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Application of response surface methodology for optimizing process parameters for the removal of Pb and Cu by *Acacia Concinna* from contaminated soil

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Abstract
This work investigates the remediation of lead (Pb) and copper (Cu) contaminated soil in batch washing experiments by using biodegradable saponin from the plant, Acacia concinna is commonly known as shikakai. The results indicate that the optimal values for the surfactant concentration (Conc), pH and soil-solution ratio (SSR) are 3.3, 3 and 28.78 respectively for Pb removal while the corresponding values for Cu are 3.70, 3 and 30.30 respectively. The predicted Pb removal efficiency was 78.17% while that for the Cu was 92.96%. The influencing parameters: conc., pH and SSR were optimised using Response surface methodology (RSM) based on the Box-Behnken design (BBD). A second-order quadratic polynomial model was used to correlate the effect of these three independent variables.

The ANOVA analysis and Pareto plot were generated using Minitab 18 software show that conc., SSR and pH were all significant ($P < 0.05$) for Pb and Cu removal while the conc. and pH were significant ($P< 0.05$) for Cu removal. The lower values of S (1.87 and 4.5) and higher values of R^2 (99.6% and 98.70%), adjusted R^2 (98.96% and 96.37%) and predicted R^2 (95.69% and 80.10%) suggested a good fit of the model to the experimental data. The high correlation between the predicted value of 78.17% and 92.96% and the experimental value of 78.79% and 90.79% for Pb and Cu respectively further confirm the adequacy as well as the applicability of this model. The results show the application of RSM as a suitable approach for optimal parameters determination in soil washing for heavy metal remediation using shikakai.

Keywords: Response surface, Shikakai, Soil washing, Contaminated soil, Copper, Lead, Box-Behnken design.

Introduction

Heavy metals belong to a class of elements having atomic numbers above 20 and a specific gravity greater than 5; these include cadmium (Cd), mercury (Hg), copper (Cu), arsenic (As), lead (Pb), chromium (Cr), nickel (Ni) and zinc (Zn).[16] Heavy metals are often described as a group of metals and metalloids that are poisonous to plants and animals even at low concentrations.[7] They are part of the natural elements of the earth's crust but can spread by geologic and anthropogenic activities.[5] They are non-biodegradable and can enter human bodies via food, drinking water and air as trace elements and can persist in the human body or system for several years.[2] Some are essential micronutrients which are needed to maintain the human body's metabolism while others are toxic even at low concentrations. The bioaccumulation of heavy metals is extremely dangerous to humans and biological organisms because of the increase in the concentration of some chemical elements over time, above the body's need for such chemicals.[2,5]

Soil pollution by heavy metals resulting from agricultural and domestic activities, mining, smelting, automobile battery production, emission from vehicles as well as industrial wastes has become a global environmental issue, which has attracted urgent attention in recent decades.[12,16] The global estimation of over 5 million sites of soil polluted by heavy metals and metalloids, covering over 500 million hectares of land, is a signal of impending disaster.[16] The global impact of this contaminated land is estimated to cost an excess of US$10 billion per year.[16] Both Pb and Cu, like other heavy metals, are known to be very toxic to humans, microorganisms, plants and the environment.[26] Soils with Pb and Cu contaminations have been reported globally.[6,14,25,27] Thus, remediation of soil polluted by Pb and Cu has become a very big challenge and needs urgent attention.

Soil remediation technologies for heavy metal contaminated land can be categorised into two major strategies, *in situ* and *ex situ* remediation methods. Remediation of heavy metal contaminated soils needs good knowledge of the source of contamination, soil physicochemical characterization, basic chemistry of elements and particles as well as some environmental considerations.[28]

Even so, the consideration of the appropriate method of soil remediation may depend on the soil characteristics, the concentration, types of contaminants to be removed and the end-use of the soil after remediation.[16]

Enhanced soil washing with surfactant has been used to remove heavy metals from the soil with high permeability such as sandy and silt soils.[1,8] Surfactants are surface-active substances that tend to reduce the surface and interfacial tension between two liquids, a gas and a liquid, or a liquid and a solid, with the help of hydrophilic heads and hydrophobic tails[20]. Biological surfactants of microbial and plant origins have enhanced the removal of heavy metals from contaminated soils.[2,20,26] To assess the performance of a soil washing technology, several reagents such as organic acids, inorganic acids, chelants and saponins have been studied under both laboratory and field remediation processes.[2,26]

Acacia concinna (shikakai) is a medicinal plant found and grown in tropical rainforests of Asia.[15] The fruits are also used for hair cleansing and conditioning.[13] Studies have shown the presence of the saponin cavity in mesocarp e.g. stone cells in the pericarp region of shikakai.[15] Previous studies have demonstrated that saponin can complex with heavy metals; the complexion with heavy metals has been attributed to the presence of the carboxyl group, the hydrophilic head and hydrophobic tails.[12] Saponins are biodegradable and re-useable; they can be separated from plants, are affordable and could offer an attractive alternative to the conventional synthetic chemicals used for the remediation of heavy metals.[4,12]

Soil washing for heavy metal removal is influenced by soil organic matter, the concentration of surfactant, pH, washing time, soil solution ratio and the level of contaminations.[26] The present study investigates the feasibility of using saponin from shikakai for the removal of Pb and Cu from contaminated soil. The Box-Behnken design (BBD), a response surface method was used for the optimization of 3 main parameters influencing Pb and Cu removal from the soil, soil-solution ratio, pH and concentration of the surfactant.

The objectives of this study are: (i) to conduct soil washing in batch experiments for the removal of Pb and Cu from contaminated soil using shikakai as a washing agent (ii) to study the influencing parameters (soil-solution ratio, pH and surfactant concentration) and (iii) to get the optimum values of these influencing parameters using BBD in Minitab 18 software.

Material and Methods

Soil samples and characterization: Fine sand and garden topsoil were procured from a garden centre in Edinburgh. The soil samples were air-dried and screened through a 2mm sieve to remove coarse sand and other aggregates. The soil was then homogenised by thoroughly mixing and stored in plastic bags for later use. The physicochemical characterisation was performed to determine the soil pH, electrical conductivity, bulk density, porosity, particle size distribution, cation exchange capacity (CEC), organic matter and moisture content. The results of the initial soil characteristics are shown in table 1.

Soil contamination procedure: The soil spiking was carried out to increase the concentration of Pb and Cu. About 1 kg of dry soil was contaminated with 1 litre of distilled water containing dissolved lead nitrate, $Pb(NO_3)_2$ and copper sulphate $CuSO_4$. The dissolved solution was thoroughly mixed with the soil into a slurry before being left to age and cured for about 6 months with frequent mixing. After the period of curing, the slurry was air-dried to a constant mass. The spiked soil was digested using a standard method of EPA 3050B; the liquid was filtered out and diluted to the required volume and the filtrate was analysed for heavy metals.

