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Evaluation of Factors Affecting Chemical Extraction of Co Ions from Contaminated Soil

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Abstract

Excessive concentrations of cobalt (Co) ions in the soil cause quality degradation and pose a significant hazard to biota. One of the options for the permanent separation of the pollutant from soil matrix is extraction by chemical reagents. In this study, response-surface methodology (RSM) was applied to evaluate the factors affecting Co extraction from contaminated calcareous soil. Solutions of disodium ethylenediaminetetraacetate (Na_2EDTA), citric acid (CA), and HCl were considered as leaching media. Reagent concentration, soil to solution ratio, and extraction time were selected as process variable, while Co extraction efficiencies and final pH values of extracts were the measured responses. The effect of factor variation between three levels was studied using Box-Behnken experimental design. By statistical analysis, the most influential factors were determined for each reagent, and the model equations were proposed for the prediction of system responses. Overlaid contour plots were used for the analysis of the effect of process conditions on both responses simultaneously. Given that each case of contamination is unique and requires extensive research before the remediation is implemented full-scale, it was shown that experimental design methodology is a smart approach for the assessment and comparison between the treatments.

Keywords: cobalt ions, soil contamination, chemical extraction, Box-Behnken design, ANOVA

1. Introduction

Cobalt (Co) is one of the essential heavy metals, which is vital at trace levels for proper functioning of the human metabolism [1]. However, at concentrations higher than optimal, essential metals become toxic. The poisoning by Co is commonly a result of drinking water contamination, high ambient air and soil concentrations, and consequent entrance and bioaccumulation of

Co in the food chain. Therefore, development and application of remediation methods are necessary in order to mitigate the negative impact of Co on the ecosystem.

The average concentration of Co in the Earth's crust is 10 mg/kg [2]. The levels of Co in the soil are influenced by the pedogenic factors, as well as by the characteristics of a parent rock material. For different climatic zones, the values of 0.05 and 300 mg/kg were reported as the minimum and maximum naturally occurring concentrations in the soil [3]. Lower amounts were found in the soils from the northern regions, which originated from the glacial deposits. The average concentrations of Co in the northern parts of Ukraine, Russia [2], and Sweden [4] are 3.5, 5.5, and 7.1 mg/kg, respectively. In contrast, naturally higher values can be found in the areas with arid or semiarid climate, like in Egypt [3].

The property which affects the manifestation of both beneficial and toxic effects is the solubility of Co in a particular environment. In respect to total concentration of Co in the soil, the fraction available to plants is more important. The accessibility to living organisms is the highest for free Co ions and water soluble complexes, while its metallic form and insoluble compounds commonly exhibit very low bioaccessibility. The available content of Co in different soil types, determined using 2.5% acetic acid as an extracting agent, was found to vary from 0.05 to 1 ppm [3]. On one hand, the lack of available Co leads to Co-deficiency in living organisms, while on the other, Co and its compounds are highly toxic in excessive amounts causing serious cell and tissue damages (LD_{50} values for intake of Co salts for rats are in the range 150–500 mg/kg of body weight [5]).

The main sources of environmental pollution with Co are industrial activities. Utilization of Co as catalyst in the chemical industry, in the production of dyes and pigments, magnetic recording media, alloys, batteries, etc., makes this element of the strategic importance for military, industrial, and commercial applications [6]. In numerous studies, Co concentrations in soil and sediments were measured to define its levels and identify the main pollution sources. Soil pollution by Co in Shenzhen soil (China) was attributed to uncontrolled discharge of industrial wastewater from factories that produce or use chemical compounds or alloys containing Co [7]. Furthermore, ceramic industry was highlighted as the source of the sediment contamination with Co and other heavy metals in Jiangsu Province (China) [8]. The highest concentrations were observed in the surface soil layer, within the 20–22 cm depth. In north greater Cairo (Egypt), direct discharge of industrial wastewaters to irrigation water canals during 30 years provoked significant contamination of soil with Co (146 mg/kg) [9]. The activity of a smelter in Zambia was found to result in dust with elevated concentrations of Co and other heavy metals, causing the contamination of soil and plants [10]. The highest measured Co concentration was 606 mg/kg found in the 0–2 cm of soil depth [11]. Furthermore, Co has been found in increased concentrations in at least 426, out of 1636 most serious hazardous waste sites in the USA, identified by Environmental Protection Agency (US EPA) [12]. The contamination of soil with Co is therefore a global problem with a tendency of steady increase.

Contaminated areas need to be treated using the techniques based either on the pollutant separation from the soil matrix or on its stabilization [13]. The levels and properties of heavy metal pollutants, as well as the physicochemical properties of the soil, govern the distribution of heavy metals which is an important factor for the selection of effective remediation method.

When soil is exposed to Co-containing solution, several processes can occur at the surface of soil constituents: electrostatic attraction, ion-exchange, complexation, co-precipitation, precipitation, occlusion, diffusion, and migration. Various single-step leaching procedures and sequential extractions are in use for the determination of metal distribution and mobility in the soil. Sequential extraction of the soil by so-called Tessier protocol is frequently applied [14]. This procedure is based on the consecutive application of selective chemical reagents in five extraction steps (F1–F5), with the aim to extract the pollutant associated with different soil fractions: ion-exchangeable (F1), acid soluble (F2), bound to Fe, Mn-oxides (F3), complexed by organic matter (F4), and incorporated in the residual fraction (F5). As the strength of the bonds between the metal and the soil constituents increases along the extraction scheme, the metal mobility decreases in the same manner.

