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Optimizing Chemical Extraction of Heavy Metals from Anaerobically Digested Sewage Sludge Using Response Surface Methodology

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Abstract: **The presence of heavy metals in digested sewage sludge presents an environmental concern of great proportions owing to the large per capita sludge volumes involved globally. Besides, sludge having high heavy metal concentration is also not suitable for agricultural purposes hence the need for heavy metal removal prior to disposal or use at the farm level. Determination of the optimal conditions for heavy metals extraction from anaerobically digested sewage sludge is thus warranted. The goal of this study was therefore to employ a response surface methodology to optimize chemical extraction of heavy metals (Zn, Cu, Pb, and Ni) using the full factorial design. The three factors considered were pH, hydrogen peroxide dosage, and extraction time. The results were analyzed statistically using analysis of variance, F-test, and lack of fit to identify the most important process variables affecting the heavy metal extraction efficiency. For the heavy metals studied, the most significant effect was ascribed to extraction time followed by Hydrogen peroxide dosage and the interaction of the two. The pH effect and the interaction between pH and time also had an influence in the heavy metal extraction efficiency. There was no significant interaction between pH and Hydrogen peroxide dosage in the extraction of heavy metals under the tested conditions. The optimal conditions of heavy metals extraction obtained were pH (3), extraction time (10 days) and Hydrogen peroxide of (1g/l). The percentage extraction at these conditions was above 98% for all the heavy metals. These results are promising for the management of digested sewage sludge.**

Keywords: **Chemical extraction, Heavy metals, Response surface, Sewage sludge.**

1. INTRODUCTION

The removal of heavy metal from sludge before disposal or application to farmland is a necessary step to achieve a more safe sludge usage or disposal [1]. Currently, methods such as membrane filtration, ion exchange, reverse osmosis and electrochemical extraction used for heavy metal removal from sewage sludge are quite expensive [2]. Therefore, efforts have to be directed toward finding strategies that are less expensive and less damaging to soil properties.

A bioleaching system produces sludge with reduced amounts of both toxic metals and pathogenic organisms [3]. Although it has the advantage of heavy metals recovery [4], its major disadvantage is the sensitivity of microorganisms to high metals toxicity levels [5]. [6] observed that Ion exchange is a versatile process which accommodates metal ion concentration variations and reasonable changes in flow rate without deterioration in performance however it has major limitations of high capital and operation costs when the heavy metals concentrations are high and the sensitivity to particles present. It has been observed that electrodialysis has main shortcomings of limited strength and high cost of the cation selective membrane. In addition high power consumption makes its industrial applications rare [7]. In adsorption method the fact that the adsorbents can be reactivated and reused is a major advantage of this method. However, treating large quantities of waste water would require large beds which will require a large inventory of expensive adsorbents leading to high capital cost. In addition adsorbents progressively deteriorate in capacity as number of cycles increases and as a result the large quantities of spent adsorbents containing heavy metals may be considered a hazardous waste [8]. The limitations associated with reverse osmosis involve the sensitivity of the membrane. Organics as well as other impurities precipitate lead causing membrane fouling. It is therefore necessary to have a consistent composition of the influent waste stream, which is hard to achieve in a wastewater treatment plant. In addition the process also requires elevated pressures that drive up the operating costs due to pumping [9].

[10], found out that heavy metals can be mobilized from sludge particles by changes in pH and ORP (oxidation-reduction potential) conditions. Chemical oxidation by addition of an oxidizing agent like Hydrogen peroxide applied before acidification increases the ORP of the sludge, promoting the oxidation of the non-soluble metal forms to crystal forms that would be dissolved at low pH. The extractive yield of Heavy metals in sludge depend on the kind and concentration of acids used [11]. According to [1] organic acids such as Citric and Oxalic acids are promising chemical extracting agents for removal of heavy metals from contaminated sludge, since they are biodegradable and can attain a higher metal extraction efficiency at mildly acidic pH compared to other extracting agents.

In this study, investigation was carried out to test the effect of PH, time and chemical oxidation on the efficiency of heavy metal extraction using Citric acid with the aim of finding the optimal conditions of heavy metals extraction. Full Factorial design was employed to model the heavy metals extraction process. The design consisted of all possible combinations of levels for all factors. Three factors and two levels design were used. A sensible low and high level for each factor was chosen to determine the experimental domain. This design was used because the factors are not more than four [12].The optimization of heavy metals extraction was performed using a multiple response method called desirability (D) function to optimize the extraction parameters (pH, hydrogen peroxide dosage and extraction time). The extraction parameters optimized by targeting maximum removal (D=1).

