

Screening and extraction of heavy metals from anaerobically digested sewage sludge

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Abstract - Heavy metals extraction from anaerobically digested sewage sludge is an important step towards achieving a safe usage of the large amounts of sewage sludge on agricultural land. The extraction reduces heavy metals accumulation in soil and their bioaccumulation in plants, animals and humans through food-chain thus reducing both human health problems and adverse environmental impacts. Chemical extraction of heavy metals from anaerobically digested sewage sludge using Citric acid was studied using the full factorial design. The three factors considered were pH, Hydrogen peroxide dosage, and extraction time at two different levels: pH (3.0 and 5.0), hydrogen peroxide dosage (1g/l and 5g/l), and extraction time (1day and 10 days) with the objective of obtaining the models for the heavy metals extractions. The results were analyzed statistically using the Student's *t*-test, analysis of variance, *F*-test, to define the most important process variables affecting the heavy metal extraction efficiency. Lead had the highest extraction at 99.90%, followed by Nickel at 99.87%, Copper at 99.80% and Zinc at 99.68%. 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 extraction efficiency of heavy metals. 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.

Key Words: Sewage sludge, Heavy metals, chemical leaching, Citric acid, Hydrogen peroxide

1. INTRODUCTION

Wastewater treatment and the management of the solids it produces are global issues, with growing challenges, that must address the concerns of all of the stakeholders, including the facility administrators and operators, the regulators, the politicians, the scientific community, the wastewater generators, the taxpayers and the general public [1]. Sewage sludge contains high heavy metal concentrations in addition to useful high quantities of nutrients and organic matter needed for plant growth. Heavy metals can accumulate in soil and in plants when sludge is applied as fertilizer. The potential accumulation of heavy metals in human tissues and biomagnification through the food-chain create both human health problems and environmental

impacts [2]. Heavy metals are harmful to both human and animals [3]. They are present in soluble form in the aqueous solution over a wide range of pH values and quite mobile in the natural environment [4]. 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 [5]. Currently, methods such as membrane filtration, ion exchange, reverse osmosis and electrochemical extraction used for heavy metal removal from sewage sludge are quite expensive [6]. Therefore, efforts have to be directed toward finding strategies that are less expensive and less damaging to soil properties.

Ideally the sludge coming out from a bioleaching system would present reduced amounts of both toxic metals and pathogenic organisms [7]. Although it has the advantage of heavy metals recovery [8], its major disadvantage is the sensitivity of microorganisms to high metals toxicity levels [9]. [10], highlighted 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 [11]. 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 [12]. 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 waste water treatment plant. In addition the process also requires elevated pressures that drive up the operating costs due to pumping [13]. The application of chemical extraction as a part of the treatment is a feasible

option, especially when it is applied as a pre-treatment aiming at heavy metals removal from sewage sludge. [14] observed 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 [15]. According to [5] 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 work, investigation was carried out using Citric acid to extract Zinc, Lead, Copper and Nickel from anaerobically digested sewage sludge. In addition, the effect of PH, time and chemical oxidation on the efficiency of the heavy metal extraction was analyzed. Full Factorial experimental 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 was 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 [16].

1.1 Sample collection and preparation

Samples of freshly deposited anaerobically digested sewage sludge were collected in standard containers from the Kariobangi sewage treatment works, in Nairobi. They were then packaged, labelled and stored.

1.2 Sample preparation

The sludge samples were 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.

2. Sludge characterization

Physical and chemical characteristics of the sewage sludge were analysed using standard methods and procedures as described by [17]. These included pH, Organic Carbon (OC), Total organic matter (OM), Total Nitrogen (TN) and Total Phosphorous, measured in percentage. Potassium and Heavy metals (Zn, Pb, Ni, Cu, Cd, Cr and Fe) were measured in mg/Kg Dry matter.

2.1 Chemical leaching of heavy metals

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 (H₂O₂) dosages were added to the samples and kept shaking. Citric acid was added to the sewage sludge solution to maintain pH at pH5 and 3pH±0.1. Samples of 15 mls were collected at times interval of 1day and 10 days and then 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.