Clean-up of the contaminated soil can be completed by the method of chemical extraction if the pollutant is distributed between relatively mobile fractions F1–F3 [15]. Extraction processes require mixing of contaminated soil with leaching solutions (solutions of acids, inorganic salts, chelating agents, surfactants, etc.) that cause a transfer of pollutant from the soil matrix into the liquid phase. If the chemical extraction is chosen among other alternative methods, the optimization of the method performance requires extensive research on the effects of a large number of variables. Some of the previous studies have addressed the impact of reagent type and concentration, reaction time, soil/solution ratio, pH, temperature, etc., on the efficiency of heavy metals extraction from the soil matrix [16–19]; however, the experiments were conducted by varying one factor at the time and little attention has been paid onto evaluation and comparison of factor effects, their interactions and process optimization.

Taking into account numerous potentially important factors, experimental design methodology (DOE) can be a useful strategy for the analysis of different soil treatments. In that sense, the present chapter aimed to explore the applicability of DOE approach for the analysis of the factors affecting chemical extraction of Co from contaminated soil and for the prediction of system responses.

2. Design of experiment (DOE)

The analysis and optimization of virtually any process can be conducted by experimental design methodology (DOE). Compared to the classical approach which implies variation of one factor at the time, DOE relies on simultaneous variation of all factors and reveals the most influential ones, the significant interactions between the factors, and the optimal levels of the factors. This methodology aims to describe or explain the variation of information under conditions that are hypothesized to reflect the variation. Therefore, DOE is a planned approach to find out the relationships between process variables and process responses, in relatively small number of experimental trials. Depending on the process under consideration, as well as on the number and the type of information of interest, different types of experimental design are in use, such as full and fractional factorial designs, response-surface designs, mixture designs, random block, Latine squares designs, etc. [20].

The response-surface methodology (RSM) was developed in order to optimize chemical reactions used on an industrial scale [21]. The application of RSM is of relevance in situations where several input variables influence the performance or quality characteristics of the process, which are called the responses. The input variables, usually denoted as independent variables, are controlled. Variation in experimental conditions provokes changes in the process response. Dependence between process responses and two process variables is a smooth surface called the response surface. The purpose of the response surface is to locate the conditions which lead to the achievement of the minimum/maximum response. Furthermore, in cases when several responses are of interest, RSM can give the optimal conditions for their target values [22]. The response values (y) are related to the process variables (x_1, x_2…) according to the model:

$$y = f(x_1, \ x_2, \ldots) + \varepsilon \tag{1}$$

In Eq. (1), $f(x_1, x_2\ldots)$ is called the response surface and represents the mean response at each x, while ε represents other sources of variability (measurement error, background noise, the effect of other variables, etc.), and it is usually treated as a statistical error.

The function $f(x_1, x_2\ldots)$ can be given as the first-order [Eq. (2)], or the second-order model [Eq. (3)]. The first-order model describes experimental conditions which provide the responses without peaks, and it is applicable for the description of local area responses without function extremes.

$$f(x_i) = \ \beta_0 + \sum \beta_i x_i + \varepsilon \tag{2}$$

In Eq. (2), β_i denotes the linear effect of the process variable x_i. Given that it includes only the main effects of the two or more variables, the form of the first-order model given by Eq. (2) is called the main effects model. In some processes, the interactions between studied variables may be significant; thus, the interaction term must be added to the first-order model, which introduce curvature into the response function.

The advantage of RSM is that the lack of fit can be estimated and the adequacy of the model can be estimated. The lack of fit test provides the answer whether the proposed model adequately describes system response (H_0—null hypothesis) or not (H_A—alternative hypotheses). If the proposed model is suitable, there is no lack of fit. When the first-order polynomial regression model is not adequate, the applicability of the second-order model is analyzed:

$$f(x_i) = \ \beta_0 + \sum \beta_i x_i + \sum \beta_{ij} x_i x_j + \sum \beta_{ii} x_i^2 + \varepsilon \tag{3}$$

The term $\beta_{i,j}$ represents the interaction effect between two factors x_i and x_j, and $\beta_{i,i}$ is the quadratic effect of factor x_i. The meanings of the other terms in Eq. (3) are the same as aforementioned. The designs that correspond to the surface response methodology are Box-Behnken design, central composite design, and optimal designs.

The results of a literature survey showed that different types of experimental design were used for the investigation of Co sorption by potential sorbent materials such as apatite, zeolite,

bauxite residue, and dried activated sludge [23–25]; however, DOE approach has not been applied, to this point, for the study of Co sorption or leaching from the soil matrix. In fact, just a few examples of RSM application for the analysis of a soil remediation process can be found [26, 27]. In this study, a three-level-three-factor Box-Behnken experimental design was selected for the evaluation of the effect of factors which influence the Co extraction from contaminated soil. Box-Behnken design is a three-level factorial design which considers factors at their low (–1) and high (+1) values, as well as at their arithmetic mean (0) [28]. This is the type of quadratic design which does not contain the factorial or fractional factorial designs but considers the midpoints of the edges of the process space and its center. In general, it is an alternative to full factorial design at three levels.

3. Materials and methods

3.1. Soil contamination and clean-up experiments

The soil was sampled from the site of Vinča Institute of Nuclear Sciences (Belgrade, Serbia), from the surface layer (0–20 cm). Prior to contamination with Co ions, soil was dried at room temperature, homogenized, grained, and sieved in order to separate the fraction of particles with the diameter <2 mm. The soil at this locality was characterized as weak alkaline (pH_{H2O} = 8, pH_{KCl} = 7), with $CaCO_3$ content of 5.4%, total organic content (TOC) of 2.1%, and cation exchange capacity (CEC) of 13 meq/100 g [29]. Mineralogical analysis revealed quartz, kyanite, and muscovite as main crystal phases, whereas mica, albite, kaolinite, and calcium, magnesium–carbonate were present in lower quantities [29].

