36	12.47	1.07	9.60

2.3. One-way soil chemical leaching experiment

In order to improve the removal rate of heavy metal Cd in soil, the effects of leaching agent concentration, leaching solution pH, and leaching time on the removal rate of heavy metal Cd in soil were studied. The leaching conditions were optimized by one-way soil chemical leaching experiment, and the preliminary range of leaching factors was determined.

The leaching experiment firstly put 2.00 g Cd contaminated soil into a 50 mL centrifuge tube. Then, 20 mL of leaching solution was added to the tube according to the soil-liquid ratio of 1:10. The pH was adjusted to the set value of the research protocol using 0.10 M HNO_3 or NaOH. The tube was tightly sealed with a screw cap and shaken in a constant temperature oscillator at 25 °C and 250 r min^{-1}. After shaking, the solution was centrifuged at 3500 r min^{-1} for 10 min. The suspension was filtered through a 0.45 μm microporous membrane, and the Cd content in the filtrate was determined by ICP-OES. The removal rate of Cd was also calculated. The experiment used distilled water as blank control, and each treatment was repeated three times.

The parameters for the single-factor experiment are as follows:

(1) pH: 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0, creating a total of 8 gradients.
(2) leaching time: 5, 10, 20, 30, 60, 120, 180 and 240 min, creating a total of 8 gradients.
(3) leaching agent concentration: 1 %, 2 %, 3 %, 4 %, 5 %, 6 %, 7 % and 8 %, creating a total of 8 gradients.

2.4. Box-Behnken experimental design

In the practical application of heavy metal contaminated soil leaching remediation, in order to reduce costs and save time, it is necessary to screen out the optimal leaching conditions to achieve higher leaching efficiency in a relatively short time. The most frequently employed optimization design techniques in China are uniform design and orthogonal design. However, the experimental precision of these methods is inadequate, and numerous variables exert an influence, resulting in a considerable increase in the number of experiments. Furthermore, the mathematical models generated are not particularly predictive. Response Surface Methodology (RSM) offers a superior predictive mathematical model. The method employs a reasonable experimental design to obtain data through experimentation, and utilises a multiple quadratic regression equation to fit the functional relationship between multiple influencing factors and response values. A statistical method for identifying the optimal process parameters through the analysis of a regression equation. In comparison to the preceding two methodologies, the RSM approach offers enhanced visualisation capabilities and enables the assessment of the influence of each parameter and the interaction between multiple variables. Its applications extend to diverse domains, including chemistry, food science and agriculture. The most commonly employed response surface methodologies at present are the Box-Behnken design (BBD), the Doehlert design (DM) and the composite centre design (CCD). BBD is typically regarded as a relatively efficient and optimal approach, particularly in comparison to CCD, which necessitates a greater number of experiments, time, and cost to establish the model equations. The number of BBD tests is typically between 15 and 62, which is fewer than the number of tests required by CCD when the factors are identical. Accordingly, in order to further ascertain the interaction between reagent concentration, solution pH and leaching time on Cd removal rate and identify the optimal process conditions, the Box-Behnken experimental design method was employed in this study. Design-Expert (V.8.0.6.1) software was utilised to optimize the parameters and elucidate the underlying mechanism. Based on the data obtained from the single factor test, the optimal design was determined, taking into account the zero level and the upper and lower limit levels.

In this research, the Box-Behnken design method was used to optimize the removal efficiency of Cd. As shown in Table 2, the codes of the 3-factor, 3-level method are −1, 0, 1. The main factors affecting the Cd removal efficiency are the initial leaching agent concentration (X_1), leaching solution pH (X_2), and laeching time (X_3). A total of 17 sets of experiments were conducted, and each experiment was repeated 3 times to reduce the influence of external factors on the experimental results.

The experimental results were fitted to the response behaviour of the variables using a second order model:

$$Y = \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} X_i X_j + \beta_0$$

where Y is the response value (heavy metal removal rate); β_0 is the intercept term; β_i, β_{ii} and β_{ij} are the linear, squared and interaction term coefficients, respectively.

Table 2
BBD design factors and levels.

Considerations	Encodings	Level (of achievement etc)		
		−1	0	+1
Leaching agent concentration	X_1	3	5	7
Leaching solution pH	X_2	3	5	7
Leaching time	X_3	30	105	180

3. Results and discussion

3.1. Efficiency of PMAS, EDTMPS, GLDA leaching for soil cadmium removal

The main factors affecting the leaching effect are leaching pH, leaching time, and leaching concentration. Optimizing the leaching process parameters can lead to the best remediation efficiency and economic benefits. Therefore, this paper investigates the effect of each factor on the removal rate of heavy metal Cd in polluted medium alkaline soil.

3.1.1. One-way test analysis of Cd removal effect in contaminated soil

3.1.1.1. Effect of pH on soil Cd removal rate. The combination of the leaching agent and Cd will affect the dissolution and elution efficiency of heavy metals in soil, and the pH value of eluent will affect the combination of leaching reagent and Cd. Fig. 1(a) illustrates the trend of Cd removal efficiency with increasing pH of PMAS. The efficiency increased until it reached the peak of 66.81 % at pH 5.00, and then decreased. This trend may be attributed to the weakening of the electrostatic field around PMAS polyions in strong acid environment, which reduces the electrostatic adsorption and washing effect. Meanwhile, under alkaline conditions, the existence of OH^- reduces the removal effect of heavy metal ions by increasing the negative charge on the surface of soil particles. This, in turn, increases the adsorption rate of heavy metal ions by soil colloids and inhibits their desorption. It is worth noting that PMAS, EDTMPS, and GLDA showed a general decreasing trend in removal efficiency with increasing pH, and the removal rate of Cd under acidic conditions was greater than that under alkaline conditions. The high concentration of H^+ in acidic environment may lead to protonation of soil colloid surface. Additionally, the adsorbed Cd can be exchanged with the leaching agents EDTMPS and GLDA by ion exchange to form soluble complexes [23].