3. Results and Discussions

The results for characterisation of anaerobically digested sewage sludge from Kariobangi sewage treatment works were as shown in table 1

Table-1: Sludge physical and chemical characteristics

	This Study	TV	HBM	EU	USA
pH	6.75±0.12	7.2	NA	6-7	NA
TN	1.21±0.02	1-8	3.5	NA	NA
TP	1.93±0.01	0.5-5	3.5	NA	NA
OM	41.85±0.07	NA	75	NA	NA
OC	14.05±0.02	5.2	NA	NA	NA
K	0.10±0.002	<1	0.2	NA	NA
Cu	486.67±12.96	800	500	1000	1500
Pb	338.25±0.47	150	200	750	300
Cr	ND	NA	NA	NA	NA
Cd	ND	NA	3	20	39
Ni	109.17±6.48	60	40	300	420
Zn	777.21±23.39	900	1000	2500	2800
Fe	4010.00±24.75	NA	NA	NA	NA

NA-Not available, ND-Not detected, HBM-Habitat Benchmark, TV-Typical values, EU-European Union

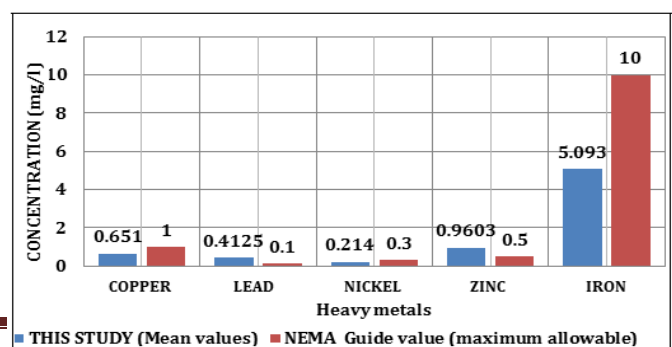


Chart-1: Heavy metals concentrations compared to NEMA Kenya standards

The mean pH value of sewage sludge was 6.75 showing that it is slightly acidic. This value was within the EU standards although lower than the typical value. Percentage Nitrogen and Phosphorous were within the NEMA, typical values and the UN habitat benchmark standards [1]. Total organic matter was lower than the UN-habitat benchmark. Organic carbon was higher than lower than the typical value. The heavy metals concentrations of copper were lower than the ceiling concentrations for all the standards considered in this study. However the concentrations of Lead and Nickel were higher than typical values, UN-habitat benchmark although within the EU standards. The concentrations of Lead and Zinc were higher than the NEMA maximum allowable value as shown on chart 1. The concentrations of Lead were higher than USA standards. Chromium and Cadmium were not detected in the sewage sludge. Iron concentration was the highest among the heavy metals as shown on chart 1. The amount of iron present (5.1 mg/l) meets the minimal threshold concentration of 3-15 mg/L Fe which 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 [18]. The Iron concentration in the sewage sludge was also within the NEMA standards as shown on chart 1. The study by [19] obtained concentrations of the heavy metals with mean values as; Zinc 1923 g/Kg, Copper 456g/Kg, Lead 410 g/Kg, Cadmium 5.8 g/Kg of dry matter. These values are comparable to those of this study with exemption of Cadmium which was not detected in this study. The high heavy metal concentrations could be attributed to the fact that Kariobangi sewage sludge plant receives waste water from industries in Nairobi and also surface runoff water from garages in the surrounding areas.

3.1 Heavy metals extraction

The percentage removal of heavy metals (Zn, Pb, Cu, Ni) at different levels was investigated at different condition of pH (A), time (B) and Hydrogen peroxide dosage (C) as shown on the experimental design matrix in table 2. The responses (Y%) i.e. percentage removal of heavy metals, for the design matrix by different conditions of pH, time and Hydrogen peroxide were presented in Table 2.

Table -2: Design matrix and mean responses.

RUN	DESIGN MATRIX			Y (%) (Zn)	Y (%) (Pb)	Y (%) (Cu)	Y (%) (Ni)
	A	B	C				
1	-1	-1	-1	92.00	86.00	92.00	93.00
2	+1	-1	-1	89.50	83.82	88.40	90.22
3	-1	+1	-1	98.54	99.02	98.15	98.87
4	+1	+1	-1	99.14	99.42	98.90	99.16
5	-1	-1	+1	99.50	99.82	99.80	99.22
6	+1	-1	+1	96.65	96.87	96.61	96.84

7	-1	+1	+1	99.68	99.90	99.64	99.87
8	+1	+1	+1	99.24	99.52	99.00	99.37

Lead had the highest extraction at 99.90%, followed by Nickel at 99.870%, Copper at 99.80% and Zinc at 99.68%.

3.2 Modelling extraction of Heavy metals

A linear regression model was fitted for the experimental data shown table 2. The model coefficients and effects of the factors and interactions are shown in Table 3 (a), (b) (c), and (d). After determining the main effects, the effect of interactions were determined by performing the analysis of variance (ANOVA). Sum of squares (SS) of each factor quantifies its importance in the process and as the value of SS increases, the significance of the corresponding factor in the process also increases [20].