The soil analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) revealed that the concentrations of Pb and Cu in the soil were approximately 3000 and 4000 mg/kg respectively. These values were far above the threshold values of 100 and 600 for agricultural and industrial soils respectively.[9]

The method used in this work for soil digestion and analysis was adopted from previous reports on similar studies.[11,29]

Table 1
Essential physicochemical properties of the original soils used for the experiments

Soil properties	Values	Units	Methods
pH	7.21		US EPA Method 9045D
Electrical conductivity	1.2	EC dS/m	Violante and Adamo method
Soil moisture content	9.2	%	ASTM D2216
CEC	8.3	meq $100g^{-1}$	Ammonium acetate method
Bulk density	1.43	g/cm^3	Gravimetric method
Porosity	49		Urum
Organic matter content	2.4	%	Loss of weight by ignition
Sand	80	%	USDA classification
Topsoil	20	%	
Lead (Pb)	11.17	mg/L	Digestion USEPA 3050B measured by ICP-OES

Preparation of plant-based surfactant: Certified pure dry organic shikakai powder was supplied by Davis Finest, Hampshire, UK while lead nitrate was supplied by Fisher Scientific Chemicals Ltd., UK. A stock solution of 10% concentration of shikakai saponin was prepared by weighing 10 g of powder and adding 100 ml of distilled water. The solution was stirred for 3 hours at room temperature and then filtered after centrifuging at 3000 rpm for 25 min following a modification of the procedure used by Zhang et al.[30] Filtrates were collected, diluted to the desired concentration and used without further purification. The solutions were prepared when needed and used immediately without storage to avoid corrosion.

Procedure for batch soil washing studies: Washing studies were conducted in batches to investigate the effect of shikakai concentration, soil solution ratio and the pH of washing solution on the removal of Pb and Cu from contaminated soil. A series of batch tests was conducted in a 125 ml conical flask over a rotary shaker at 200 rpm for 8 hrs at room temperature (24^0C) and then aliquots were collected and centrifuged at 9000 g for 15 mins.[17] The initial pH of the surfactant solution was modified either by the addition of hydrochloric acid or sodium hydroxide.[21] The supernatants were collected after filtration using Whatmann filter paper. The samples were preserved with 1 drop of nitric acid and stored for ICP-OES analysis. The details of the experimental conditions and variables are shown in table 2.

The response was recorded as a percentage of Pb and Cu removed from the washing experiment and calculated using a similar equation as reported by Wuana et al. The pH values of the solutions before washing and those of the supernatants after washing were recorded. To ensure precision, all the experiments were performed in replicate and the results were presented as an average of the replication.[31]

$$\text{Percentage metal removal (\%)} = \frac{C_1 V_1}{C_s M_S} \text{X}\, 100 \qquad (1)$$

where C1 (mg/l) *and* CS (mg/kg), are the concentrations of metal in supernatant and soil respectively, Vl is the volume of supernatant (litres) and MS is the dry mass of the soil (kg).

Experimental design: Response surface methodology (RSM) is a collection of mathematical and statistical techniques that were applied for the analysis of research questions and models, in which the response is influenced by several independent variables and the main goal is an optimization of the process variables.[8] Response surface methodology is also used to quantify the relationship between the controllable input parameters and the obtained response surfaces.[3] RSM has two major design approaches: Box-Behnken Design (BBD) and Central Composite Design (CCD). BBD is widely applied in statistical analysis. A major advantage of using BBD is that it requires fewer treatment combinations than CCD in cases for which 3 and 4 factors are involved. The application of BBD can make the experiments more time-efficient while maintaining efficiency. In this study, BBD was employed to check the effects of pH, soil-solution ratio (SSR) and surfactant concentration (Conc) on the removal of Pb and Cu from the contaminated soil. Three factors at 3 levels were investigated in coded levels of +1 (high), 0(middle) and -1 (low). The process variables and their levels are shown in table 2. The number of experiments (N) in BBD, where each variable was varied three times, is defined by eq. 2:[8]

$$N = 2k\,(k-1) + Co \qquad (2)$$

where N is the no of experiments, k is the number of variables (3 for each Box-Behnken design) and Co is the number of central points. In this study, 3 centre points were used to estimate the pure error and therefore the total number of experimental runs was 15. A second-order quadratic polynomial model eq. 3 was used to correlate the effect of these three independent variables with Pb and Cu removal while the corresponding removal efficiency can be expressed:[3,8,26]

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii}\, x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta ij x_i\, x_j + \varepsilon \quad (3)$$

where Y = predicted response (% removal of Pb and Cu), β_0 = constant-coefficient term or the intercept, β_i = linear effect of the factors, β_{ii} = quadratic coefficient of the factors, β_{ij} = first-order interaction coefficient between the input parameters, x_i and x_j = coded levels of the independent variables and ε = the model error.

The statistical analysis was carried out with the aid of Minitab 18 software. The second-order polynomial model was validated at a 95% confidence level and demonstrated using analysis of variance (ANOVA)[8]. The model was assessed by the correlation coefficient (R^2) and related terms. The effect of correlation coefficients of linear and quadratic terms as well as the interaction of the experimental data was analysed by using ANOVA followed by the F-test at a 95% confidence level.

Table 2
Experimental variable of the independent factors and their levels

Independent variables	Coding	Level		
		-1	0	+1
Surfactant Concentration	Conc.	1	3	5
pH	pH	3	4	5
Soil-solution ration	SSR	10	25	40

The optimization of parameters using Minitab prediction tools was also carried out to determine the optimum points of the dependent variable and their expected responses. These predicted values were put to test experimentally to find out if there is an agreement or correlation between predicted and experimental responses.

Results and Discussion

Physicochemical analysis of soil: Table 1 shows the results of the physicochemical properties of the virgin soil. The soil used in this study is made up of fine sand and topsoil. The topsoil consists of loam soil and organic matter used as a soil amendment for both garden and other agricultural needs. The soil combination is a good example of a typical soil used for the cultivation of crops and can be classified as loamy sand according to the USDA soil classification triangle. Sandy soils are known to have low retention capacity for both water and heavy metals. On the other hand, the addition of topsoil would retain water and heavy metals because of the organic matter content which is known to have a great affinity for heavy metals and retention of water.[28]

Physicochemical test further shows that the soil pH is near neutral (Table 1). The neutral pH favours the growth of plants while a lower soil pH is necessary for heavy metal desorption from the soil. Electrical conductivity (EC) is the measure of the salinity of the soil. High EC is not good for the survival of plants as well as microorganisms in the soil. The EC value of 1.2 dS/m is within the normal range for agricultural soil.