In the first step, the soil was artificially contaminated by Co ions. The solution containing 0.0012 mol/L of $Co(NO_3)_2$(Merck, p.a.) was mixed with 100 g of dried soil at the solid/liquid ratio 1:20. After 24 h of equilibration, the liquid phase was separated from the soil by filtration and the contaminated sample was dried in the air atmosphere. The concentration of Co ions sorbed by the soil was calculated as the difference between its initial and the residual concentration.

Soil clean-up was conducted using the method of chemical extraction. Based on the high extraction efficiencies observed in the previous study [18], the solutions of disodium ethylenediaminetetraacetate (Na_2EDTA), citric acid (CA), and HCl were selected as extracting agents. The contaminated soil was mixed with the reagent solutions in the centrifuge tubes which were placed on the rotary shaker and agitated at the constant speed (10 rpm) at ambient temperature (20 ± 2°C).

The effects of the variation of reagent concentration, solid/liquid ratio, and contact time, among three levels, were investigated. Experimental variables and their levels are given in **Table 1**. The matrix with the experimental conditions for simultaneous variation of process parameters (**Table 2**) was generated using Minitab Release Software 13.1.

Extraction of Co ions was performed using each of the selected reagents, according to the conditions given in **Table 2**. After specified contact times, the suspensions were centrifuged for 10 min at 10,000 rpm and the extracted concentrations of Co ions were measured in clear supernatants. The chemical extraction experiments were conducted in duplicate.

Independent factor	Symbol	Level 1 coded value (−1)	Level 2 coded value (0)	Level 3 coded value (−1)
Reagent concentration (mol/L)	A	0.0005	0.05025	0.1
Soil/solution ratio	B	5	15	25
Contact time (h)	C	1	3.5	6

Table 1. Experimental factors and their levels used in the Box-Behnken design.

Experimental run	Independent factor		
	A	B	C
1	1	1	0
2	−1	0	−1
3	0	1	−1
4	−1	0	1
5	0	0	0
6	1	−1	0
7	0	1	1
8	−1	−1	0
9	0	0	0
10	0	−1	1
11	1	0	−1
12	0	−1	−1
13	1	0	1
14	−1	1	0
15	0	0	0

Table 2. Combinations of factors and their levels according to Box-Behnken design matrix.

In the sorption and extraction experiments, Co concentrations were determined by Perkin Elmer 3100 atomic absorption spectrometer (AAS), using a wavelength of 252.1 nm. Standards for instrument calibration were prepared by diluting certified Perkin Elmer standard (1000 mg/L), and the calibration was repeated after every 10-sample measurement. The detection limit was 0.05 mg/L, whereas the deviations among five replicate measurements for each sample were lower than 3%.

The percentages of the extracted Co ions were used as the main response function of the process. In addition, pH values of the leaching solutions after the completion of the process (denoted as final pH) were measured using WTW InoLab pH-meter, and also considered as system response.

3.2. Statistical analysis

Mean values of measured parameters, obtained from duplicate extraction experiments, were used as system responses for data interpretation and statistical analysis. Experimental point designation, analysis of variance (ANOVA), fitting of regression polynomial models, and graphical presentations (ternary plots) were performed using the statistical software MINITAB Release 13.2. The statistical analysis was done at the confidence level $\alpha = 95\%$.

4. Results and discussion

4.1. System responses at different experimental conditions

After the contamination step, the total amount of Co ions sorbed by the investigated soil was found to be 1390 mg/kg. High sorption affinities of soils and soil components toward Co are well documented [24, 30–32]. The sorbed amount is in agreement with the results of a previous study in which the soil from the same location was contaminated with Co under the range of experimental conditions [18].

The variation of chemical reagents and other experimental conditions according to the Box-Behnken design resulted in variation of system responses (**Figure 1**).

The mean values of Co extraction efficiency were found to fluctuate in the range 10–72% for Na_2EDTA, 1–66% for CA, and 0–71% for HCl as extracting agent (**Figure 1a**). The results signify that, at certain levels of the considered factors, amounts of extracted Co can reach high values using tested reagents. It is evident that the change of experimental conditions differently affects the performance of tested reagents and that effect of HCl was the lowest when compared to other reagents under the same sets of experimental conditions.

The final pH values were also largely dependent on the type of reagent and process variables (**Figure 1b**). The initial pH values of extracting solutions at their lower, middle, and higher selected concentrations were: 4.4, 4.6, and 4.9 for Na_2EDTA, 2.0, 2.2, and 3.5 for CA, and 1.0, 1.3, and 3.3 for HCl. After the reaction of contaminated soil with Na_2EDTA solutions, pH values were in the range 4.4–8.8, while using solutions of CA and HCl, pH values varied between 2.8–7.8 and 1.6–7.6, respectively. The observed increase in pH, after interaction with the soil, can be attributed to the buffering capacity of the soil which mainly originates from its carbonate content [18].