Table -3: Regression coefficients of model terms and their effects on heavy metals extraction.

(a) Zinc					
Factor / Term	Effect	Coefficient	S-Error	Low (-) (95% CI)	High (+) (95% CI)
Intercept	-	96.78	0.14	92.00	99.24
A	-1.30	-0.65	0.14	97.43	96.13
B	4.74	2.37	0.14	94.41	99.15
C	3.97	1.99	0.14	94.79	98.77
AB	1.38	0.69	0.14	96.09	97.47
AC	-0.35	-0.17	0.14	96.95	96.61
BC	-3.35	-1.68	0.14	98.46	95.11
ABC	-0.17	-0.086	0.14	96.87	96.69
(b) Lead					
Intercept	-	95.55	0.14	83.82	99.52
A	-1.28	-0.64	0.14	96.18	94.91
B	7.84	3.92	0.14	91.63	99.47
C	6.96	3.48	0.14	92.06	99.03
AB	1.29	0.64	0.14	94.90	96.19
AC	-0.39	-0.195	0.14	95.74	95.35
BC	-6.47	-3.235	0.14	98.78	92.31
ABC	0.00	0.00	0.14	95.55	95.54
(c) Nickel					
Intercept	-	97.07	0.14	93.00	99.37
A	-1.34	-0.67	0.14	97.74	96.40
B	4.50	2.25	0.14	94.82	99.32
C	3.51	1.76	0.14	95.31	98.82
AB	1.24	0.62	0.14	96.45	97.69
AC	-0.10	0.00	0.14	97.12	97.02
BC	-2.91	-1.45	0.14	98.52	95.61
ABC	-0.30	0.00	0.14	97.22	96.92
(d) Copper					
Intercept	-	96.56	0.14	92.00	99.00
A	-1.67	-0.84	0.14	97.40	95.73
B	4.72	2.36	0.14	94.20	98.92
C	4.40	2.20	0.14	94.36	98.76

AB	1.73	0.86	0.14	95.70	97.43
AC	-0.25	-0.13	0.14	96.69	96.44
BC	-3.61	-1.80	0.14	98.37	94.76
ABC	-0.45	-0.23	0.14	96.79	96.34

The model coefficients were obtained by dividing the effects by two. The resultant models are represented as follows:

Zinc:
 $Y\% = 96.78 - 0.65A + 2.37B + 1.99C + 0.69AB - 0.17AC - 1.68BC$ (1)

Lead:
 $Y\% = 96.78 - 0.65A + 2.37B + 1.99C + 0.69AB - 1.68BC$(2)

Nickel:
 $Y\% = 97.07 - 0.67A + 2.25B + 1.76C + 0.62AB - 1.45BC$(3)

Copper:
 $Y\% = 96.56 - 0.84A + 2.36B + 2.20C + 0.86AB - 1.80BC - 0.225ABC$ (4)

Where Y% is the percentage heavy metal extracted.
 The ANOVA results for the heavy metals extraction from sewage sludge were presented in Table 4 (a), (b), (c) and (d).

Table -4: ANOVA results for heavy metals extraction

(a) Zinc						
F	SS	MS	F ₀	F _t	Sf	α
A	0.00067	0.00067	129.74	5.32	S	0.05
B	0.00898	0.00898	1730.34	5.32	S	0.05
C	0.00631	0.00631	1216.97	5.32	S	0.05
AB	0.00076	0.00076	146.31	5.32	S	0.05
AC	0.00005	0.00005	9.31	5.32	S	0.05
BC	0.00449	0.00449	866.35	5.32	S	0.05
ABC	0.00001	0.00001	2.29	5.32	NS	0.05
Error	0.00004	0.00001				
Total	0.02132					
(b) Lead						
A	0.0007	0.0007	49.09	5.32	S	0.05
B	0.0246	0.0246	1846.60	5.32	S	0.05
C	0.0194	0.0194	1456.65	5.32	S	0.05
AB	0.0007	0.0007	49.89	5.32	S	0.05
AC	0.0001	0.0001	4.5078	5.32	NS	0.05
BC	0.0168	0.0168	1258.92	5.32	S	0.05
ABC	0.0000	0.0000	0.0001	5.32	NS	0.05
Error	0.0001	0.0000				
Total	0.0622					
(c) Nickel						
A	0.0007	0.0007	6.46	5.32	S	0.05
B	0.0081	0.0081	72.61	5.32	S	0.05
C	0.0049	0.0049	44.28	5.32	S	0.05
AB	0.0006	0.0006	5.51	5.32	S	0.05
AC	0.0000	0.0000	0.03	5.32	NS	0.05
BC	0.0034	0.0034	30.39	5.32	S	0.05
ABC	0.0000	0.0000	0.32	5.32	N	0.05
Error	0.0009	0.0001				