3.1.2. Effect of leaching time on soil Cd removal rate

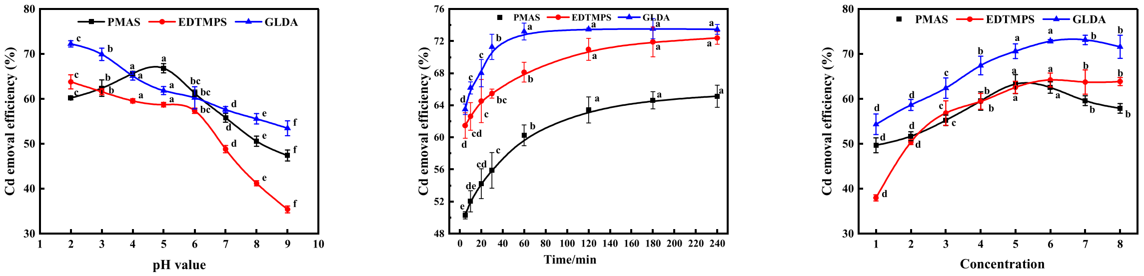
In general, a longer soil leaching time is more favourable for the leaching agent to complex heavy metals in the soil and improving the removal rate of heavy metals. Sun X et al. [24] utilised biodegradable citric acid (CA) modified with sodium lignosulfonate (LS) derived from waste paper to purify soil. It was found that the washing rate of Cd, Pb and Zn increased exponentially with time ($p < 0.05$), and reached a level after 120.0 min. Fig. 1(b) shows that the washing efficiency of PMAS, EDTMPS, and GLDA on soil Cd increased gradually with time. At 120 min, the removal rates of Cd were 63.41 %, 66.00 % and 74.48 %, respectively. However, with the increase of leaching time, the increasing speed slows down. The study found that the removal of heavy metal Cd by Dai Zhucheng using hydroxylamine hydrochloride enhanced citric acid was consistent with the obtained result [25]. The desorption of heavy metals by PMAS, EDTMPS and GLDA can be divided into two processes: rapid desorption in the first 2 h and then slow release. The possible reasons for this situation are as follows: in the first stage, the leaching agent destroyed the weak chemical bond between soil and heavy metals, causing the initial release of easily extractable heavy metal ions. In the second stage, the release of heavy metals from the organic state was activated, resulting in a slight increase in the removal rate [26].

3.1.3. Effect of leaching concentration on soil Cd removal rate

The concentration of the leaching agent is the crucial factor that affects the efficiency of heavy metal removal during soil leaching. Generally, the heavy metal removal rate increases as a power function of the concentration [27]. It is important to note that a high concentration of the leaching agent will involve more functional groups in chemical reactions. Fig. 1(c) shows that PMAS achieved the highest Cd removal rate (63.30 %) at 5 %, while EDTMPS and GLDA reached peak Cd removal rates of 64.19 % and 72.82 % at 6 %, respectively. After 7 %, the removal rate of all Cd decreased, which may be due to the complexation of Cd in soil, which can form a stable chelate with the leaching agent [28]. The results indicated that the removal rate of Cd decreased after 7 %.

3.2. Optimization of soil Cd removal process by leaching reagents

To enhance the comprehensibility of the effects of variables and their interaction on the response variable (Cd removal rate), we



(a) (b) (c)

Fig. 1. Influence of pH (a), concentration (b) and time (c) of PMAS, EDTMPS and GLDA on Cd removal rate.

analysed three-dimensional response surface plots of PMAS, EDTMPS and GLDA. These figures simulate the predictions of PMAS, EDTMPS and GLDA on the removal rate of heavy metal Cd in polluted medium-alkaline soil.

3.2.1. Model building and analysis of variance (ANOVA)

The rate of removal of the heavy metal Cd was calculated for 17 groups of optimization experiments using Eq. (1) as the response value. A quadratic term regression equation was established by fitting the concentration of the leaching agent ($X_{1)}$, the pH of the leaching solution (X_2), and the reaction time (X_3) according to Eq. (1) in Response Surface Analysis software Design Expert 8.0. The relationship between the removal rate of heavy metals in soil and leaching factors can be expressed by the following equation:

(1) PMAS on the heavy metal Cd:

$$Y_{Cd} = 39.325 - 1.941X_1 + 8.83X_2 + 0.018X_3 - 0.03156X_1X_2 - 4.83 \times 10^{-3}X_1X_3 - 0.003X_2X_3 + 0.336X_1^2 - 1.094X_2^2 + 2.6 \times 10^{-4}X_3^2$$

(2) EDTMPS for the heavy metal Cd:

$$Y_{Cd} = 52.67 + 3.097X_1 + 0.7018X_2 - 0.001519X_3 + 0.04531X_1X_2 + 0.0018X_1X_3 - 0.00633X_2X_3 - 0.3385X_1^2 - 0.3048X_2^2 + 2.155 \times 10^{-4}X_3^2$$

(3) GLDA on the heavy metal Cd:

$$Y_{Cd} = 56.53 + 2.169X_1 - 0.8483X_2 + 0.05953X_3 - 0.06875X_1X_2 + 0.003292X_1X_3 - 0.01098X_2X_3 - 0.1927X_1^2 - 0.04553X_2^2 + 1.05 \times 10^{-5}X_3^2$$

where Y_{Cd} is the Cd removal efficiency in soil predicted by PMAS, EDTMPS, and GLDA washing, and X_1, X_2, and X_3 are the concentration of leaching solution, pH of leaching solution, and leaching time, respectively.