The knowledge of the nature and the strength of the bonds established between added Co ions and soil constituents are important for interpretation and understanding the effect of different chemical reagents. By means of the sequential extraction analysis, the portions of Co bonded in different fractions of the investigated soil were previously analyzed [18]. Considering various contamination levels and aging times (1 h to 30 days), Co ions were found to be associated with Fe, Mn-oxide fraction (F3), carbonate/acid soluble (F2), and ion-exchangeable (F1) fraction (F1 + F2 + F3 > 92%). For the comparison, the majority of naturally occurring Co in the soil from the Vinča locality was found in F3 and residual (F5) phase [29], indicating that sorbed
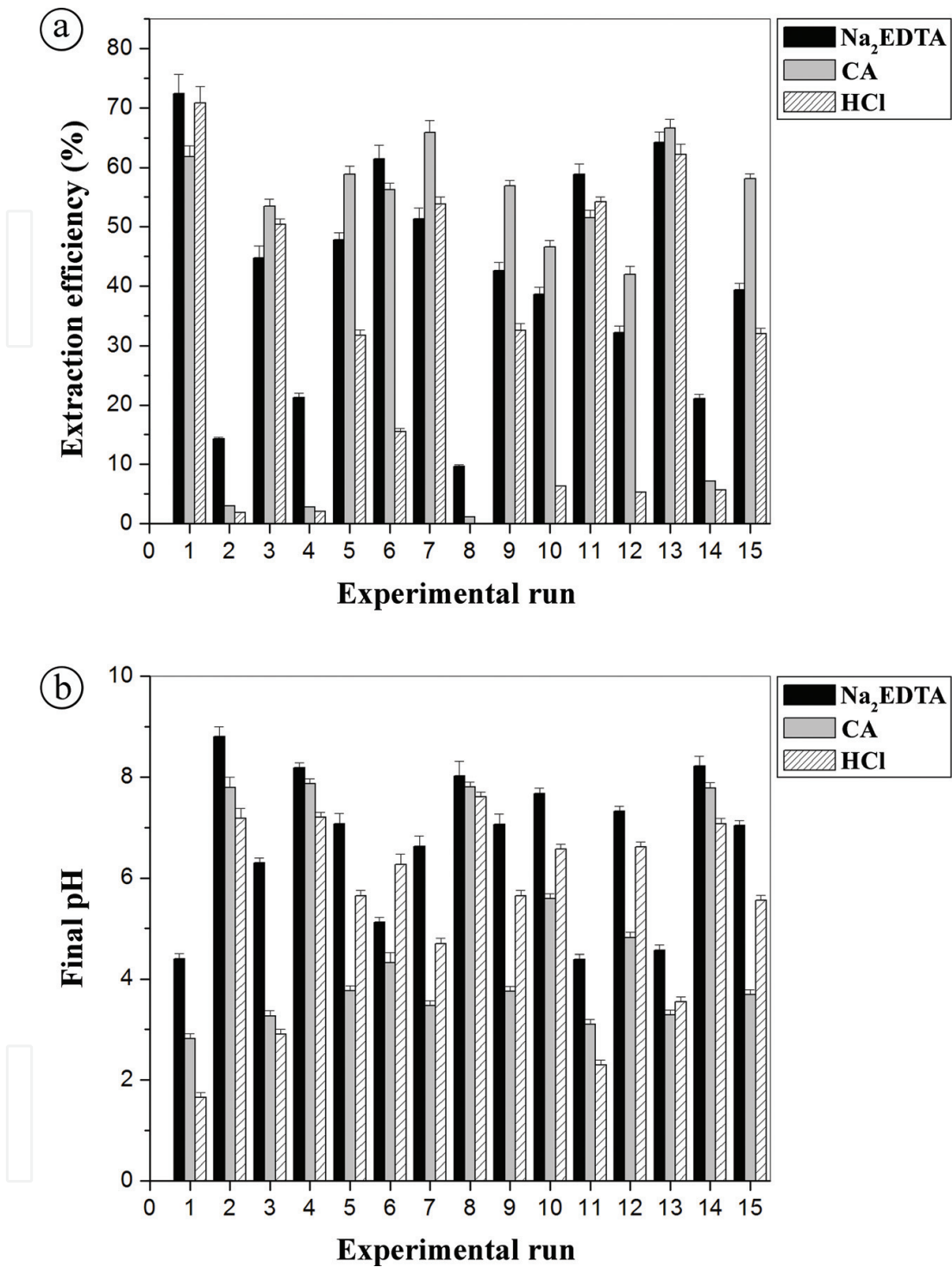
Figure 1. System responses obtained for different extracting agents under experimental conditions defined in **Table 2**: (a) extraction efficiency of Co ions from the contaminated soil and (b) final pH of extracts.

cobalt ions have significantly higher mobility. These results signify that chemical extraction can be considered for soil clean-up [33].

Fe- and Mn-oxides and hydroxides have been generally recognized as the major substrates for Co ions in the soil [34]. High affinities of such minerals toward Co ions were also revealed

in the studies of Co sorption by Fe- and Mn-oxides [35–37], as well as by geochemical modeling of Co speciation in different soil samples [38]. The amounts of Co found in F2 phase of the sequential extraction correspond to the fraction associated with carbonates, as well as the fraction chemisorbed on the surface of soil components. The crystal lattice of calcium-carbonate can accommodate high quantities of Co and other divalent metals, implying that calcite is an important sorbent for metals in calcareous soils [39]. In addition, carbonate phase is of a crucial importance for high soil pH, which results in higher stability of sorbed metal ions [40]. Finally, the ion-exchange between Co and other divalent cations contained in the soil minerals also contributes to Co retention in the soil [41].

Taking into account the effects achieved by investigated reagents (**Figure 1a**), it can be concluded that both complexing agents and the mineral acid can release Co ions sorbed within different soil fractions. The extraction potential of HCl solutions is governed by the changes of pH. As the pH becomes more acidic, the dissolution of soluble soil constituents occurs, as well as the exchange reactions between H^+ and metal ions, and the protonation of active surface sites which become more positively charged [31, 42, 43]. Depending on the pH, these reactions cause the liberation of metal ions bonded by ion-exchange mechanism, specifically sorbed, and associated with carbonates and oxide minerals. Solubility of metal ions in the soil is also enhanced in the presence of chelating anions. These organic ions form multiple bonds with the metal cation, essentially in the form of a ring, which exhibits high stability in aqueous media. The chelating agents have a potential to extract the metal ions bonded to all non-residual fractions [44].