Total	0.0187					
(d) Copper						
A	0.0011	0.0011	133.13	5.32	S	0.05
B	0.0089	0.0089	1062.01	5.32	S	0.05
C	0.0077	0.0077	923.47	5.32	S	0.05
AB	0.0012	0.0012	142.03	5.32	S	0.05
AC	0.0000	0.0000	2.89	5.32	NS	0.05
BC	0.0052	0.0052	620.29	5.32	S	0.05
ABC	0.0001	0.0001	9.61	5.32	S	0.05
Error	0.0001	0.0000				
Total	0.0243					
CI - Confidence Level, Sf- Statistical Significance, S-Significant, NS-Not Significant, SS- Sum of Squares, MS-Mean Square, α -Alpha, F-factor, Ft-F table						

In order to determine the important effects of heavy metals extraction from sewage sludge the F distribution (F_0) and F_{table} value were employed. Since $F_{table} = 5.32$, the value of 95.0% confidence level, all the effects in Table 4 giving F_0 greater than 5.32 have statistical significance [20]. Therefore ABC interaction had insignificant effect in the extraction of heavy metals (Zn, Lead and Nickel) and can be discarded because F_0 is less than F_{table} . In addition AC interaction had insignificant effect in the extraction of heavy metals (Lead, Nickel and Copper) and was discarded. To determine whether calculated effects were significant, Student's t -test was used. It was observed that for a 95% confidence level, the t -value was equal to 4.30265 for all the heavy metals. Those evaluations are illustrated by means of Pareto charts 2, 3, 4 and 5.

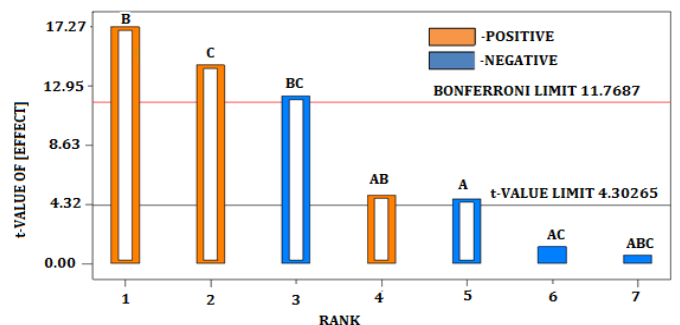


Chart -2: Pareto plot for effects of individual factors and interactions for Zinc extraction.

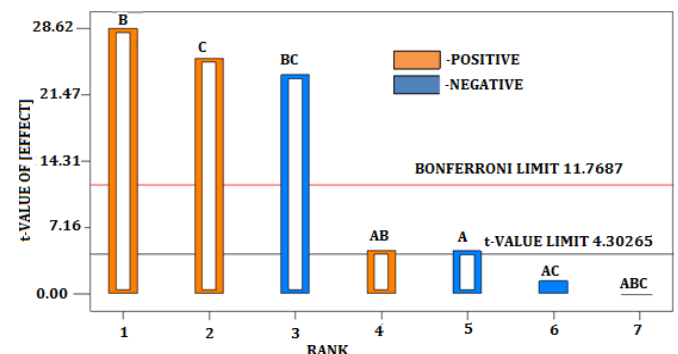


Chart -3: Pareto plot for effects of individual factors and interactions for Lead extraction.

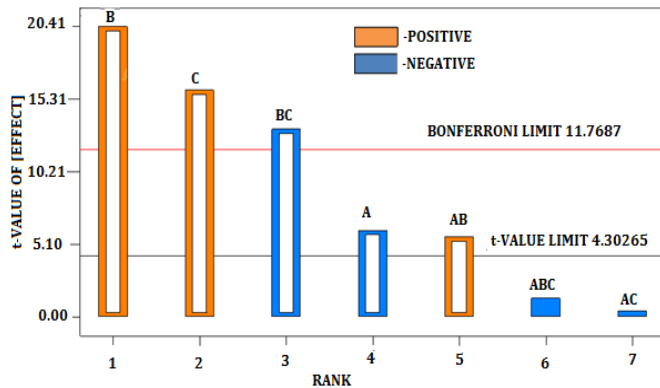


Chart -4: Pareto plot for effects of individual factors and interactions for Nickel extraction.