2. MATERIALS AND METHODS

2.1 Experimental Procedure:

Samples of freshly deposited anaerobically digested sewage sludge were collected in standard containers from the Kariobangi sewage treatment works, in Nairobi, air dried, crushed and sieved through 2mm sieve. A representative sample of 250 gms was retained by coning and quartering. The samples were then ground in a mortar in order to pass through a 60 mesh screen. Physical and chemical characteristics of the sewage sludge were analysed using standard methods and procedures as described by [13]. These included pH, Total Nitrogen and Total Phosphorous and Heavy metals **(Zn, Pb, Ni, Cu, Cd, Cr and Fe)**.

2.2 Analysis for heavy metals:

The standard series, suitably diluted sample and blank digests were aspirated into the AAS calibrated for heavy metal measurement at the appropriate wavelength and absorbance measured. The concentation of the heavy metals in the samples and blanks was then determined. The concentration of the heavy metal in the dried sample was calculated as follows,

$$\text{Hm (mg/Kg)} = \left[\frac{(a-b) \, x V x \; f \; x1000}{1000 x \, W}\right]$$

Where; a= Concentration of Hm in the solution, b= Concentration of Hm in the mean values of the blanks, V= Final volume of the digestion process, W= Weight of the sample, f= Dilution factor, Hm= Heavy metal, [13].

2.3 Extraction of heavy metals from sewage sludge:

7 g of sewage sludge were mixed with 140 ml of distilled water in 500 ml Erlenmeyer flask. Citric acid was added to the sewage sludge solution to adjust pH to pH5 and 3pH.The mixtures were stirred continuously at 125 rpm at room temperature for 2hrs. Hydrogen peroxide (H_2O_2) dosages were added to the samples and kept shaking. Citric acid was added to the sewage sludge solution to maintain pH atpH5 to 3pH±0.1.Samples of 5 mls were collected at times interval

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of 1day and 10 days). The 15mls samples were centrifuged at 4000 rpm for 30 minutes. The supernatant was filtered through a filter paper. The filtrate was analysed for heavy metals (Cu, Pb, Ni and Zn) using AAS. The experiments were carried out in duplicate.

2.4 Experimental design:

A two-level, three-factor full factorial experimental design was used. Design © Expert9 software was used in ANOVA and regression analysis. A total of 16 experiments, including replicates were conducted. For each experiment a control experiment was also setup. The three independent factors considered were pH, Hydrogen peroxide dosage, and extraction time at two different levels were, pH (3.0 and 5.0), hydrogen peroxide dosage (1g/l and 5g/l), and extraction time (1day and 10 days). The codes A, B and C, represented the independent variables pH, Extraction time and Hydrogen peroxide dosage respectively. The experimental design matrix is shown on table 1.

Table-1: Experimental design matrix

RUN	A (pH)	B (Time)	C (H_2O_2)
1	3	1	1
2	5	1	1
3	3	10	1
4	5	10	1
5	3	1	5
6	5	1	5
7	3	10	5
8	5	10	5

The general mathematical model for full factorial design in coded values tested was:

$$Y\% = X_O + X_1A + X_2B + X_3C + X_4AB + X_5AC + X_6BC + X_7ABC \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$ [14],

where, *Y%* is the percentage of heavy metals (Zn, Pb, Cu, Ni) extracted from the sewage sludge, X_o is the global mean, X_i represents the other regression coefficients and A, B and C are the coded symbols for the factors under study as shown in table 1. After determining the main effects, the effect of interactions were obtained by performing the analysis of variance (ANOVA).

3. RESULTS AND DISCUSSIONS

The observed characteristic properties of anaerobically digested sewage sludge are as given in table 2.