4.2. Evaluation of the effects of factors by Box-Behnken design

By using actual values of process variables, the response variable (y) was fitted to a second-order polynomial model as follows:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j \qquad (4)$$

where y is system response, β_0 is the intercept, β_i is the linear effect, and β_{ii} is the quadratic effect of the process variable x_i, while $\beta_{i,j}$ is the effect of the interaction between two independent process variables x_i and x_j.

Applicability of different models was tested by ANOVA. In order to determine which mathematical model adequately fits the obtained experimental results, full quadratic model was initially applied [Eq. (4)]. Statistical calculations were assessed on the basis of the F- and p-values. F-values are obtained from Fisher's test and represent the ratio of the mean square due to regression and mean square due to residual error, whereas p-value is defined as the smallest level of significance which leads to the rejection of null hypothesis. Therefore, higher F and lower p-values ($p < 0.05$) represent statistically significant terms. By omitting the insignificant terms ($p > 0.05$) and considering the values of determination coefficients (R^2) together with the results of lack of fit, the most appropriate models were found.

For Na_2EDTA as Co leaching reagent, the most suitable model included only linear terms, following the equation:

$$Co(Na_2EDTA) = 41.142 + 23.798A + 5.935B + 3.138C \tag{5}$$

According to the proposed Eq. (5), Co desorption efficiency was dependent on the linear effect of all selected factors. However, by observing the values of coefficients next to the respective factors, it can be concluded that the highest effect on the process response was achieved by the change of initial reagent concentration, followed by the effect of applied reagent volume, and finally the effect of contact time. The positive signs of the calculated coefficients indicate that leached amounts of Co increase with the increased levels of factors.

The coefficient of determination (R^2) was calculated according to the equation:

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}} \tag{6}$$

where SS_{res} denotes the sum of squares of the residuals, while SS_{tot} is the total sum of squares. SS_{tot} was calculated as the sum of squared differences between the different system responses values (y_i) and its mean. Furthermore, the SS_{res} is the sum of the squared differences between each system variable and its value predicted by the model. Knowing that the R^2 values increase with the number of terms in the model even if their effect is insignificant, an incorrect model could be proposed if R^2 magnitude is solely considered. Therefore, the value of the adjusted determination coefficient (R^2_{adj}) was included. In contrast to their effect on R^2 values, insignificant terms in the model provoke the decrease in R^2_{adj} values.

The summary of ANOVA, F and p-values obtained for significant model terms and the results of the lack of fit are given in **Table 3**. Using the experimental results obtained for Na_2EDTA extraction efficiency, calculated R^2 and R^2_{adj} values were 99.02 and 98.76%, respectively. Practically, the predicted model adequately describes even 99.02% of experimental results. Giving that F-value was <1 and p-value was >0.05, the proposed model can be regarded as adequate.

The following model was developed for CA as a leaching reagent:

$$Co(CA) = 54.527 + 27.779\,A + 5.304\,B + 3.990\,C - 23.238A^2 \tag{7}$$

The extraction of Co ions with CA solutions was found to be dependent on all investigated factors with the statistical significance. Changes in the level of reagent initial concentration have caused the highest impact on the leaching efficiency. Furthermore, the squared term in the derived equation (A^2) indicates the existence of curvature in the response surface. The obtained Eq. (7) fitted 97.88% of the experimental results, with the calculated R^2_{adj} value of 97.03%.

The extraction of Co using HCl can be described by the model which includes the following linear and interaction terms:

$$Co(HCl) = 28.31 + 24.15\,A + 19.20\,B + 12.39AB \tag{8}$$

For the proposed model, determined R^2 was 94.69%, while R^2_{adj} was 93.25%. The analysis of factors affecting the efficiency of applied inorganic acid indicates that the changes of contact

	Na$_2$EDTA		CA		HCl	
	F	p	F	p	F	p
Extraction efficiency						
Regression	371.70	<0.0001	115.50	<0.0001	65.45	<0.0001
A	1032.90	<0.0001	333.90	<0.0001	111.29	<0.0001
B	64.24	<0.0001	12.17	<0.006	70.40	<0.0001
C	17.96	0.001	6.89	0.025	/	/
A^2	/	/	109.04	<0.0001	/	/
AB	/	/	/	/	14.65	0.003
Lack of fit	4.48	0.196	5.37	0.160	3.13	0.310
Final pH of extracts						
Regression	86.21	<0.0001	96.28	<0.0001	77.93	<0.0001
A	318.98	<0.0001	219.89	<0.0001	269.36	<0.0001
B	9.91	0.01	18.17	0.001	132.38	<0.0001
A^2	13.48	0.004	50.79	<0.0001	/	/
C	/	/	/	/	10.61	0.012
C^2	/	/	/	/	8.95	0.017
AB	/	/	/	/	38.40	<0.0001
BC	/	/	/	/	7.86	0.023
Lack of fit	2.51	0.151	6.37	0.06	5.14	0.18

Table 3. Analysis of variance.

time did not significantly influence on the amount of leached cobalt. On the other hand, changes in the concentration and volume of the reagent were significant, as well as the interaction of these two parameters.

Furthermore, the models for the description of final pH values were developed. Considering the data obtained using Na$_2$EDTA, the following equation was found suitable, with calculated values of $R^2 = 96.48\%$ and $R^2_{adj} = 95.52\%$:

$$pH(Na_2EDTA) = 7.0186 - 1.8438A - 0.3250B - 0.5548A^2 \qquad (9)$$

The final pH values of the CA extracts can be described ($R^2 = 96.33\%$, $R^2_{adj} = 95.33\%$) by Eq. (10):

$$pH(CA) = 4.0400 - 2.2175A - 0.6375B + 1.5600A^2 \qquad (10)$$

Eqs. (9) and (10) indicate that variation of initial concentration and volume of both investigated complexing agents had an effect on final pH. The negative signs of the corresponding

coefficients denote that increased concentration levels and increased levels of applied volume influenced the decrease in pH.