The soil has low organic matter due to the greater percentage of sand; organic matter is known to offer binding strength to various heavy metals as well as other pollutants. CEC is the capacity of soil to retain a particular group of nutrients called cations. It is known that CEC comes from clay and organic matter present in the soil. Therefore, the low value of CEC was due to low organic matter. Thus, the low values of EC, CEC, organic matter and moderate porosity recorded from the physicochemical analyses of the soil mean that the soil was permeable and will be suitable for leaching of heavy metals with a possibility of remediation washing.[28] Soil analysis also revealed low levels of lead concentration and thus spiking with lead nitrate was required to increase the level of heavy metal concentration.

Results of BBD experiments and development of regression model: The response surface model applies a three-dimensional surface structure to create and show the influence of experimental factors and response values. BBD of 3 factors at 3 levels was used for the optimization of the Pb and Cu removal from contaminated soil in this study. The experimental arrangement and runs for BBD were generated by using Minitab 18 software as shown in table 3 to study the influence and interaction effect of the independent variables including pH, soil-solution ratio (SSR) and surfactant concentration (Conc.). The experiments were conducted according to BBD as shown in table 2. The experimental design arrangement and details along with the response values as well as predicted values are shown in table 3. The second-order polynomial regression equations were generated by Minitab 18 software to describe the Pb and Cu removal efficiencies. The equations are expressed in an uncoded form as shown in eqs. 4 and 5:

$$\% \text{ Cu removed} = 4.6 + 24.14 \text{ Conc.} - 3.8 \text{ pH} + 5.822 \text{ SSR} - 5.126 \text{ Conc.*Conc.} - 2.17 \text{ pH*pH} - 0.1108 \text{ SSR*SSR} + 1.54 \text{ Conc.*pH} + 0.1830 \text{ Conc.*SSR} - 0.153 \text{ pH*SSR} \quad (4)$$

$$\% \text{ Pb removed} = 16.4 + 4.32 \text{ Conc.} + 3.06 \text{ pH} + 4.674 \text{ SSR} - 3.056 \text{ Conc.*Conc.} - 2.398 \text{ pH*pH} - 0.08331 \text{ SSR*SSR} + 2.436 \text{ Conc.*pH} + 0.2980 \text{ Conc.*SSR} - 0.2866 \text{ pH*SSR} \quad (5)$$

where % Cu removed and % Pb removed are the predicted Cu and Pb removal efficiencies. Conc., pH and SSR are the uncoded independent variables representing surfactant concentration, pH of the solution and soil-solution ratio respectively.

ANOVA study: Table 3 presents the summary of the ANOVA analysis of Cu and Pb removal experiments. ANOVA is an effective statistical tool for determining the influence of the experimental parameter on the response. ANOVA was carried out to assess the variations, adequacy and significance of the regression model. In this study, the effects of the 3 factors influencing Cu and Pb removal from contaminated soil and their interactions were analysed (Table 3).

The F-statistic tool was used to test the significance of each of the parameters studied and the effect of their interactions. The model terms with P-value less than 0.05 are considered significant while P-values greater than 0.05 are considered not significant. The significance of a parameter means that changes in that parameter can influence their responses. The regression model equation for the second-order polynomial is showing the relationship between the Cu and Pb removal rate and the 3 independent variables are presented in uncoded units in eqs. 4 and 5 respectively.

Table 4 indicates that the model has P-values of <0.0001 for Pb and Cu (ANOVA) which further implies that the model is significant and adequate to predict the removal of Pb and Cu from contaminated soil based on the fitted data. The model single parameters: Conc., pH and SSR as well as their 2-way interactions: Conc. *pH, Conc.*SSR and pH.*SSR were all significant ($P < 0.05$) for Pb removal. However, for Cu removal, conc. and pH were all significant while SSR was not significant at ($P<0.5$). The 2-way interactions of conc., pH and SSR for Cu removal were not significant as in the case of Pb removal. Fig. 1 shows the absolute values of standardized effects of the parameters influencing Pb and Cu removal and clearly explained their significance; not least because their interactions clearly show the level of their significance.

Table 3
Details of BBD experimental arrangements and the results obtained from the soil washing experiments

Run Order	Conc.	pH	SSR	% Cu removed Experimental	% Cu removed Predicted	% Pb removed Experimental	% Pb removed Predicted
1	1	4	40	20.6001	18.0739	22.6781	21.0078
2	3	3	40	75.1388	72.8591	65.9562	66.4177
3	1	5	25	20.3149	19.5574	20.8468	21.6047
4	1	3	25	61.7577	66.5637	62.1006	63.3094
5	3	5	40	24.1376	27.4213	24.9479	25.8603
6	5	4	40	44.0152	45.5375	51.3210	51.6175
7	5	4	10	25.4962	28.0224	24.3910	26.0613
8	1	4	10	24.0449	22.5226	31.5067	31.2103
9	3	4	25	74.5461	73.9786	65.2085	63.4438
10	3	5	10	23.1992	25.4789	27.2416	26.7801
11	5	5	25	47.0044	42.1984	45.2879	44.0791
12	3	3	10	65.0187	61.7350	51.0565	50.1441
13	3	4	25	72.2076	73.9786	63.2529	63.4438
14	3	4	25	75.1821	73.9786	61.8699	63.4438
15	5	3	25	76.1287	76.8861	67.0537	66.2958

Table 4
Response surface analysis of variance for the fitted quadratic polynomial model

		Pb removal			Cu removal		
Source	DF	Adj SS	F-Value	P-Value	Adj SS	F-Value	P-Value
Model	9	4702.87	148.91	<0.0001#	7728.32	42.26	<0.0001#
Linear	3	2484.97	236.05	<0.0001#	3965.61	65.05	<0.0001#
Conc.	1	324.12	92.37	<0.0001#	543.29	26.74	<0.004#
pH	1	2042.97	582.19	<0.0001#	3336.95	164.21	<0.0001#
SSR	1	117.87	33.59	0.002#	85.37	4.20	0.096*
Square	3	1729.39	164.27	<0.0001#	3583.09	58.77	<0.0001#
Conc.*Conc.	1	551.72	157.22	<0.0001#	1552.58	76.40	<0.0001#
pH*pH	1	21.22	6.05	0.057*	17.41	0.86	0.397*
SSR*SSR	1	1297.47	369.74	<0.0001#	2295.47	112.96	<0.0001#
2-Way Interaction	3	488.52	46.40	<0.0001#	179.61	2.95	0.138*
Conc.*pH	1	94.95	27.06	0.003#	37.94	1.87	0.230*
Conc.*SSR	1	319.67	91.10	<0.0001#	120.60	5.93	0.059*
pH*SSR	1	73.90	21.06	0.006#	21.08	1.04	0.355*
Error	5	17.55			101.61		
Lack-of-Fit	3	11.92	1.41	0.440*	96.70	13.14	0.072*
Pure Error	2	5.63			4.91		
Total	14	4720.42			7829.92		
	Model summary						
S	1.87327				4.50792		
(R^2)	99.63%				98.70%		
(Adjusted R^2)	98.96%				96.37%		
(Predicted R^2)	95.69%				80.10%		

DF= degree of freedom: Adj SS = adjusted sum of square: # = significant (P<0.05): * = not significant (P > 0.05): SSR = Soil solution ratio: Conc. Concentration of surfactant

The ANOVA (Table 4) further shows that the "lack of fit" is not significant for both Pb and Cu removal. This further suggests that there is a lack of evidence to conclude that the model did not fit the data very well. This also implies that this model can be used to describe the functional relationship between the experimental parameters (Conc., pH and SSR) and the response variable (Pb and Cu removal) satisfactorily.