Table-2: Sludge physical and chemical characteristics

Heavy Metal	NEMA Guide value (max allowable)	THIS STUDY (Mean values)
Chromium(mg/l)	2	ND
Cadmium (mg/l)	0.01	ND
Copper (mg/l)	1.0	**0.6510**
Lead (mg/l)	0.1	**0.4125**
Nickel (mg/l)	0.3	**0.2140**
Zinc (mg/l)	0.5	**0.9603**
pH	6.5-8.5	**6.75**
TOTAL N (%)	2	**1.21**
TOTAL P (%)	2	**1.93**
Iron(mg/l)	10	**5.093**

The mean values of **pH,** Copper, Iron, and Nickel concentrations and Percentage Nitrogen, Phosphorous, were lower than the National Environment Management Authority (NEMA) ceiling values [15]. However the concentrations of Lead and Zinc were higher than the NEMA maximum allowable value. Chromium and Cadmium were not detected in the sewage sludge. Iron concentration was the highest among the heavy metals. The amount of iron present (5.1 mg/l) met the

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minimal threshold concentration of 3-15 mg/l Fe that allows the Fenton reaction to proceed within a reasonable period of time regardless of the concentration of organic material during chemical extraction of heavy metals [16].

3.1 Model equations for heavy metals extraction:

The selected factorial models values were as shown on table 3 while the ANOVA for the selected factorial models is shown in table 4. The Model F-value of 140.94 (Zn), 413.54 (Pb), 182.79 (Ni) and 92.18 (Cu) implied the models are significant. From the *P* values the main effect of each factor and the interaction effects are statistically significant when $P < 0.05$. In this case A, B, C, AB, and BC are significant model terms. Values of "Prob> F" less than 0.0500 indicate model terms are significant. There is only a 0.71%, 0.24%, 0.54%, 1.08%, for Zn, Pb, Ni, and Cu respectively, chance that an F-value this large could occur due to noise.

Table-3: Selected heavy metals extraction models Coefficients

(a)					**Zinc**
	Coefficient		**Standard**	**95% CI**	**95% CI**
Factor	**Estimate**	**df**	**Error**	**Low**	**High**
Intercept	96.78	1	0.14	96.19	97.37
A	-0.65	1	0.14	-1.24	-0.058
B	2.37	1	0.14	1.78	2.96
C	1.99	1	0.14	1.40	2.58
AB	0.69	1	0.14	0.099	1.28
BC	-1.68	1	0.14	-2.27	-1.09
(b)					**Lead**
	Coefficient		**Standard**	**95% CI**	**95% CI**
Factor	**Estimate**	**df**	**Error**	**Low**	**High**
Intercept	95.55	1	0.14	94.96	96.13
A	-0.64	1	0.14	-1.23	-0.050
B	3.92	1	0.14	3.33	4.51
C	3.48	1	0.14	2.89	4.07
AB	0.64	1	0.14	0.055	1.23
BC	-3.24	1	0.14	-3.83	-2.65
(c)					**Nickel**
	Coefficient		**Standard**	**95% CI**	**95% CI**
Factor	**Estimate**	**df**	**Error**	**Low**	**High**
Intercept	97.07	1	0.11	96.59	97.54
A	-0.67	1	0.11	-1.14	-0.20
B	2.25	1	0.11	1.77	2.72
C	1.76	1	0.11	1.28	2.23
AB	0.62	1	0.11	0.15	1.09
BC	-1.45	1	0.11	-1.93	-0.98
(d)					**Copper**
	Coefficient		**Standard**	**95% CI**	**95% CI**
Factor	**Estimate**	**df**	**Error**	**Low**	**High**
Intercept	96.56	1	0.18	95.78	97.34
A	-0.84	1	0.18	-1.61	-0.057
B	2.36	1	0.18	1.58	3.14
C	2.20	1	0.18	1.42	2.98
AB	0.86	1	0.18	0.084	1.64
BC	-1.80	1	0.18	-2.58	-1.02
Cl - Confidence Level, A-pH, B-Extraction Time, C-Hydrogen Peroxide Dosage, df- Degrees Of Freedom					

The "Predicted R-Squared" of 0.9547(Zn), 0.9845 (Pb), 0.9651 (Ni) and 0.9309 (Cu) is in reasonable agreement with the "Adjusted R-Squared" of 0.9901 (Zn), 0.9966 (Pb), 0.9924 (Ni) and 0.9849 (Cu); i.e. the difference is less than 0.2.R^2 was used to check the goodness of fit of the model. The R^2 values provide a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions. The R^2 value is always between 0 and

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1. The closer the R^2 value is to 1, the stronger the model is and the better it predicts the response [17]. When expressed as a percentage, R^2 is interpreted as the percent variability in the response explained by the statistical model. In this case, the value of the determination coefficient (R^2= 0.9972 (Zn), 0.9990 (Pb), 0.9978 (Ni) and 0.9957 (Cu)) indicate that 99.72% (Zn), 99.9% (Pb), 99.78% (Ni) and 99.57% (Cu) of the variability in the response could be explained by the models. In addition, the values of the adjusted determination coefficient (Adjusted R^2= 0.9901(Zn), 0.9966(Pb), 0.9924(Ni), 0.9849 (Cu)) were also very high to advocate for a high significance of the model. These ensured a satisfactory adjustment of the polynomial model to the experimental data. The adjusted R^2 corrects the R^2 value for the sample size and the number of terms in the models. In this case, the adjusted R^2values were very close to the R^2 values and therefore the models were good for all the heavy metals under this study.