The complex mathematical model was obtained for describing the solution pH values after soil leaching with HCl:

$$pH(HCl) = 5.6386 - 1.9150A - 1.3425B + 0.3800C - 0.511C^2 - 1.0225AB + 0.4625BC \quad (11)$$

The adequacy of Eq. (11) was confirmed by high R^2 and R^2_{adj} values (98.32% and 97.06%, respectively). The model indicates that the variation of all studied factors, as well as AB and BC interactions, significantly affected the pH of resulting extracts. The HCl concentration and volume exhibited negative correlation with pH, while the contact time and pH were positively correlated.

Inside the range of experimental conditions covered by the design, the efficiency of Co extraction can be predicted using the mathematical models proposed by Eqs. (5), (7), and (8). The graphical interpretation of these equations, that help visualize the shape of the response surface, is given in **Figure 2** in form of contour plots. The graphs express the relationships between calculated
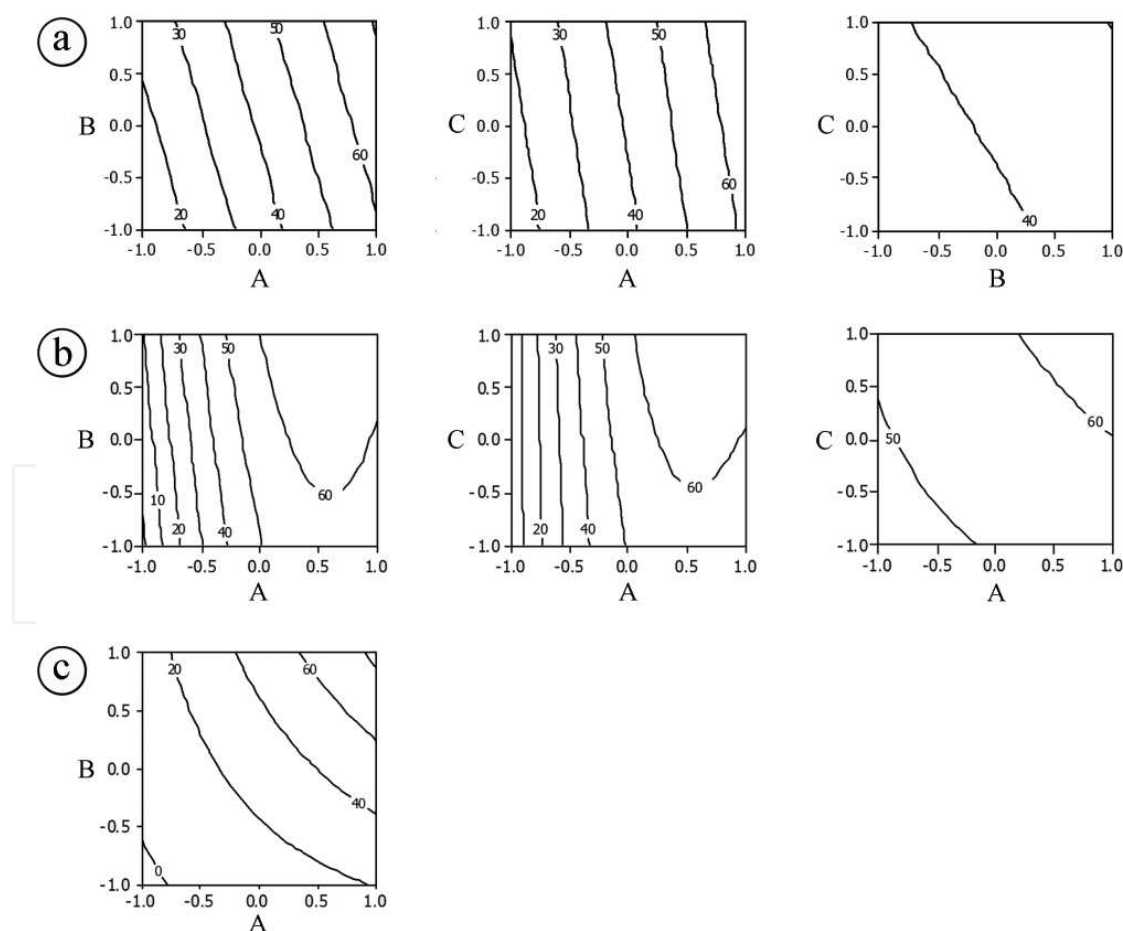
Figure 2. Contour plots for cobalt extraction efficiency using: (a) EDTA, (b) CA, and (c) HCl solutions, presenting the relationships between calculated responses and statistically significant factors, at the constant intermediate value of the third factor (A—reagent concentration, B—soil/solution ratio, C—extraction time).
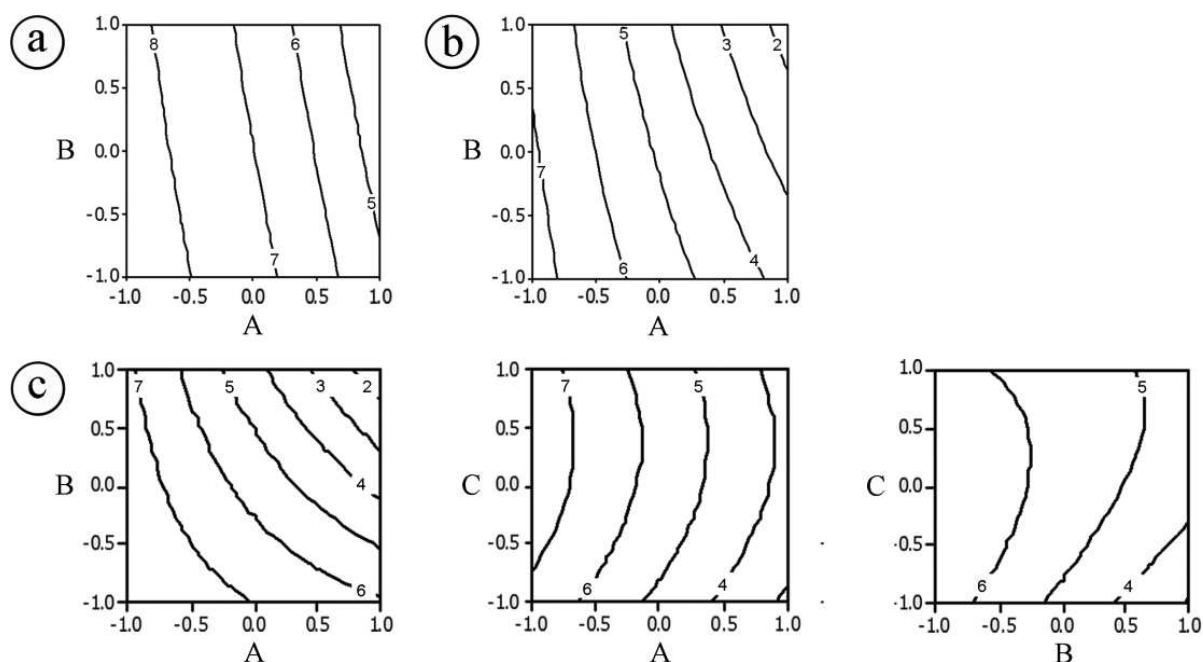
responses and statistically significant variables, at the constant intermediate value of the third parameter. The lines on the graphs represent constant values of the system response.