To verify the accuracy and reliability of the above fitting model, one-way ANOVA was performed. Tables 2–4 show that the model was highly significant ($P < 0.001$) and all misfit terms were greater than 0.05, indicating that the model is effective for data analysis and can better simulate the effects of three independent variables: pH, time, and concentration on the removal rate of Cd [29]. The correlation coefficients (R^2) were all greater than 0.97, which indicates that the fitting values of the regression model are highly consistent with the measured values [30]. The experiment considered all the main influencing factors that affect soil Cd leaching efficiency. In addition, the coefficients of variation (CV) were less than 10 %, indicating the reliability of the second-order model [31]. Additionally, all signal-to-noise ratios (SNR) were greater than 20, demonstrating sufficient signal resolution and better reflecting the fitting effect of the model [32].

The regression equation for PMAS leaching in heavy metal contaminated soil (Table 3) shows that the constant term coefficients have P-values less than 0.05, indicating that the reagent concentration, pH, and leaching time significantly affect the removal rate of Cd. The sum of squares for Cd removal by leaching indicates that $X_2 > X_3 > X_1$, showing that leaching agent pH has the greatest effect on Cd removal, followed by leaching time and leaching agent concentration. The coefficients for the interaction terms indicate that the interaction of these factors was not significant.

Table 3

Response surface fitting quadratic model ANOVA of PMAS for soil Cd removal.

Factors	Degrees of freedom d_f	Square sum (e.g. equation of squares)	Mean square	F-value	P-value
Modelling	9	378.05	42.01	46.47	<0.0001
X_1	1	18.20	18.20	20.13	0.0028
X_2	1	213.57	213.57	236.29	<0.0001
X_3	1	50.35	50.35	55.71	0.0001
$X X_{12}$	1	0.064	0.064	0.071	0.7982
$X X_{13}$	1	2.10	2.10	2.33	0.1710
$X X_{23}$	1	0.81	0.81	0.90	0.3753
X_1^2	1	7.61	7.61	8.42	0.0230
X_2^2	1	80.62	80.62	89.20	<0.0001
X_3^2	1	9.01	9.01	9.97	0.0160
Residual	7	6.33	0.90		
Anomaly	3	4.77	1.59	4.07	0.1043
Pure error	4	1.56	0.39		
Aggregate	16	384.38			

Y_{Cd}: $R^2 = 0.9835$ $R^2_{adj} = 0.9624$ CV(%) = 1.76 Signal-to-noise ratio = 22.269.

Table 4

Response surface fitted quadratic model ANOVA for soil Cd removal by EDTMPS.

Factors	Degrees of freedom df	Square sum (e.g. equation of squares)	Mean square	F-value	P-value
Modelling	9	295.47	32.83	53.45	<0.0001
X_1	1	0.52	0.52	0.84	0.3891
X_2	1	253.74	253.74	413.16	<0.0001
X_3	1	17.23	17.23	28.05	0.0011
$X X_{12}$	1	0.13	0.13	0.21	0.6577
$X X_{13}$	1	0.29	0.29	0.47	0.5130
$X X_{23}$	1	3.96	3.96	6.45	0.0387
X_1^2	1	7.72	7.72	12.57	0.0094
X_2^2	1	6.26	6.26	10.19	0.0152
X_3^2	1	6.19	6.19	10.07	0.0156
Residual	7	4.30	0.61		
Anomaly	3	3.42	1.14	5.19	0.0728
Pure error	4	0.88	0.22		
Aggregate	16	299.77			

Y_{Cd}: $R^2 = 0.9857$ $R^2_{adj} = 0.9672$ CV(%) = 1.41 Signal-to-noise ratio = 27.831.

However, the results of Cd removal by EDTMPS leaching are slightly different. As shown in Table 4, the P value of the constant term coefficients, other than X_1, is less than 0.05. The sum of squares coefficient is $X_2 > X_3 > X_1$, which indicates that pH has the greatest effect on the removal of Cd by EDTMPS leaching. Furthermore, only the P values of X_2X_3 was less than 0.05 in the interaction terms, indicating a significant interaction between the pH and time factors when EDTMPS washed the alkaline soil.

The regression equation of GLDA (Table 5) shows that the P-values of the constant term coefficients of X_2 and X_3 were less than 0.05, while the P-value of X_1 was greater than 0.05. This suggests that pH and time may have a stronger effect on the removal of Cd from contaminated agricultural soils by leaching than concentration. Additionally, the interaction term coefficient X_2X_3 is less than 0.05, indicating a strong interaction between pH and time of leaching when treating the soil.

Fig. 2(a)–. (b) and (c) represent residual normal probability graphs of heavy metal Cd removal by PMAS, EDTMPS and GLDA respectively. Fig. 2 shows that all points are uniformly distributed and lie near a straight line. This indicates that the residuals of the quadratic term model fitted to the heavy metal removal rate follow the normal distribution, and it is confirmed that the difference between the predicted value and the measured value is due to randomness rather than systematic deviation. Therefore, the response surface regression model has a good prediction effect.