Table-4: ANOVA for selected factorial models

(a)						**Zinc**
	Sum of		**Mean**	**F**	**p-value**	**Statistical**
Source	**Squares**	**df**	**Square**	**Value**	**Prob> F**	**significance**
Model	106.08	5	21.22	140.94	0.0071	significant
A	3.37	1	3.37	22.36	0.0419	significant
B	44.88	1	44.88	298.15	0.0033	significant
C	31.57	1	31.57	209.70	0.0047	significant
AB	3.79	1	3.79	25.21	0.0375	significant
BC	22.47	1	22.47	149.28	0.0066	significant
Residual	0.30	2	0.15			
Cor Total	106.38	7				
R^2 = 0.9972 , Adjusted R^2=0.9901, Predicted R^2=0.9547						
(b)						**Lead**
	Sum of		**Mean**	**F**	**p-value**	**Statistical**
Source	**Squares**	**df**	**Square**	**Value**	**Prob> F**	**Significance**
Model	310.20	5	62.04	413.54	0.0024	Significant
A	3.27	1	3.27	21.77	0.0430	Significant
B	122.89	1	122.89	819.15	0.0012	Significant
C	96.94	1	96.94	646.17	0.0015	Significant
AB	3.32	1	3.32	22.13	0.0423	Significant
BC	83.78	1	83.78	558.46	0.0018	Significant
Residual	0.30	2	0.15			
Cor Total	310.50	7				
R^2 = 0.9990, **Adjusted R^2**=0.9966, **Predicted R^2**=0.9845						
(c)						**Nickel**
	Sum of		**Mean**	**F**	**p-value**	**statistical**
Source	**Squares**	**df**	**Square**	**Value**	**Prob> F**	**significance**
Model	88.68	5	17.74	182.79	0.0054	significant
A	3.60	1	3.60	37.08	0.0259	Significant
B	40.43	1	40.43	416.71	0.0024	Significant
C	24.66	1	24.66	254.13	0.0039	Significant
AB	3.07	1	3.07	31.63	0.0302	Significant
BC	16.92	1	16.92	174.40	0.0057	Significant
Residual	0.19	2	0.097			
Cor Total	88.87	7				
R^2 = 0.9978, **Adjusted R^2**=0.9924, **Predicted R^2**=0.9651						
(d)						**Copper**
	Sum of		**Mean**	**F**	**p-value**	**statistical**
Source	**Squares**	**df**	**Square**	**Value**	**Prob> F**	significance
Model	120.88	5	24.18	92.18	0.0108	significant
A	5.59	1	5.59	21.30	0.0439	Significant
B	44.56	1	44.56	169.90	0.0058	Significant
C	38.75	1	38.75	147.74	0.0067	Significant

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AB	5.96	1	5.96	22.72	0.0413	Significant
BC	26.03	1	26.03	99.23	0.0099	significant
Residual	0.52	2	0.26			
Cor Total	121.40	7				
R^2 = 0.9957**, Adjusted R^2**=0.9849**, Predicted R^2**=0.9309						
Cl - Confidence Level, A-pH, B-Extraction Time, C-Hydrogen Peroxide Dosage, df- degrees of Freedom						

Final heavy metals extraction model equations in terms of coded factors were as follows on eliminating the terms with no statistical significance:

$$Y\% = 96.78 - 0.65A + 2.37B + 1.99C + 0.69AB - 1.68BC$$ ………….. (Eqn. 4.5) for Zinc,

$$Y\% = 95.55 - 0.64A + 3.92B + 3.48C + 0.64AB - 3.24BC$$ ………….. (Eqn. 4.6) for Lead,

$$Y\% = 97.07 - 0.67A + 2.25B + 1.76C + 0.62AB - 1.45BC$$ …………… (Eqn. 4.7) for Nickel,

$$Y\% = 96.56 - 0.84A + 2.36B + 2.20C + 0.86AB - 1.80BC$$ …………….(Eqn. 4.8) for Copper.