Furthermore, S is used to evaluate how well the model describes the response. A lower S means that the model describes the response very well. In this study, the value of S is 1.87 for Pb and 4.5 for Cu. This implies that the standard deviation of the data points around the fitted values is 1.87 and 4.5 respectively for Pb and Cu, indicating a better fit. R^2 is measured in percentage and normally used to determine how well the model fits the data. The higher is the value of R^2, the better fitting the model is to the data. The R^2 values of 99.63 and 98.70% for Pb and Cu removal respectively obtained in this study imply that the model fits well with the data.

Also, this indicates that only 0.57% and 1.30% of the total variations in response were not explained by the model. Adjusted R^2 compares the number of predictors in the model with the number of observations. The higher the value is, the better is the model fitting signifying a better prediction of response. The goodness of fit requires a low variation between R^2 and adjusted R^2. In this study, the adjusted R^2 of 98.96% and 96.37% were obtained for Pb and Cu respectively. The differences between R^2 and adjusted R^2 were within the marginal range confirming that the model fits well with the experimental data.

Also, the higher value of predicted R^2 (95.69% and 80.10% for Pb and Cu respectively) further indicates that the model was reliable for the data and could be used to predict future observations. This predictive ability of the model is very important to avoid over-fitting.

Additionally, the normal probability plot, the residual plot and the histogram of the residuals (Fig. 2) are all in agreement with the earlier assertion that the model adequately represents the data and can be used to predict new observations. This also implies that this model can be effectively applied and replicated for the prediction of Pb and Cu removal from contaminated soils with similar physicochemical properties and similar washing conditions.

Response surface analysis of the effect of pH and Soil-solution ratio on Pb and Cu removal: Contour plot and three-dimensional (3D) response surface analysis are effective tools used to explore the potential relationship between two and three variables respectively. In this study, the contour plot and 3D wireframe plots were used to demonstrate the relationship and interaction between the three parameters was studied along with the Pb and Cu removal efficiency. Fig. 3 shows the interactions that occurred between pH and SSR and the percentage of Pb and Cu removed in the experiments while keeping the effect of conc. at the central point of 3%.

It is shown in fig. 3 that pH ranges from 3 to 5 while the soil-solution ratio ranges from 10 to 40. Both parameters influenced the removal of Pb and Cu significantly as shown in fig. 3. Pb and Cu removal increased with an increase in the soil-solution ratio but decreased with an increase in the pH of the washing solution. The range for which pH gives the highest removal efficiency is between the values of 3-3.5 while the highest removal efficiency can be obtained in soil: solution range of 18 -38 (Fig. 3). Low pH is known to influence the removal efficiency of heavy metals since acidic conditions tend to aid heavy metal desorption from contaminated soil.[29]

This is because metals tend to form insoluble mineral oxides, phosphates and carbonates at high pH which makes them difficult to remove from the soil surface. However, at low pH, heavy metals would form free ionic complexes with saponin molecules, making them easy to remove during the washing processes.[24]

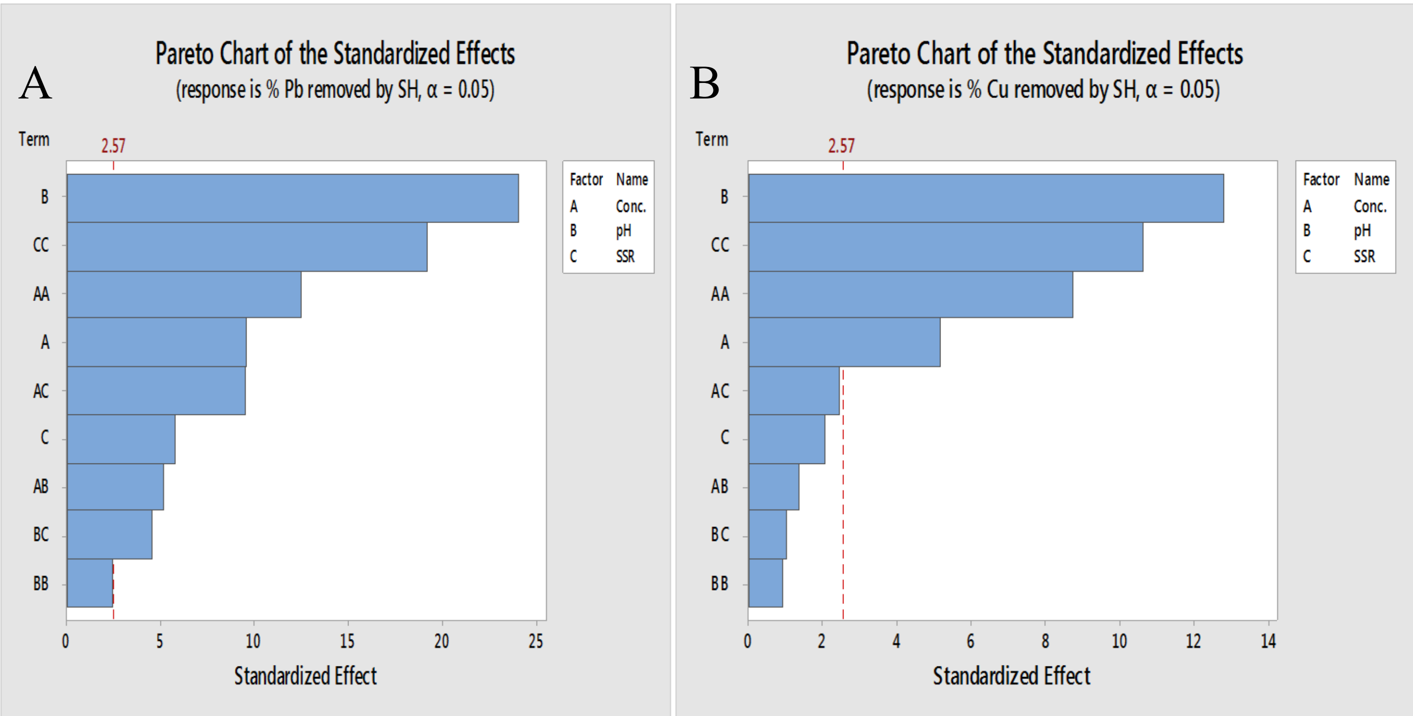

Figure 1: Pareto chart of standardized effect of Pb (A) and Cu (B) removal from contaminated soil using shikakai (SH).