3.2.2. Contour map analysis of Cd removal by PMAS, EDTMPS and GLDA leaching

The study indicates that the removal rate of soil heavy metals is more affected by individual leaching factors and their interaction when the contours are more concentrated and elliptical [33]. Conversely, the effect is smaller when the contour lines are more sparse and circular.

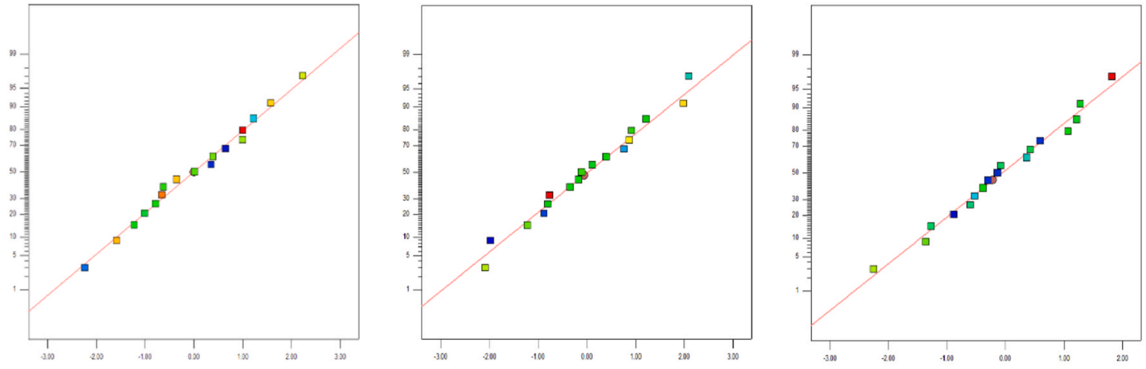
The isocontour density along the pH direction is greater than that in the direction of reagent concentration in the contour plots Fig. 3(a), (b) and (c) of the removal of Cd by PMAS, Fig. 3(d), (e) and(f) of the removal of Cd by EDTMPS, and Fig. 3(g), (h) and (i) of the removal of Cd by GLDA. These findings are further corroborated by the isoline plots between the pH of Fig. 3(c)–(f), and (i) and the leaching time, which demonstrate that pH exerts a predominant influence on the efficiency of soil leaching. Furthermore, it can be observed that the contour density of time is marginally greater than that of concentration in all contour maps. However, the contour density of the interaction effect between the two is markedly smaller than that between other factors, and is circular, indicating that leaching time is the second factor affecting the removal rate of Cd, Pb and Zn, and that the concentration and time of reagents have a

Table 5

Response surface fitted quadratic model ANOVA for soil Cd removal by GLDA.

Factors	Degrees of freedom df	Square sum (e.g. equation of squares)	Mean square	F-value	P-value
Modelling	9	292.11	32.46	34.48	<0.0001
X_1	1	1.90	1.90	2.01	0.1988
X_2	1	250.99	250.99	266.64	<0.0001
X_3	1	24.38	24.38	25.90	0.0014
$X X_{12}$	1	0.30	0.30	0.32	0.5885
$X X_{13}$	1	0.98	0.98	1.04	0.3426
$X X_{23}$	1	10.86	10.86	11.53	0.0115
X_1^2	1	2.50	2.50	2.66	0.1470
X_2^2	1	0.14	0.14	0.15	0.7115
X_3^2	1	0.015	0.015	0.016	0.9040
Residual	7	6.59	0.94		
Anomaly	3	4.25	1.42	2.43	0.2055
Pure error	4	2.33	0.58		
Aggregate	16	298.70			

Y_{Cd}: $R^2 = 0.9779$ $R^2_{adj} = 0.9496$ CV(%) = 1.69 Signal-to-noise ratio = 21.015.



(a) (b) (c)

Fig. 2. Residual normal probability diagram of heavy metal Cd removal by leaching with PMAS (a), EDTMPS (b) and GLDA (c).

negligible influence on the removal of Cd in soil.

3.2.3. Response surface analysis of Cd removal by PMAS, EDTMPS and GLDA rinsing

Xu et al. [34] found that the shape of the response surface can directly reflect the size of the interaction effect between two factors. If the slope of the response surface is steeper and the shape is closer to the saddle type, it shows that the response value is sensitive to the change of experimental factors. Conversely, if the slope of the response surface is relatively gentle, the surface presents a rounded and smooth type, indicating that the change of treatment conditions has little effect on the response value.

From Fig. 4(a)–(d) and (g), it can be seen that the removal rate of Cd increased when the leaching time was fixed at 105 min, due to the interaction of EDTMPS, GLDA concentration, and pH, while the removal rate of Cd by PMAS showed different trendsand convex changes. The leaching efficiency of Cd showed a smooth increasing trend with the increase of EDTMPS and GLDA concentration, and the decrease of leaching solution pH. On the other hand, the leaching effect showed a trend of rapid increase and then levelling off with the decrease of the pH of PMAS. Fig. 4(b)–(e) and (h) show that when the pH value of the leaching solution was 5, and the concentration and duration of the leaching agent were increased simultaneously, the removal rate of Cd gradually increases and tends to be stable. This shows that the interaction between the concentration of PMAS, EDTMPS, GLDA, and the time and pH had little effect on the removal of Cd.