Where Y% is the percentage heavy metal extracted.

3.2 Normal Probability Plot:

The normal probability plot of the residuals of the heavy metals under study percentage extraction from sewage sludge were as shown in Figures1, 2, 3, and 4.

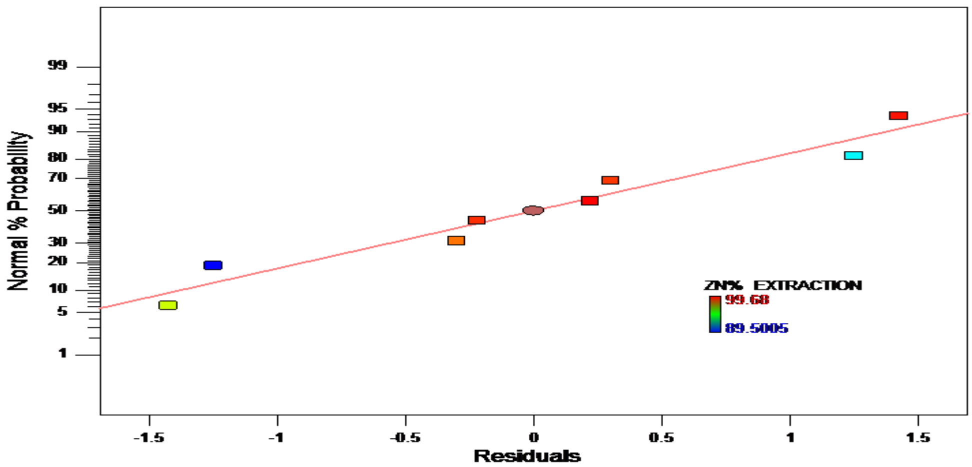

Figure 1: Normal probability plot of residuals for Zinc extraction

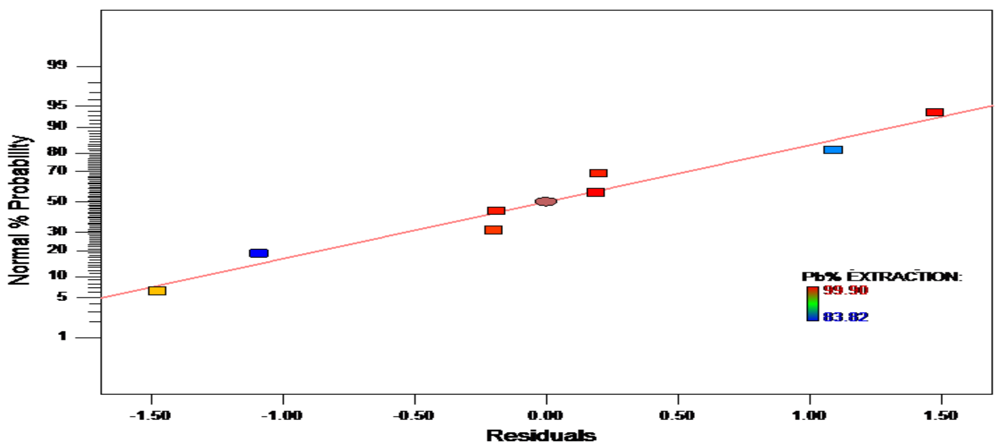

Figure 2: Normal probability plot of residuals for Lead extraction

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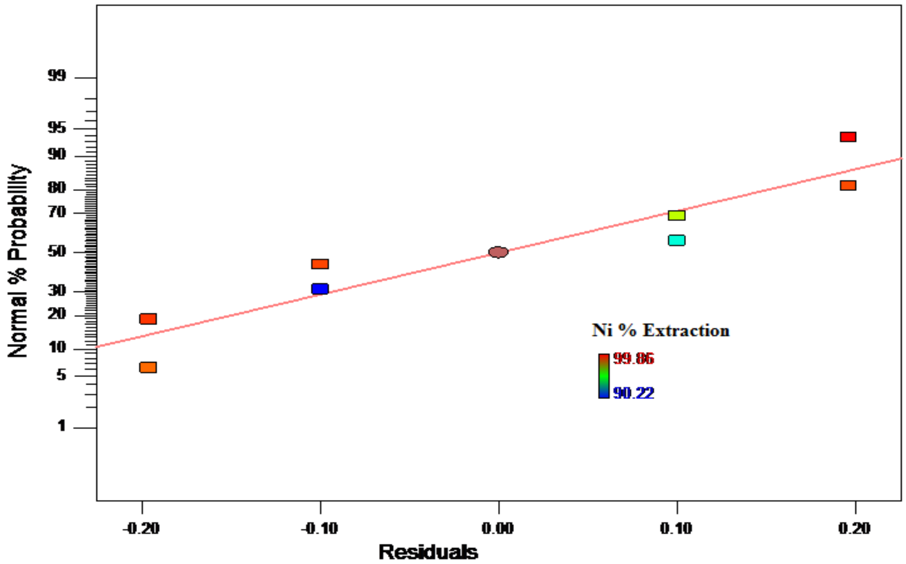