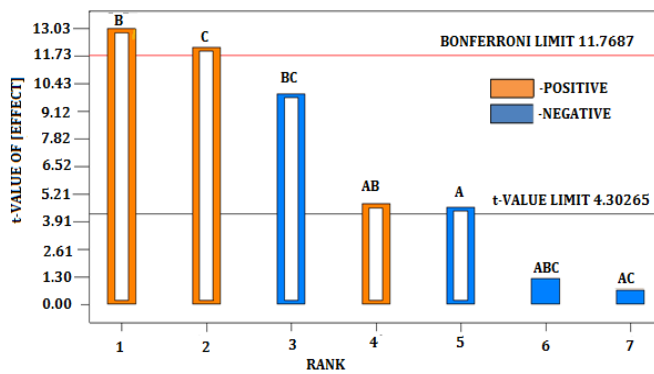


Chart -5: Pareto plot for effects of individual factors and interactions for Copper extraction.

The horizontal line indicates minimum statistically significant effect magnitude for a 95% confidence level. Effects above t-value (4.30265) limit are significant terms in the model. The main factors of Extraction time (B), Hydrogen peroxide dosage (C) and A (pH) and interactions such as BC significantly influenced the extraction of all the heavy metals. ABC and AC interaction were found to be of no importance in the extraction of all heavy metals from sewage sludge. Any factor or interaction of factors above Bonferroni limit (11.7687) had a major influence in the extraction of heavy metals.

3.3 Main Effects in extraction of heavy metals

The main factors and their effect on the extraction of heavy metals were shown graphically in chart 6, 7 and 8. The main effect plots are helpful in visualizing which factors affect the response the most (Nuran, 2007) [21]. The sign of the main effect indicates the direction of effect. A negative effect means that the response is higher at the low setting.

3.4 Effect of pH

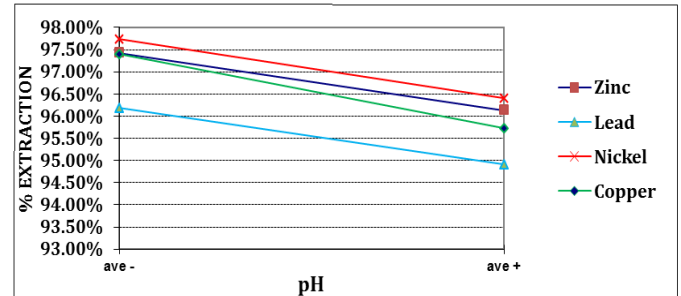


Chart -6: Effect of pH

As the pH lowered, the extraction of all the heavy metals increased as shown in chart 6. These results concur with the observation of [5] that a low pH value is required for the heavy metals to solubilize where the acid acts as a proton donor. In this case therefore, a low pH was necessary for solubilisation of the heavy metals with the highest value being 97.43% (Zinc), 96.18% (Lead) 97.74% (Nickel) and 99.34% (Copper). [14] states that a lower pH favours the solubilisation process hence the increase in percentage of heavy metals extracted as the pH decreased. Effect of pH on extraction of Nickel was highest among the heavy metals and it was least on extraction of lead. This suggested that Nickel-Organic bond strength is least among the heavy metals and it is highest in Lead. Among the main factors pH effect was ranked lowest as shown on the Pareto plot charts 2, 3 and 4 and 5. This could be explained from the fact that the change in pH was the smallest (between 3 and 5) among the main factors because Citric acid is a weak acid.

3.5 Effect of Hydrogen peroxide dosage

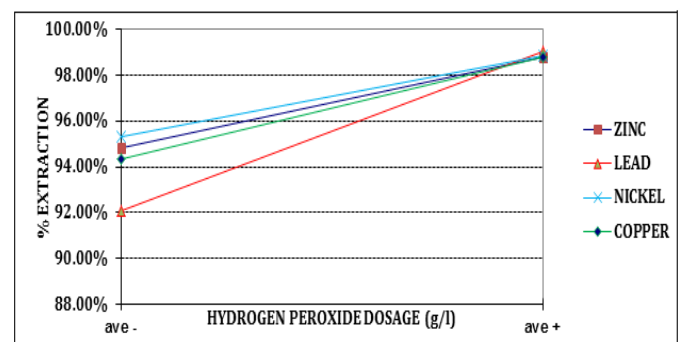


Chart -7: Effect of hydrogen peroxide dosage

As the Hydrogen peroxide dosage increased the percentage extraction of heavy metals from sewage sludge increased with the highest percentage extraction being 98.77% (Zn), 99.03% (Pb), 98.82% (Ni), 98.76% (Cu) as shown on chart 7. According to [14], in anaerobic sludges the heavy metals are present usually in their most reducible form, e.g., metal sulphides. [18] observed that the addition of Hydrogen