Fig. 4(c)–(f) and (i) show that when the concentration of the eluent is 5 %, the removal of Cd generally exhibited a convex trend with decreasing pH and increasing leaching time when using EDTMPS and GLDA. This is consistent with the research results of Qian Yuanyu et al. [35], who used response surface analysis to investigate the effects of pH, extraction time, and soil-liquid ratio on soil Cd leaching rate. The interaction effects of pH and leaching time of EDTMPS and GLDA on the removal rate of Cd were found to be significant, which is consistent with the ANOVA results.

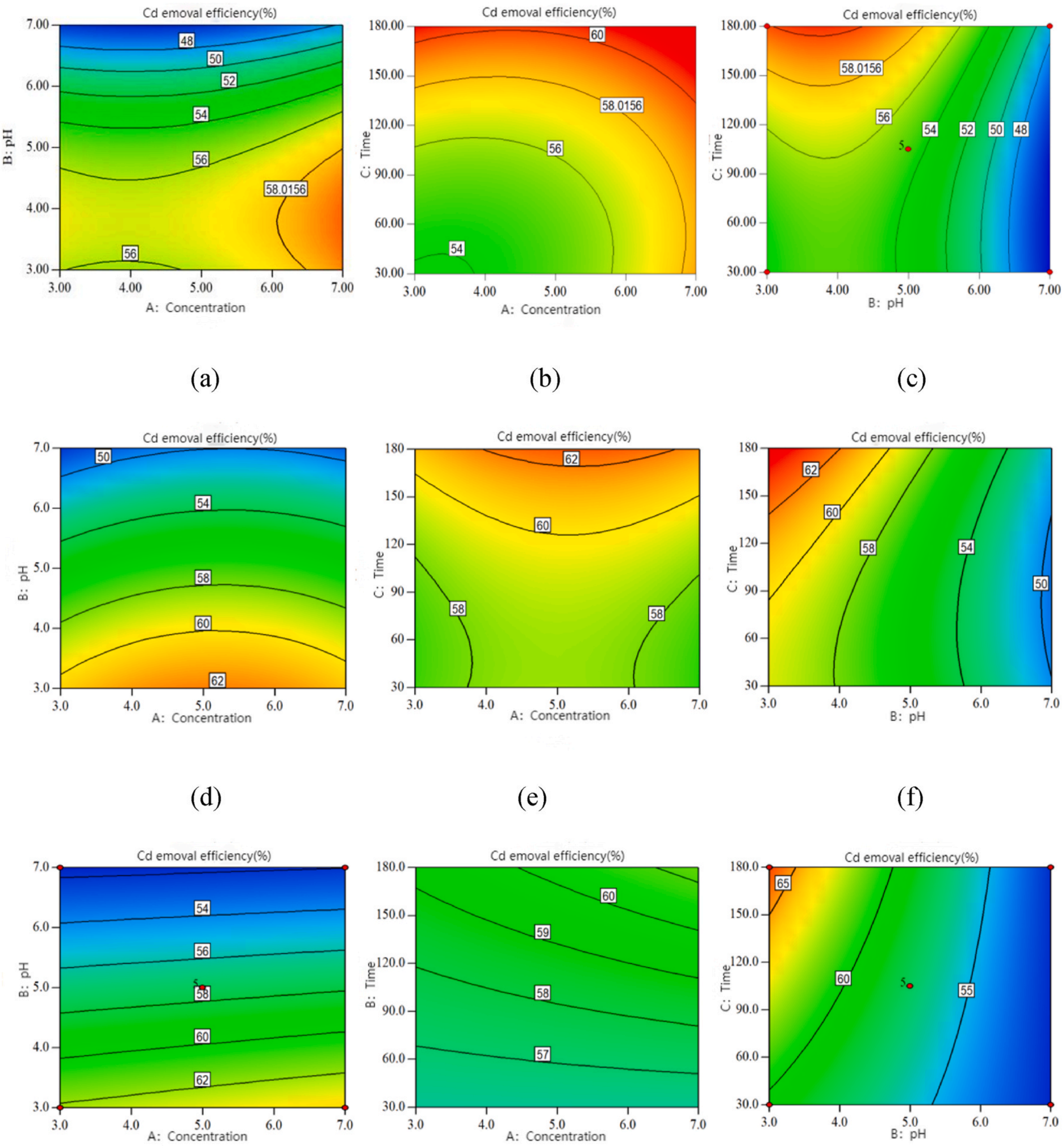
3.2.4. Optimization of response factor levels

The main objective of this study is to optimize the leaching factors, including reagent concentration, pH, and leaching time, in order to improve the removal rate of Cd in contaminated soils. To achieve this, numerical optimization was performed to determine the maximum point of the fitting equation and identify the optimum process parameters for heavy metal removal. The range of the 3-factor study was optimized using Design Expert 8.0.6 to find the stabilization point of maximum soil heavy metal removal and its corresponding factor level. Table 6 shows the optimal conditions for Cd removal by PMAS, EDTMPS and GLDA. For PMAS, the optimal conditions were concentration of 7 %, pH of 3.61, and reaction time of 180 min. For EDTMPS, the optimal conditions were concentration of 4.94 %, pH of 3.0, and reaction time of 180 min. For GLDA, the optimal conditions were a concentration of 4.96 %, pH of 3.0, and a reaction time of 180 min. The model predicted the maximum removal of Cd from the soil to be 62.65 %, 64.47 %, and 66.63 %, respectively.