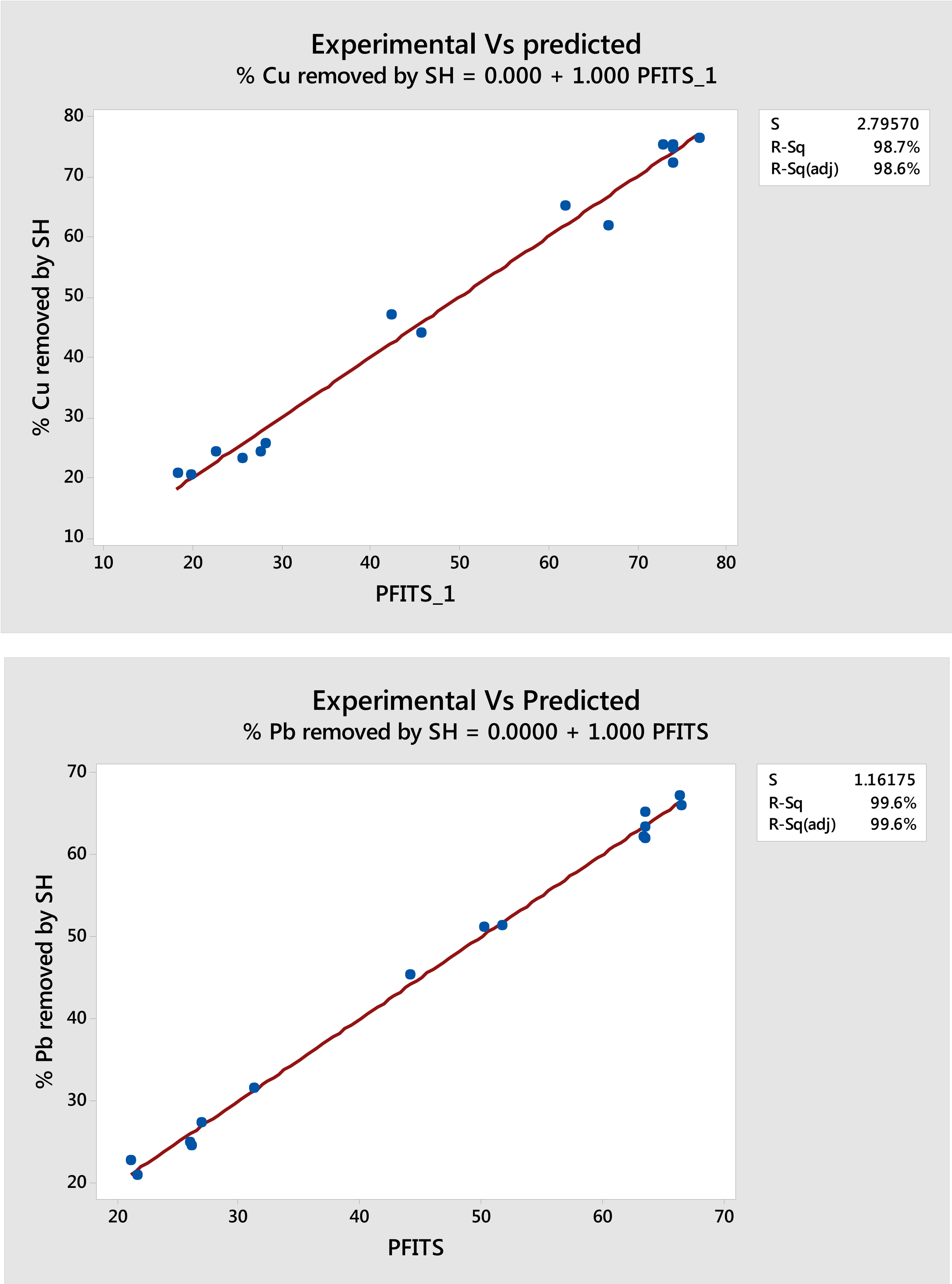

Figure 2: The relationship between the predicted variable and experimental data for Pb and Cu removal using shikakai