peroxide after acidification increases the oxidation-reduction potential of the sludge which results in solubilisation of more heavy metals in the presence of iron ions in the solution. Iron ions were abundant in the solution of the sewage sludge under study as shown in chart 1 and could not be exhausted at low hydrogen peroxide dosage. This applied for the extraction of the heavy metals in this study. Among the main factors, Hydrogen peroxide dosage effect was ranked intermediate as shown on the Pareto plot 2, 3, 4 and 5. Effect of Hydrogen peroxide dosage on extraction of Zinc was highest at high dosage among the heavy metals while it was lower than that of Nickel at low dosage. Its effect on extraction of Lead was lowest at low dosage and highest at high dosage. The highest extraction of Zinc increased from 97.43% due to pH to 98.77% due to Hydrogen peroxide dosage. Such behaviour could be justified by the destruction of organic matter due to Hydrogen peroxide treatment, which does not occur by only Citric acid acidification due to the high stability of Zinc complexes with organic matter. [14], observed that the rise in Oxidation-Reduction Potential (ORP) of the sludge promotes the oxidation of the non-soluble metal forms to crystal forms that would be dissolved at low pH. Oxidation-Reduction Potential (ORP) of the sewage sludge must have increased with addition of Hydrogen peroxide leading to increased extraction of Zinc.

3.6 Effect of leaching time

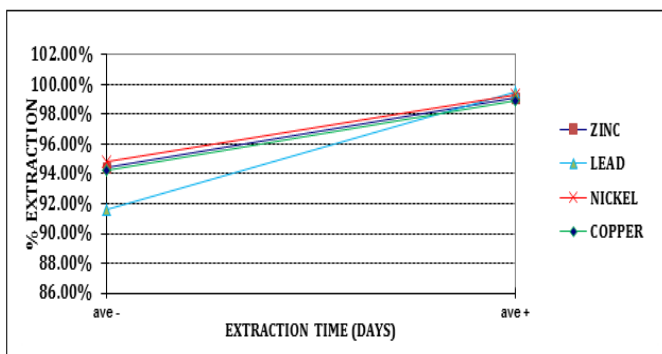


Chart -8: Effect of leaching time

As the leaching time increased the percentage extraction of all heavy metals increased as shown in chart 8. This could be attributed to the fact that as the extraction time increased the more stable heavy metals complexes were broken down hence releasing more heavy metals into solution with the highest percentage being 99.15% (Zn), 99.47% (Pb), 99.24% (Ni) and 98.86% (Cu). Among the main factors extraction time effect was ranked highest as shown on the Pareto plot 2, 3, 4 and 5. Extraction time plays a major role because it determines how well the other factors interact for effective extraction of the heavy metals. Effect of leaching time on extraction of Zinc was highest among the heavy metals at the beginning while it was highest on extraction of Lead at the end of the extraction time. This means that Zinc-Organic

bond is broken faster and therefore Zinc is solubilised faster than the other heavy metals.

3.7. Interaction Effects

Charts 9 to 20 show the two-factor interactions for heavy metals extraction from sewage sludge. The interactions of different factors influenced the response significantly can be observed from the Pareto chart 2, 3, 4 and 5. From table 4 the interaction effects of Time * hydrogen peroxide dosage (BC) and pH*extraction time (AB) are seen to be significant in the extraction of all the heavy metals.