To assess the applicability and validity of the fitted equations, three validation experiments were conducted under optimal conditions (refer to Table 7). The results obtained were similar to those of the numerical optimization, with a difference of less than 3.0 %. This indicates that the model can accurately describe the effects of the three significant factors and their interactions on Cd removal rate. The results suggest that BBD is a dependable approach for optimizing the biodegradable chelator PMAS to reduce soil Cd leaching.

4. Conclusion

This study investigates the effects of concentration, leaching pH, and leaching time of three biodegradable chelating agents, PMAS, EDTMPA and GLDA, on the efficiency of removing Cd from contaminated soil. The response surface methodology (RSM) of Box-Behnken design was used to analyse the interactions between the factors and derive the optimal leaching conditions based on the equilibrium points of concentration, pH and time in the single factor experiment. The study found that, (1) the removal rate of Cd in soil increased with an increase in leaching time and concentration, and a decrease in leaching pH within the three-factor study range



(a) (b) (c)

(d) (e) (f)

(g) (h) (i)

Fig. 3. Contour plot of soil Cd removal rate by different leaching parameters PMAS (a), (b), (c) EDTMPS (d), (e), (f) and GLDA (g), (h), (i) (Note: Colour change from blue to green to red indicates increasing elution efficiency.).

(leaching concentration 1–8%, leaching pH 2–9, and leaching time 5–240 min). The intervals of 3–7% concentration, 30–180 min time, and pH = 3–7 showed strong changes in Cd removal rate, indicating the research range of the response surface analysis method. (2) The secondary modelling analysis of the data was carried out by using the software Design Expert 8.0.6, which revealed that the removal rate of Cd was significantly affected by the concentration of the leaching, leaching time, and pH of the leaching solution. Additionally, the interaction between pH and leaching time also had a significant effect on the removal rate. (3) Based on the analysis, the optimum conditions for Cd removal by PMAS were found to be concentration of 7 %, pH of 3.61, and reaction time of 180 min. The optimal conditions for removing Cd using EDTMPS were found to be concentration of 4.94 %, pH of 3.0, and reaction time of 180 min. Similarly, the optimal conditions for Cd removal using GLDA were concentration of 4.96 %, pH of 3.0, and reaction time of 180 min. The validation test results showed that the deviation from the experimental value is less than 3 % under the theoretically optimal