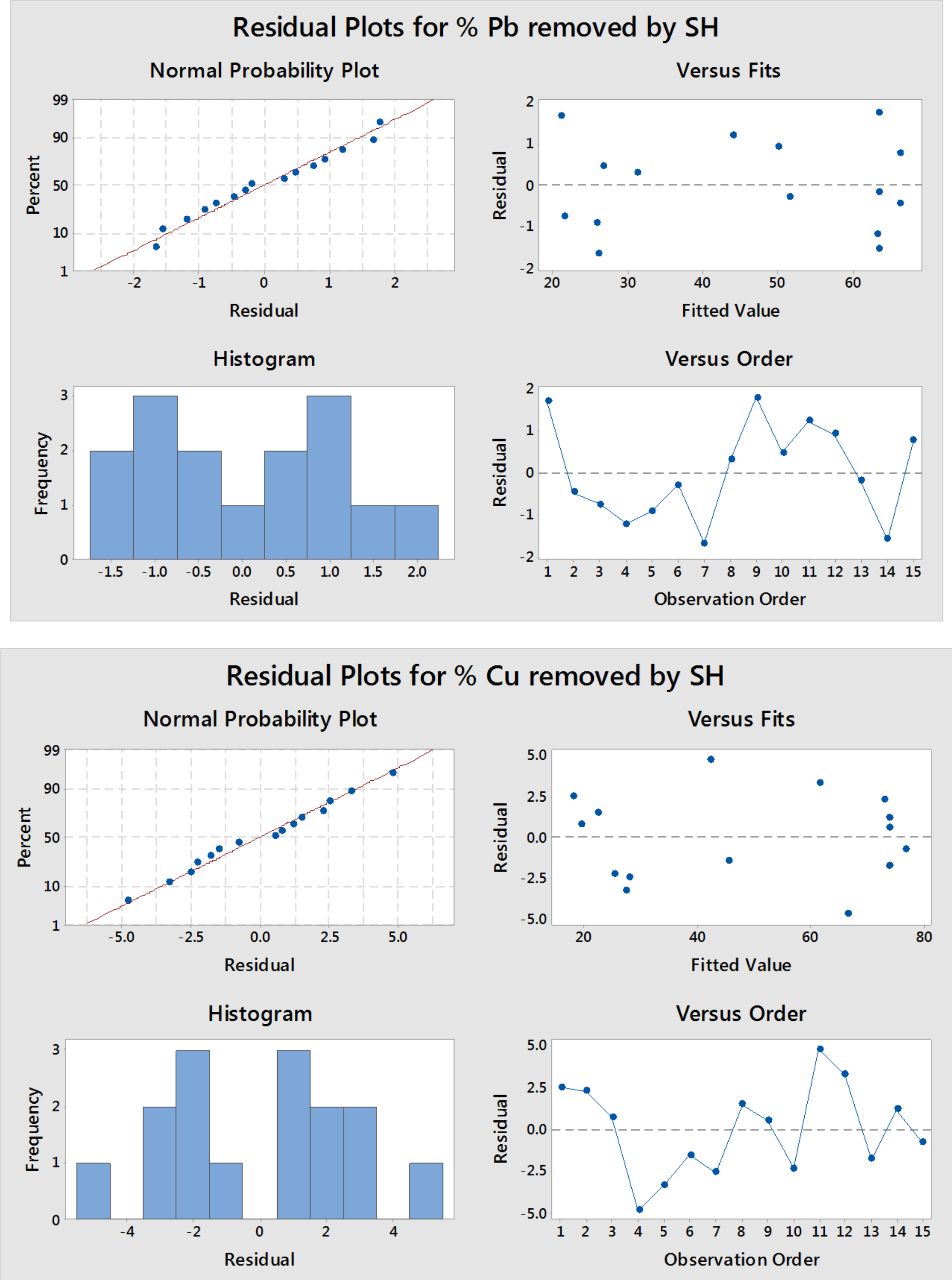

Figure 3: Residual plots for Pb (A) and Cu (B) removal from contaminated soil using shikakai (SH)

A high soil-solution ratio on the other hand is known to improve the removal efficiency of heavy metals. This may be attributed to the fact that an increase in the quantity of liquid solution will increase the number of micelles formation as well as complex formation with the heavy metals.[19,31] Previous studies also reported that acidic conditions and an increase in soil-solution ratio enhanced heavy metal removal from the soil during the washing process.[10,12,18,22,23]

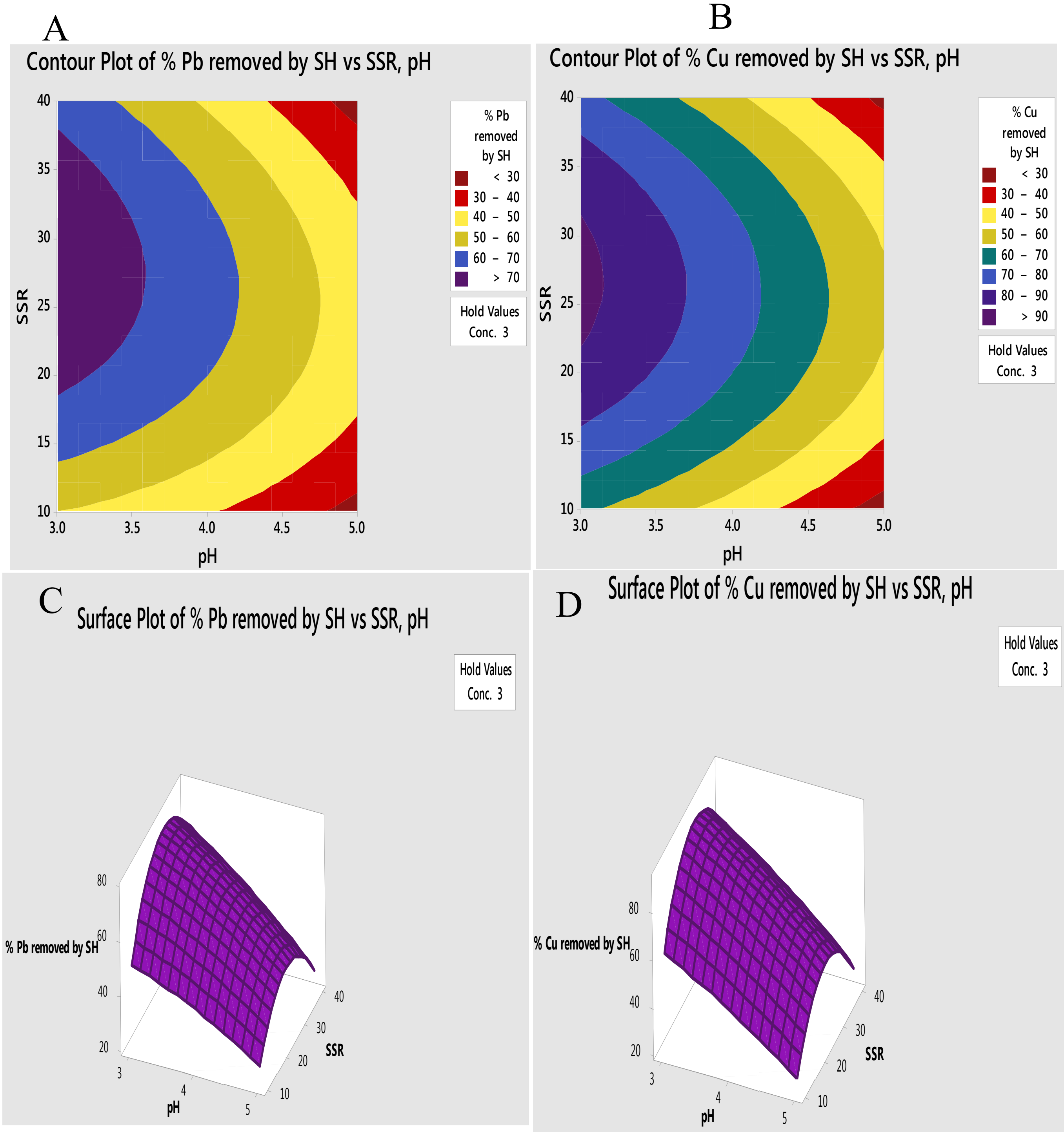

Figure 4: The interactions between pH and soil-solution ratio and their responses (Pb and Cu removal efficiency). A and B are the Contour plots while D and C are the three-dimensional wireframe plots for Pb and Cu respectively

Response surface analysis of the effect of concentration and soil-solution ratio on Pb and Cu removal: The concentration of washing agents is especially important factor to consider when planning the soil washing process. It has a strong bearing on the removal efficiency of heavy metals. In this study, the concentration of shikakai was found to influence the removal efficiency of Pb and Cu from the contaminated soil. ANOVA (Table 4) and the Pareto plot (Fig. 1) clearly show that surfactant concentration was statistically significant for both Pb and Cu removal. Fig. 4 shows the interaction effect of concentration and soil-solution ratio on the removal efficiency of Pb and Cu.