The parallel lines on the contour plots in **Figure 2a** refer to the linear effect of process variables on Co desorption efficiency by Na_2EDTA, with the highest yield of extraction achieved at their maximum levels. The curvature in system responses occurred in case when CA was used as reagent, due to the quadratic term in the model equation, whereas in case of HCl due to the significant interaction effect between the reagent concentration and applied volume.

Similar predictions were made for final pH values as response functions, using Eqs. (9)–(11), and the contour plots are given for statistically significant parameters (**Figure 3**).

The contour graphs, as well as the ANOVA results, signify that increase of the initial reagent concentration provoked decrease in the final pH. Furthermore, pH declined with increased volume of the reagents. In contrast, longer reaction times contribute only to higher pH of HCl solution.

If multiple system responses are considered in the same experiment, their simultaneous analysis could be essential to optimize the process. Construction of overlaid contour plots enables determination of the ranges of process variable which lead to the achievement of the target effect. These plots are constructed by overlaying the contour plots of each considered response. The responses defined in the presented study, final pH values of the filtrate and extraction efficiency, are related: the lower the pH—the higher extraction yield (**Figures 2** and **3**). However, high acidity of extracting solutions may cause the degradation of soil vital properties due to significant degradation of both mineral and organic phase [43], making the soil inappropriate for on-site disposal and re-vegetation after completion of the treatment. Furthermore, the

Figure 3. Contour plots for the final pH of extracts: (a) EDTA, (b) CA, and (c) HCl, presenting the relationships between calculated responses and statistically significant factors, at the constant intermediate value of the third factor (A—reagent concentration, B–soil/solution ratio, C—extraction time).

obtained filtrates represent liquid waste which requires further management (neutralization, metal recovery, reagent recovery, etc.). Thus, both the wastewater and the processed soil would need to be neutralized, increasing the complexity and cost of the treatment.