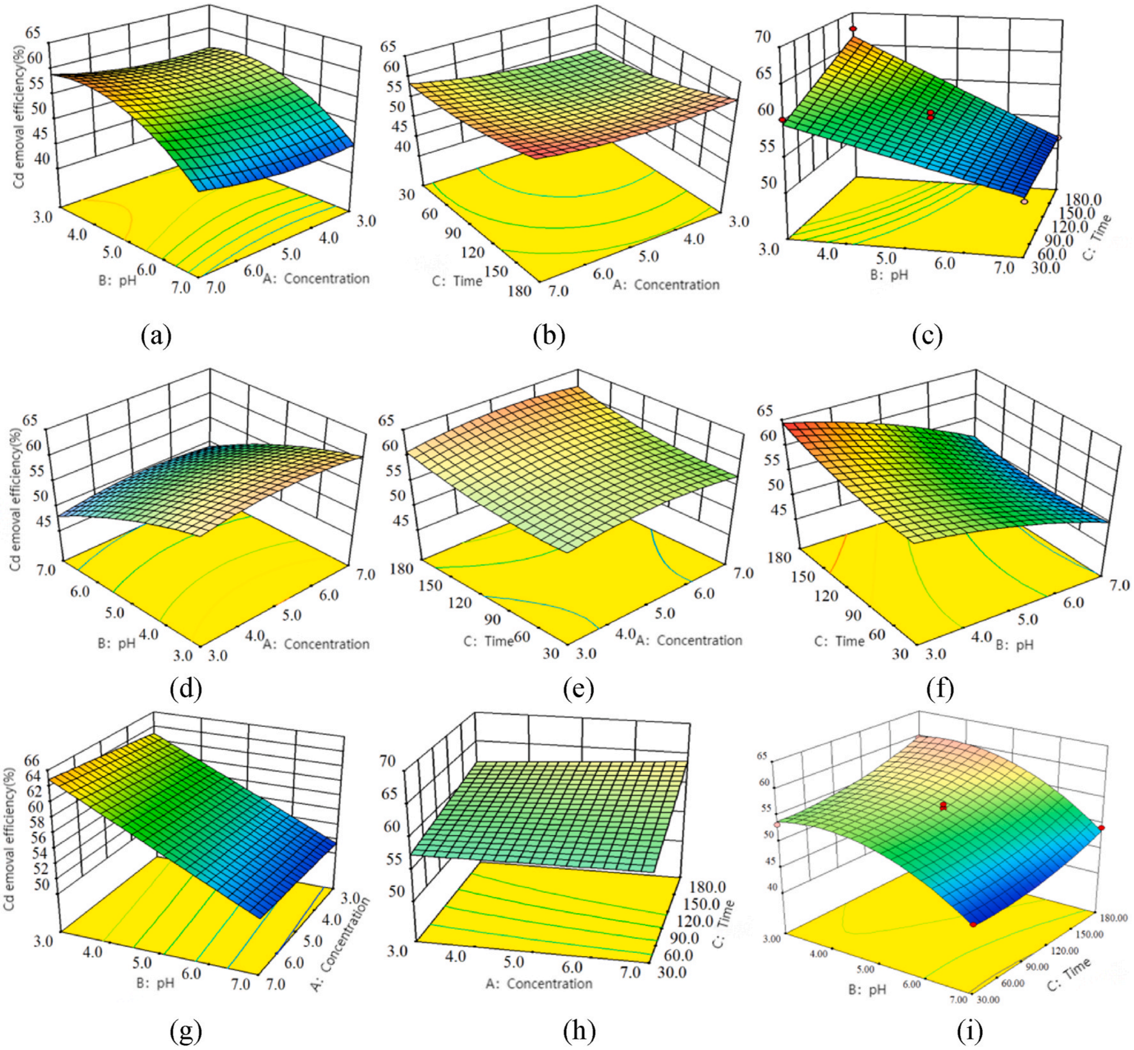


Fig. 4. 3D response surface diagram of different leaching parameters PMAS(a), (b), (c) EDTMPS(d), (e), (f) GLDA(g), (h), (i) on the removal rates of Cd in soil. (Note: Colour change from blue to green to red indicates increasing elution efficiency.).

Table 6
Optimization of leaching parameters for maximum Cd removal rates.

Optimization factor	Concentration (%)	pH	Time (min)	Cd removal (%)
PMAS	7.00	3.61	180.00	62.65
EDTMPS	4.94	3.00	180.00	64.47
GLDA	4.96	3.00	180.00	66.63

Table 7
Comparison of the removal rates of Cd under optimal leaching parameters with the predicted values of the model.

Optimization factor	PMAS	EDTMPS	GLDA
	Cd	Cd	Cd
Forecast (%)	62.65	64.47	66.63
Measured value (%)	63.37	64.38	67.54

washing conditions. In conclusion, the biodegradable chelating agents PMAS, EDTMPS and GLDA have broad application prospects in the remediation of Cd-contaminated soils. The response surface methodology is suitable for optimizing the leaching parameters for the removal of Cd in contaminated soils.

Institutional review board statement

(Not applicable).

Informed consent statement

(Not applicable).

Data and code availability

All the relevant data are included in the manuscript. No separate repository is attached.

CRediT authorship contribution statement

Jiajia He: Writing – original draft, Investigation, Data curation. **Ruidong Mi:** Writing – review & editing, Formal analysis. **Zilin He:** Writing – review & editing, Methodology. **Jiyuan Jin:** Writing – review & editing, Resources, Funding acquisition. **Jie Liu:** Validation, Formal analysis. **Jian Lang:** Resources, Conceptualization. **Gang Yang:** Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work is supported by the Power Construction of China (P42819, DJZDXM-2019-42) and Sichuan Science and Technology Program (2022YFN0025).

References

[1] T. Zhao, K. Zhang, J. Chen, et al., Changes in heavy metal mobility and availability in contaminated wet-land soil remediated using lignin-based poly(acrylic acid), J. Hazard Mater. 368 (2019) 459–467.

[2] Z.A. Begum, I.M.M. Rahman, H. Sawai, et al., Effect of extraction variables on the biodegradable chelant-assisted removal of toxic metals from artificially contaminated European reference soils, Water, Air, Soil Pollut. 224 (3) (2013) 1381.

[3] S. Gluhar, A. Kaurin, D. Lestan, Soil washing with biodegradable chelating agents and EDTA: technological feasibility, remediation efficiency and environmental sustainability, Chemosphere 257 (2020) 127226.

[4] C. Boente, C. Sierra, E. Rodríguez-Valdés, et al., Soil washing optimisation by means of attributive analysis: case study for the removal of potentially toxic elements from soil contaminated with pyrite ash, J. Clean. Prod. 142 (2017) 2693–2699.

[5] N. Bolan, A. Kunhikrishnan, R. Thangarajan, et al., Remediation of heavy metal(loid)s contaminated soils - to mobilise or to immobilise? J. Hazard Mater. 266 (2014) 141–166.

[6] X. Yuan, N. Xue, Z. Han, A meta-analysis of heavy metals pollution in farmland and urban soils in China over the past 20 years, J. Environ. Sci. 101 (2021) 217–226.

[7] H. Bian, J. Wan, T. Muhammad, et al., Computational study and optimisation experiment of nZVI modified by anionic and cationic polymer for Cr(VI) stabilization in soil: kinetics and response surface methodology (RSM), Environ. Pollut. 276 (2021) 116745.

[8] S. Khalid, M. Shahid, N.K. Niazi, et al., A comparison of technologies for remediation of heavy metal contaminated soils, J. Geochem. Explor. 182 (2017) 247–268.

[9] A. Piccolo, R. Spaccini, A. De Martino, et al., Soil washing with solutions of humic substances from manure compost removes heavy metal contaminants as a function of humic molecular composition, Chemosphere 225 (2019) 150–156.

[10] S. Satyro, M. Race, F. Di Natale, et al., Simultaneous removal of heavy metals from field-polluted soils and treatment of soil washing effluents through combined adsorption and artificial sunlight-driven photocatalytic processes, Chem. Eng. J. 283 (2016) 1484–1493.

[11] J. Beiyuan, D.C.W. Tsang, M. Valix, et al., Combined application of EDDS and EDTA for removal of potentially toxic elements under multiple soil washing schemes, Chemosphere 205 (2018) 178–187.

[12] Q. Wang, J. Chen, A. Zheng, et al., Dechelation of Cd-EDTA complex and recovery of EDTA from simulated soil-washing solution with sodium sulfide, Chemosphere 220 (2019) 1200–1207.