3.8 Effect of pH*time interaction on the extraction of heavy metals.

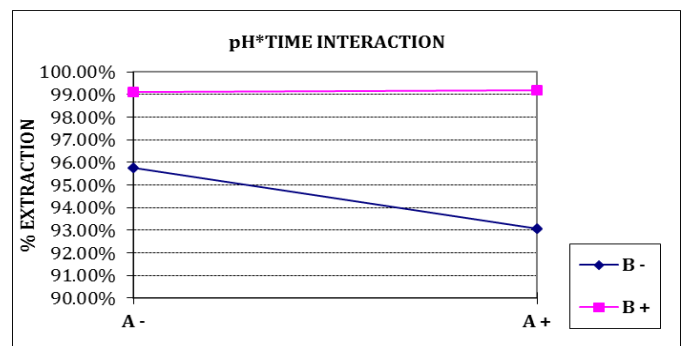


Chart-9: Effect of pH*time interaction on the extraction of Zinc

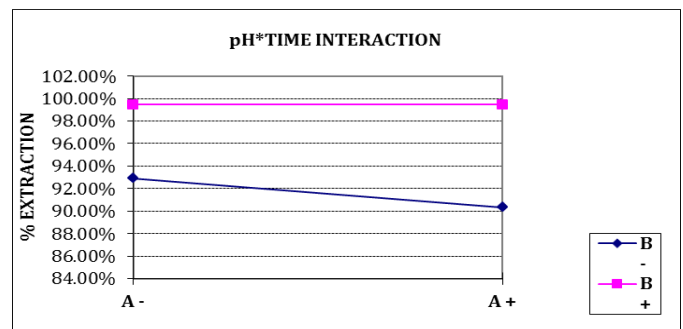


Chart -10: Effect of pH*time interaction on the extraction of Lead

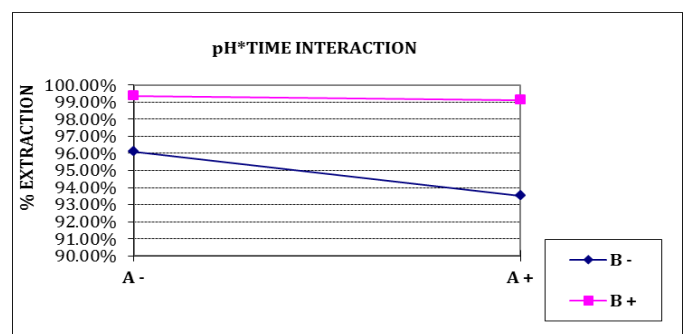


Chart -11: Effect of pH*time interaction on the extraction of Nickel.

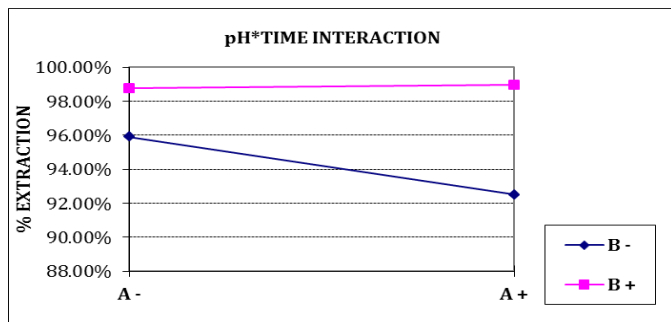


Chart -12: Effect of pH*time interaction on the extraction of Copper.

The heavy metals percentage extraction plots on chart 9, 10, 11 and 12 are not parallel and therefore there was interaction between pH (A) and time (B) during the extraction. The highest heavy metals percentage extraction due to this interaction was Zn (95.75%), Pb (99.46%), Ni (99.37%) and Cu (98.95%). The effect of this interaction to the extraction of all heavy metals was low but significant as shown on chart 2, 3, 4 and 5 with a t-value effect above than the t-value limit.

3.9 Effect of pH*Hydrogen peroxide dosage interaction on heavy metals extraction.

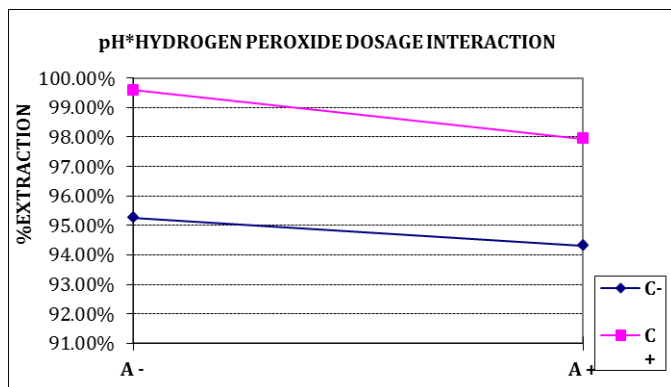


Chart 13: Effect of pH*Hydrogen peroxide dosage interaction on the extraction of Zinc.

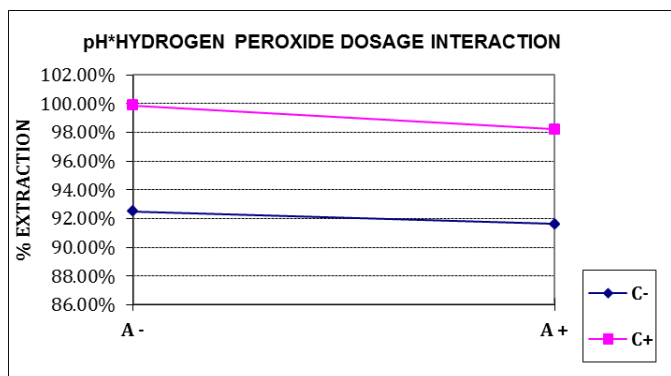


Chart 14: Effect of pH*Hydrogen peroxide dosage interaction on the extraction Lead