Figure 3: Normal probability plot of residuals for Nickel extraction

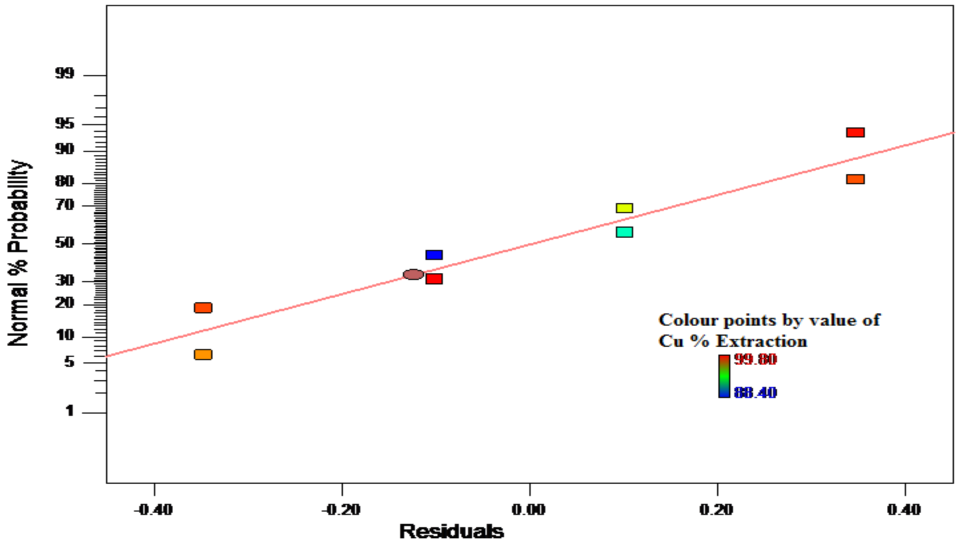

Figure 4: Normal probability plot of residuals for Copper extraction

The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. The normality of the data can be checked by plotting a normal probability plot of the residuals (differences between the predicted (model) and the observed (experimental) ones). If the data points fall fairly close to the straight line, then the data is normally distributed [18]. The statistical analysis of the data in terms of the residual was conducted to verify the normality of the data. The data points fairly close to the straight line indicate that the experiments came from a normally distributed population. Checking the adequacy of the model needs all of the information on lack of fit, which is contained in the residuals. The normal percentage probability plot of the residuals is an important diagnostic tool to detect and explain the systematic departures from the assumptions that errors are normally distributed and are independent of each other and that the error variances are homogeneous [17]. The normal probability plot of the residuals indicates almost no violation of the assumptions underlying the analyses of heavy metals Zn, Pb, Ni and Cu.

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3.3. Optimization for heavy metals extraction

The 3D surface plot of the heavy metals extraction is shown in Figure 5, 6, 7, and 8.