[13] Y. Cao, S. Zhang, Q. Zhong, et al., Feasibility of nanoscale zero-valent iron to enhance the removal efficiencies of heavy metals from polluted soils by organic acids, Ecotoxicol. Environ. Saf. 162 (2018) 464–473.

[14] L. Li, Y. Wang, Y. Sun, et al., Novel and green hydroxyperylene imide based fluorescent polymer for calcium sulfate scale inhibition, J. Mol. Liq. 344 (2021) 117730.

[15] Y. Han, C. Zhang, L. Zhu, et al., Effect of alternating electromagnetic field and ultrasonic on CaCO3 scale inhibitive performance of EDTMPS, J. Taiwan Inst. Chem. Eng. 99 (2019) 104–112.

[16] T. Das, A. Shinto, K.K. Kamaleshwaran, et al., Radiochemical studies, pre-clinical investigation and preliminary clinical evaluation of 170Tm-EDTMP prepared using in-house freeze-dried EDTMP kit, Appl. Radiat. Isot. 122 (2017) 7–13.

[17] J. Guo, C. Yuan, Z. Zhao, et al., Soil washing by biodegradable GLDA and PASP: effects on metals removal efficiency, distribution, leachability, bioaccessibility, environmental risk and soil properties, Process Saf. Environ. Protect. 158 (2022) 172–180.

[18] Q. Wu, Y. Cui, Q. Li, et al., Effective removal of heavy metals from industrial sludge with the aid of a biodegradable chelating ligand GLDA, J. Hazard Mater. 283 (2015) 748–754.

[19] Jianping Han, L.O.C.K. Yongpeng, Theory and application of hydrostatic correction of structural finite element model based on response surface method, Earthq. Eng. Eng. Vib. 33 (5) (2013) 128–137.

[20] Wei-deng Chen, Application of response surface analysis method in silt curing proportion design, Fujian Construction Science and Technology 5 (2018) 35–37+69.

[21] M. Ebba, P. Asaithambi, E. Alemayehu, Development of electrocoagulation process for wastewater treatment: optimization by response surface methodology, Heliyon 8 (5) (2022) e09383.

[22] A.D. Tura, H.B. Mamo, Characterization and parametric optimization of additive manufacturing process for enhancing mechanical properties, Heliyon 8 (7) (2022) e09832.

[23] L. Soto-Muñoz, L. Palou, M. Argente-Sanchis, et al., Optimization of antifungal edible pregelatinised potato starch-based coating formulations by response surface methodology to extend postharvest life of 'Orri' mandarins, Sci. Hortic. 288 (2021) 110394.

[24] X. Sun, Y. Yi, Acid washing of incineration bottom ash of municipal solid waste: effects of pH on removal and leaching of heavy metals, Waste Manag. 120 (2021) 183–192.

[25] Zhuqing Dai, Wenwen Peng, Mingxin Wang, et al., Remediation of heavy metal contaminated soil by citric acid leaching reinforced with hydroxylamine hydrochloride, J. Ecol. Rural Environ. 36 (9) (2020) 1218–1225.

[26] L. Peng, P. Liu, X. Feng, et al., Kinetics of heavy metal adsorption and desorption in soil: developing a unified model based on chemical speciation, Geochem. Cosmochim. Acta 224 (2018) 282–300.

[27] Z. Xia, S. Zhang, Y. Cao, et al., Remediation of cadmium, lead and zinc in contaminated soil with CETSA and MA/AA, J. Hazard Mater. 366 (2019) 177–183.

[28] Chunle Chen, Ting Yang, Xianmei Zou, et al., Leaching remediation and kinetic characterisation of heavy metal contaminated soil by biodegradable chelating agents iminodisuccinic acid and glutamic acid N,N-diacetic acid, J. Ecol. Rural Environ. 37 (3) (2021) 394–401.

[29] X. Zhu, H. Zhang, Optimization of [CnPy]Cl (n=2,4,6) ionic liquid aqueous two-phase system extraction of papain using response surface methodology with box-behnken design, Process Biochem. 77 (2019) 113–121.

[30] N. Jalal, M. Zidi, Influence of experimental conditions on visco-hyperelastic properties of skeletal muscle tissue using a Box-Behnken design, J. Biomech. 85 (2019) 204–209.

[31] R. Singh, P. Bhunia, R.R. Dash, Optimization of bioclogging in vermifilters: a statistical approach, J. Environ. Manag. 233 (2019) 576–585.

[32] E. Bazrafshan, T.J. Al-Musawi, M.F. Silva, et al., Photocatalytic degradation of catechol using ZnO nanoparticles as catalyst: optimising the experimental parameters using the Box-Behnken statistical methodology and kinetic studies, Microchem. J. 147 (2019) 643–653.

[33] X. Zhao, Y. Zhang, H. Zhao, et al., Principal component analysis and response surface methodology: optimisation for H2 evolution from water catalyzed adopting V-Bi under visible light, Mater. Today Chem. 25 (2022) 100920.

[34] X.U. Yuan, S.H.I. Ruiqi, Dajun Huang, et al., Optimisation of Co O_{34} preparation and its photocatalytic performance by response surface method, Journal of Chongqing University of Technology (Natural Science) 35 (5) (2022) 74–79.

[35] Yuanyu Qian, Ke Liu, Optimisation of soil cadmium leaching process by response surface method, J. Environ. Eng. 12 (12) (2018) 3448–3455.