It can be observed that an increase in concentration leads to an increase in removal efficiency. It was previously reported by Mulligan et al[21] and Mukhopadhyay et al[19] that an increase in surfactant concentration above the CMC will improve the performance of the saponin solutions. This is because more micelles are formed and released into the solution, resulting in enhanced solubilisation and mobilization of heavy metals. Also, an increase in heavy metal removal might have resulted from the reduction in the surface tension of the solution and an increase in micelle formation when more surfactant molecules are introduced into the solution.[19]

It can also be seen (Fig. 4) that the highest removal efficiency can be achieved when surfactant concentration is above 2.5% and the soil-solution ratio is at a range of 20-35 while holding pH [SA6] at 4. The ANOVA (Table 4) and Pareto plot (Fig. 1) further show that there is a significant interaction between SSR and Conc. for Pb removal but not significant for Cu removal.

Response surface analysis of the effect of pH and concentration on Pb and Cu removal: Fig. 5 shows the contour and response surface plots of the interaction effect between pH and surfactant concentration at the soil-solution ratio of 25. It can be seen from the Pareto plot (Fig. 1) that the interaction between surfactant concentration and pH is significant for Pb removal but not significant for Cu removal.

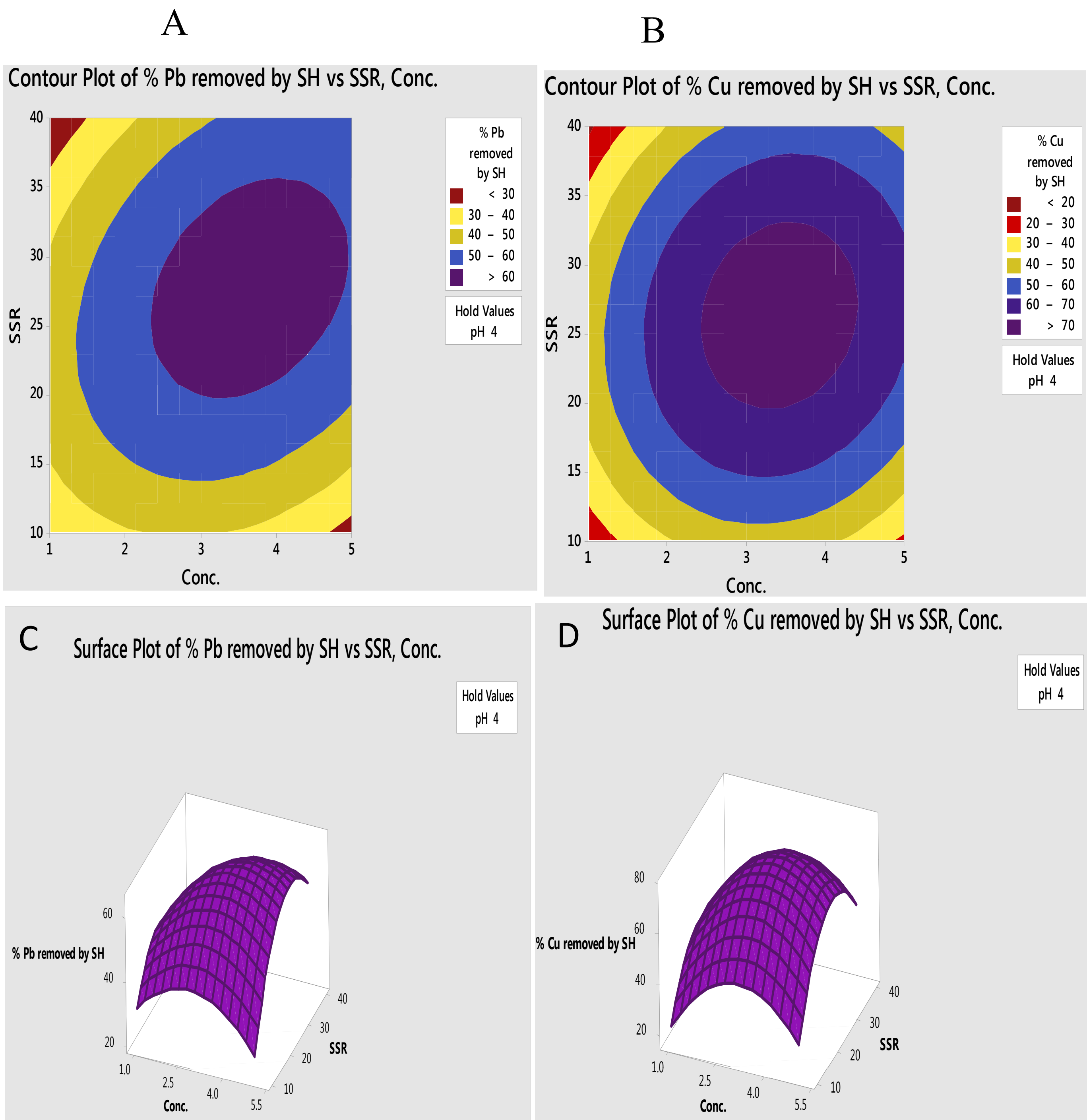

Figure 1: The interactions between concentration and soil-solution ratio and their responses (Pb and Cu removal efficiency), A and B are the Contour plots and C and D are the three-dimensional wireframe plots