Therefore, the performance of different reagents was compared using near neutral final pH (5–7) and Co extraction efficiency >50%, as target values. Under these conditions, overlaid contour plots were constructed for Na$_2$EDTA and CA (**Figure 4a** and **b**). On the other hand, desired response values could not be reached simultaneously using HCL, and the target value of Co extraction was decreased to >40% (**Figure 4c**).
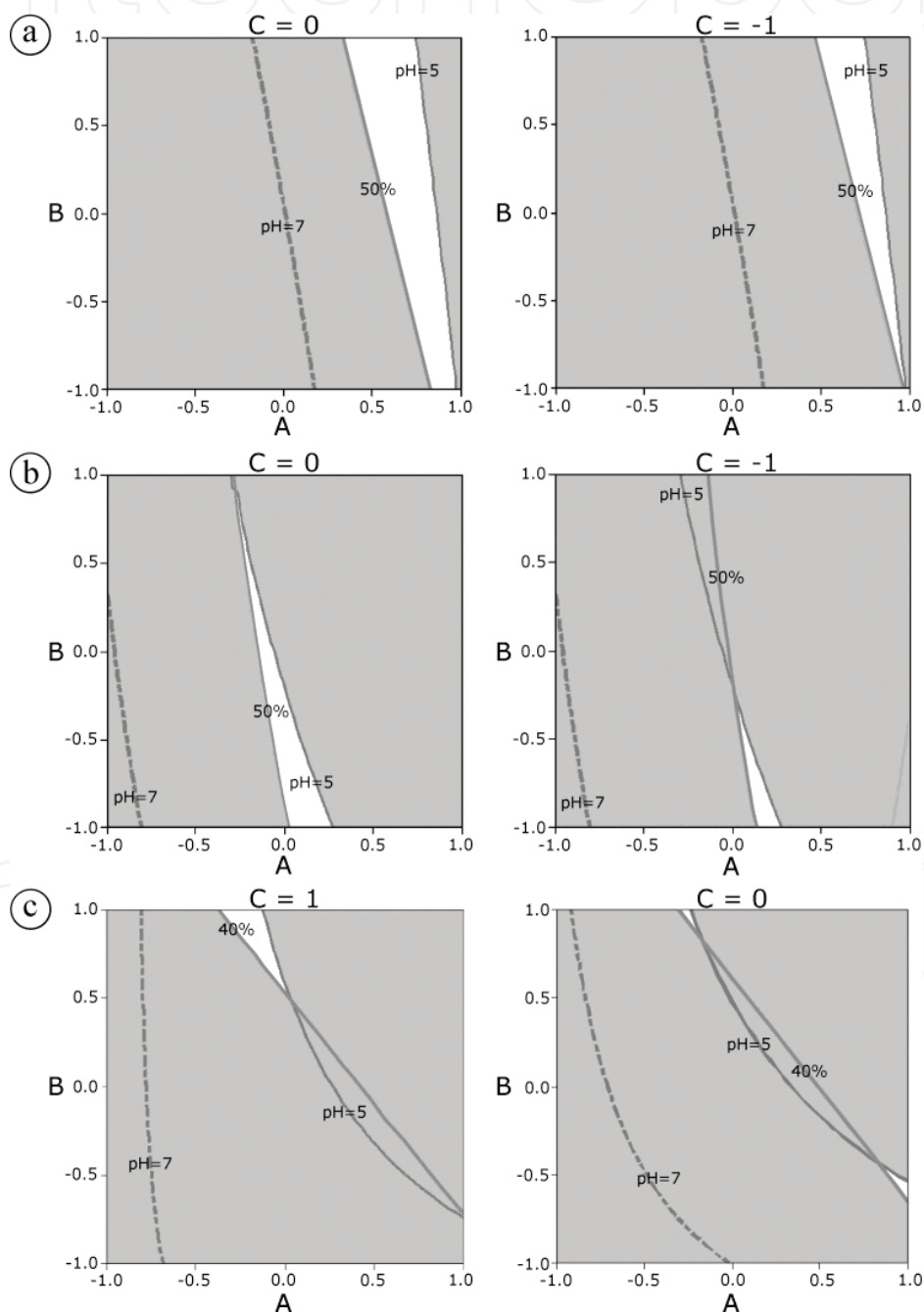
Figure 4. Overlaid contour plots for determination of process conditions which lead to achievement of target system responses using (a) Na$_2$EDTA, (b) CA, and (c) HCl (A—reagent concentration, B—soil/solution ratio, C—extraction time).

The white areas in the constructed plots present the ranges of factors A and B that provide given responses, at different contact times (C). Using Na$_2$EDTA, target response values can be obtained for contact times of 1 h, as well as 3.5 h, by selecting reagent concentration and volume in the designated ranges. Designated area is wider for 3.5 h, which practically means that if the duration of extraction is increased the desired responses can be gained at lower reagent concentrations. For the same extraction times, using CA instead of Na$_2$EDTA (**Figure 4b**), target values of Co desorption efficiency and solution pH can be obtained using initial concentrations and volumes of the reagent in much lower ranges. The effect of HCl was limited since it is governed by pH decrease (**Figure 4c**). Approximately 40% of sorbed Co ions can be leached under conditions that simultaneously assure target pH of the extract, at higher contact times (6 and 3.5 h).

Such results may be indicative for further evaluation of reagents. Consideration of the advantages and disadvantages related to the application of a chemical reagent includes the environmental impact and overall costs. Although HCl is often used for chemical leaching at full-scale, its effect is limited in calcareous soils. Consumption of high amounts of acid reagent would be necessary to provide efficient Co separation, which would in turn results in dissolution and degradation of soil matrix, creation of acidic waste water and soil residue. On the other hand, by selection of factor levels, complexing agents provide more efficient decontamination, even at near neutral pH conditions. Leaching of soil by chelating agents is potentially detrimental to its quality if a part of the chelating agent remains in the soil. As a natural compound, CA undergoes biodegradation process more easily compared to Na$_2$EDTA [45]. Furthermore, CA is less expensive chelating reagent [46], which supports the selection of CA among the tested reagents.

5. Conclusion

The Box-Behnken design was applied for screening and analyzing the factors affecting soil chemical extraction process using the sample of calcareous soil artificially contaminated with Co ions. Using Na$_2$EDTA, CA, and HCl as reagents, the effect of variation of three factors (concentration of the chemical reagent, soil/liquid ratio, and the contact time between the phases) between three levels was analyzed in respect to extraction efficiency and final pH values. The adequacy of different mathematical models, with inclusion of linear or quadratic terms, was tested for the description of experimental results. The extraction efficiency was highly dependent of the applied chemical reagent. Analysis of variance of the chosen responses revealed that Co separation was predominantly affected by the variation of the reagents concentrations. Effect of applied reagents volume had smaller statistical significance, while the contact time played an important role in the performance of complexing agents. Mathematical models were developed to describe the effect of each independent parameter and their interactions on system response. Predicted values of Co recovery, obtained using model equations, were in good agreement with the experimental data. Treatments by different reagents were compared using overlaid contour plots, taking into consideration extraction efficiencies in near neutral range of final pH values. The results demonstrate limited effect of HCl in cancerous soil, while chelating agents can exhibit high efficiencies by selection of factor

levels. CA stands out as the most suitable agent, due to its performance, price, and biodegradability. The applicability of RSM for fast assessment and comparison of soil treatments was verified, highlighting the significance of DOE in practical applications.

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