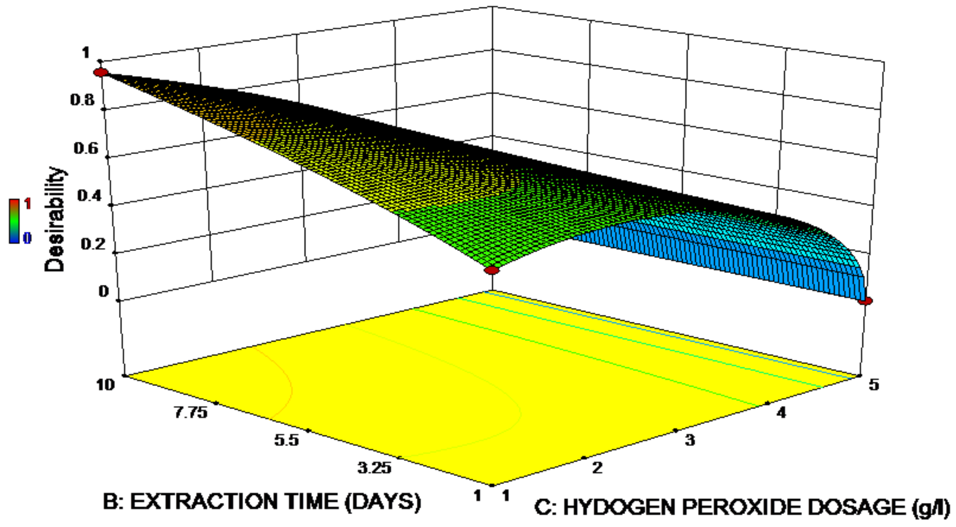

Figure 5: Desirability fitted 3D surface plot for Zinc extraction at pH3.

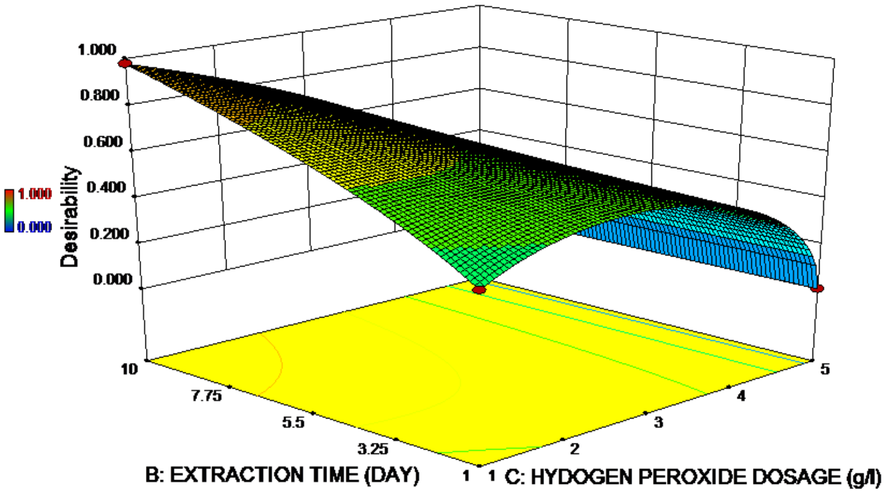

Figure 6: Desirability fitted 3D surface plot for Lead extraction at pH3.

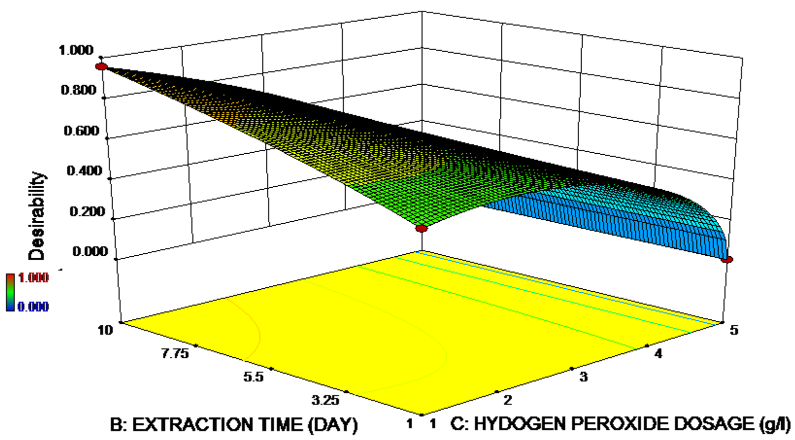

Figure 7: Desirability fitted 3D surface plot for Nickel extraction at pH3.