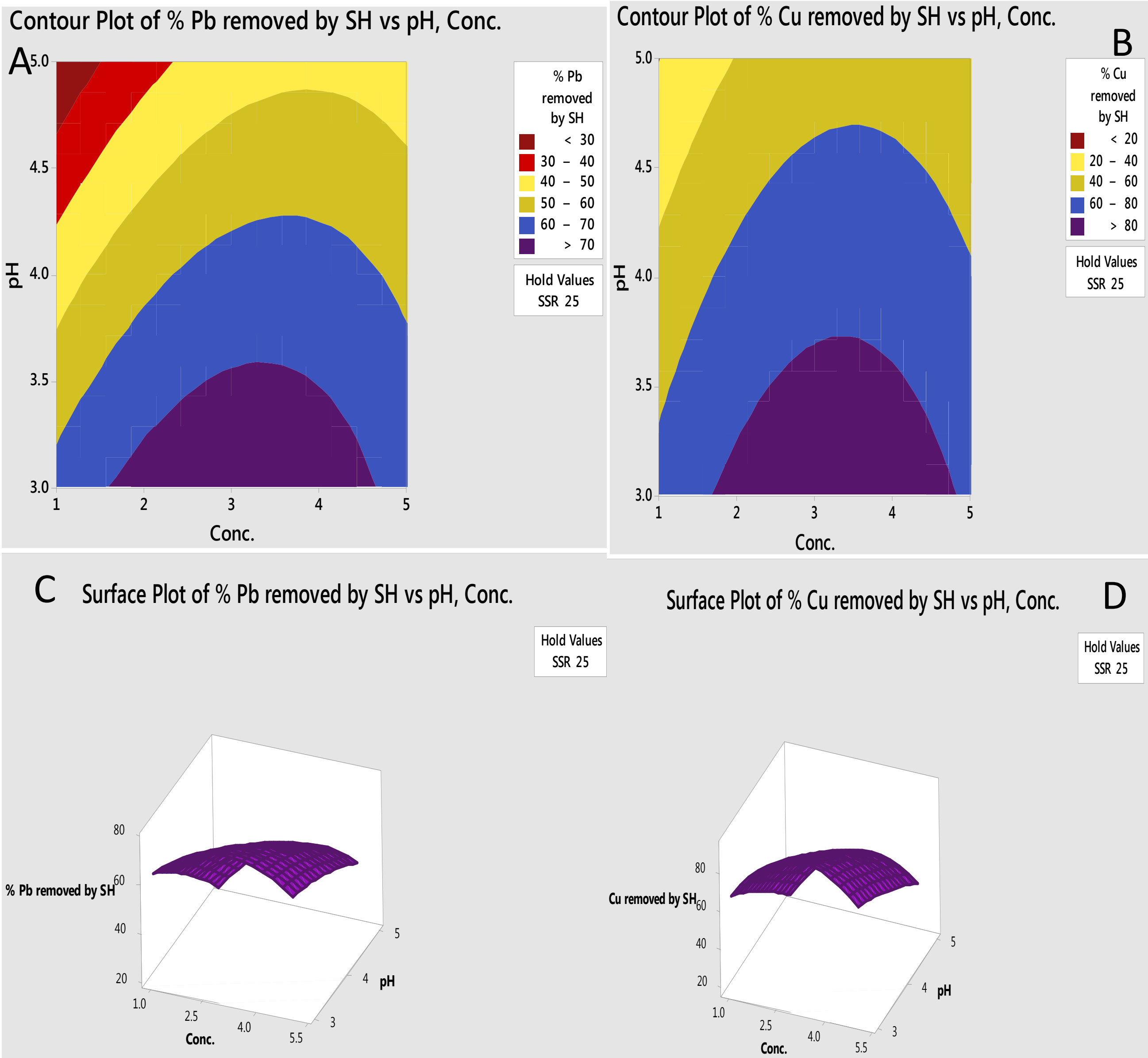

Figure 6: The interactions between concentration and pH and their responses (Pb and Cu removal efficiency). A and B are the Contour plots and C and D are the three-dimensional wireframe plots

However, the surface and contour plots (Fig. 5) show that removal efficiency increases with an increase in concentration but decreases with an increase in the pH of the washing solution. A maximum response can be achieved at a pH range of 3 - 3.5 and surfactant concentration between 1.8 – 4.7%. Therefore, under low pH and high surfactant concentration, Pb and Cu removal rates could improve while holding the soil-solution ratio at 25.

Optimization of washing parameters for Pb and Cu removal by shikakai: One of the major purposes of this study is to obtain the optimum conditions to maximize Pb and Cu removal from contaminated soil using saponin from shikakai. Multiple response prediction of operational parameters was carried out by using Minitab 18 software to determine these optimal operational conditions[8]. The variable settings and the optimized values obtained from the calculation are presented in table 5. The results indicate that the optimal values for surfactant concentration, pH and soil-solution ratio are 3.3, 3 and 28.78 respectively for Pb removal while that of Cu are 3.70, 3 and 30.30 respectively. The predicted Pb removal efficiency was given as 78.17% with the desirability of 1.0 and a standard error of 1.19% while that for Cu was 92.96% at the same desirability and standard error of 3.61.

The optimum surfactant concentration in the present study is consistent with the previous report of Hong et al[12] and Gusiatin et al[9,10] in which saponin was reported to be effective at the concentration of 3%. Predicted pH conforms to the fact that acidic conditions enhance heavy metal removal. Although, acidic conditions are not suitable for the micro-organisms and other living organisms in the soil, necessary care must be taken to ensure that the remediation is designed toward the targeted use of the soil after heavy metal removal.

Table 5
Validation of multiple response prediction of optimal conditions of process parameters for Pb and Cu removal

	Pb removal		**Cu removal**	
Variable	**Predicted values**	**Validation experiments**	**Predicted values**	**Validation experiments**
Surfactant concentration (Conc.)	3.3	3.3	3.70	3.70
pH	3	3	3	3
Soil-solution ratio (SSR)	28.79	28.79	30.30	3.30
Percentage removal	78.17	78.93	92.96	90.79

Increasing the pH will favour the existence of living organisms in the soil whereas low pH is suitable for improved soil remediation. The optimal soil-solution ratio is quite reasonable to avoid increasing surfactant solution which will generate a larger volume of wastewater as effluent. Such effluents are normally treated and can also be re-used for another soil washing process instead of using fresh surfactant solution.[8]

To validate the adequacy of the multiple response prediction models, soil washing experiments were conducted in triplicate on the same contaminated soil sample using the variable optimum conditions.[8,22] Table 5 shows that the result of 76.69% Pb removal was obtained from the experiments under the optimum conditions while 90.79% of Cu removal was obtained under an experimental condition. This result is in close agreement with the predicted values of 78.17% and 92.96% which were estimated by the optimization model providing a piece of further evidence for the validity of the model.

Conclusion

Three significant parameters for washing Pb and Cu from contaminated soil by using saponin from shikakai have been studied with the help of Box–Behnken design and the Response surface methodology model. A second-order quadratic polynomial model was used to correlate the effect of three independent variables: surfactant concentration, soil-solution ratio and pH of the washing solution on Pb and Cu removal. ANOVA and Pareto plot generated using Minitab 18 software show that conc., SSR and pH were all significant ($P < 0.05$) for Pb removal while conc. and pH were significant ($P< 0.05$) for Cu removal. The lower values of S (1.87 and 4.5) and high values of R^2 (99.6% and 98.70%), adjusted R^2 (98.96% and 96.37%) and predicted R^2 (95.69% and 80.10%) suggested good fits of the model to the experimental data.

Based on the multiple response prediction of variables, the optimal conditions of process parameters for Pb and removal were: (Conc. 3.3% and 3.7), (SSR 28.79 and 30.30) and (pH 3) for Pb and Cu respectively which are in agreement with similar previous reports. The high correlation between the predicted values of 78.17% in comparison with the experimental values of 78.79% and 90.70% for Pb and Cu further confirms the adequacy as well as the applicability of this model. Possible mechanisms for Pb removal by surfactant are the formation of micelles, complexion with metals on the soil surface, ion exchange and precipitation of sorbed metals onto a solution for possible extraction.

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