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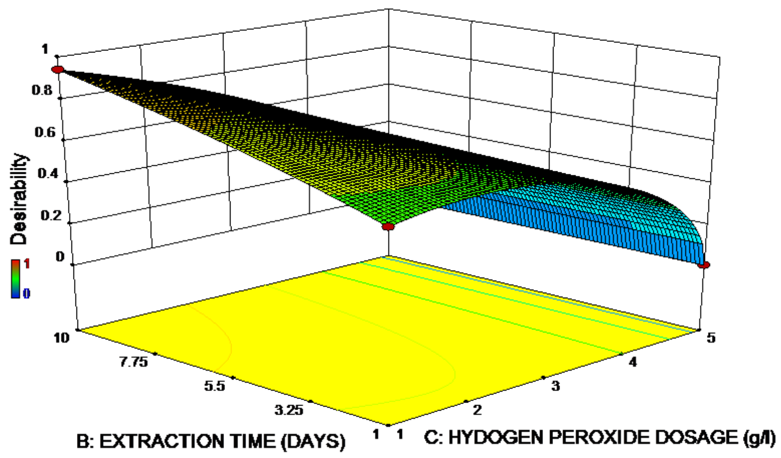

Figure 8: Desirability fitted 3D surface plot for Copper extraction at pH3.

Optimization of the heavy metals removal was performed by using a multiple response method called desirability (D) function to optimize the extraction parameters (pH, Hydrogen peroxide dosage and extraction time). The main factors pH, Hydrogen peroxide dosage and extraction time were optimized by targeting maximum removal (D=1) of the heavy metals. Hydrogen peroxide dosage was set to be minimised, extraction time were set to be within the studied range, whereas pH was set to lowest (pH3). Hydrogen peroxide dosage and extraction time were targeted for the optimum within the range. This was done in consideration of cost in extraction process and given that the holding time for sewage sludge during treatment is long enough to give the allowance of the studied range of up to 10 days. The optimisation process desirability, D=0.956 (Zn), 0.978 (Pb), 0.958 (Ni), 0.941 (Cu) which was close to the targeted value of 1 for all the heavy metals studied.

3.4. Validation Experiments for heavy metals extraction:

Verification of the optimized results was done by performing an experiment under predicted conditions by the developed models. The models predicted 98.8% (Zn), 99.22% (Pb), 99.07% (Ni) and 98.5% (Cu) removal at pH3, hydrogen peroxide dosage of 1mg/L, and extraction time 10 days. The experimental values obtained at these conditions are 98.41% (Zn), 98.78% (Pb), 98.62% (Ni), 98.15% (Cu) and is closely in agreement with the result obtained from the model and hence validated the findings of the optimization. This extraction percent was higher than that obtained using Citric acid by [1] who obtained 68% (Zn), 66% (Pb), 65% (Ni) and 51% (Cu) using effect of pH and extraction time only. This can be attributed to the use of hydrogen peroxide causing rise in ORP of the sludge that promoted the oxidation of the non-soluble metal forms to crystal forms that would be dissolved at low pH.

4. CONCLUSION & RECOMMENDATIONS

4.1 Conclusions:

The results showed that the anaerobically digested sewage sludge from Kariobangi sewage treatment plant contains high amounts of Nitrogen, Phosphorous. This implies that it can be used as an organic fertilizer in agriculture. The high heavy metals content of the sludge clearly indicated that they must be extracted before its application on agricultural land. The option of using Citric acid and chemical oxidation with Hydrogen peroxide was investigated and found to be a feasible option. The use of factorial design allowed the identification of the most important parameters for extraction of heavy metals Zn, Pb, Ni and Cu under tested conditions. For heavy metals Zn, Pb, Ni and Cu the most significant effect was ascribed to extraction time followed by Hydrogen peroxide dosage and the interaction of the two. The pH effect and the interaction between pH and time also had an influence in removal heavy metals Zn, Pb, Ni and Cu efficiency. There was no significant interaction between pH and Hydrogen peroxide dosage in the extraction of heavy metals Zn, Pb, Ni and Cu under tested conditions. The optimal conditions of heavy metals Zn, Pb, Ni and Cu extraction from anaerobically digested sewage sludge were pH (3), extraction time (10 days) and Hydrogen peroxide of (1gm/l). The percentage extraction at these conditions was Zn (98.4%), Pb (98.8%), Ni (98.6%) and Cu (98.2%). This percentage extraction reduced the heavy metals concentration to below the NEMA maximum allowable values. Full factorial experiment design and response surface methodology are good techniques for studying the influence of major process parameters on responses because they help in reducing the number of experiments and henceforth, saving time, energy, and money. From this study it is evident that extraction of heavy metals using Citric acid from sewage sludge with chemical oxidation using hydrogen peroxide is an efficient and viable option.

4.2 Recommendation:

Chemical oxidation using Hydrogen Peroxide with Citric acid acidification was found to be an excellent heavy metals extraction method from anaerobically digested sludge. Further studies should be carried-out to establish its efficiency in other types of sewage sludges.

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