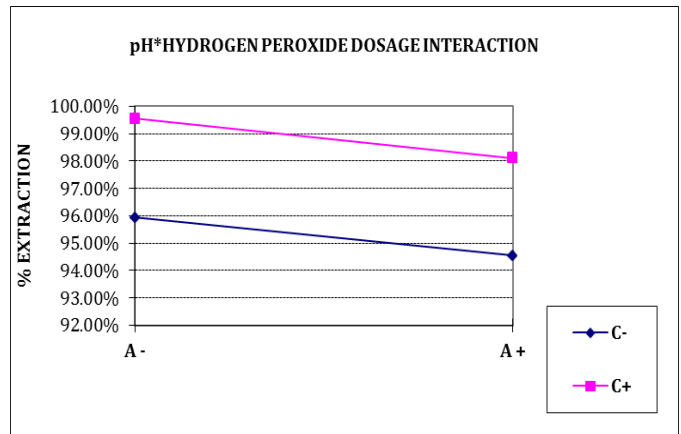


Chart 15: Effect of pH*Hydrogen peroxide dosage interaction on the extraction Nickel

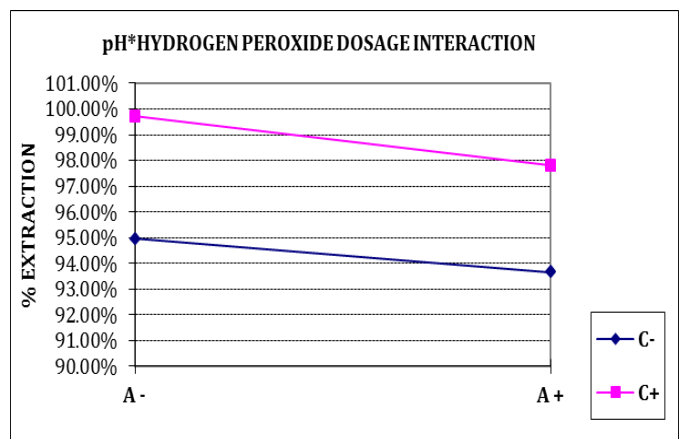


Chart 16: Effect of pH*Hydrogen peroxide dosage interaction on the extraction Copper

The heavy metals percentage extraction plots on chart 13, 14, 15 and 16 are parallel showing that there was no interaction between the pH and hydrogen peroxide dosage. As a result this interaction had no significance in the extraction of all the heavy metals under study. This is confirmed by its t-value being less than the t-value limit as shown the Pareto plot chart 2, 3, 4, and 5 for heavy metals extraction. This can be attributed to the fact that effect of Hydrogen peroxide dosage oxidation reaction is dependent on the presence of Iron ions in solution [18]. The Iron ions were abundant in the sewage sludge and could be taken as a constant because they were in large amounts as shown in chart 1.

3.10 Effect of Hydrogen peroxide dosage *time interaction on heavy metals extraction.

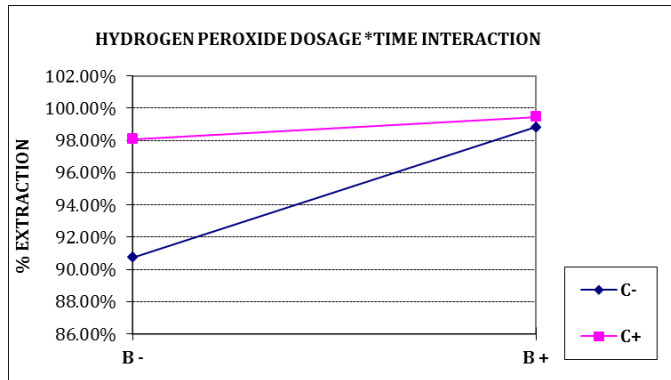


Chart 17: Effect of Hydrogen peroxide dosage *time interaction on Zinc extraction

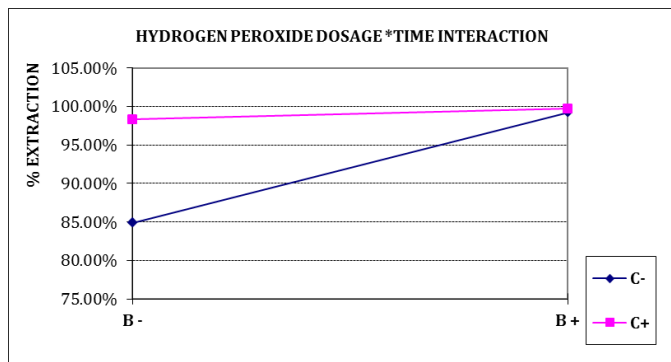


Chart 18: Effect of Hydrogen peroxide dosage *time interaction on Lead extraction

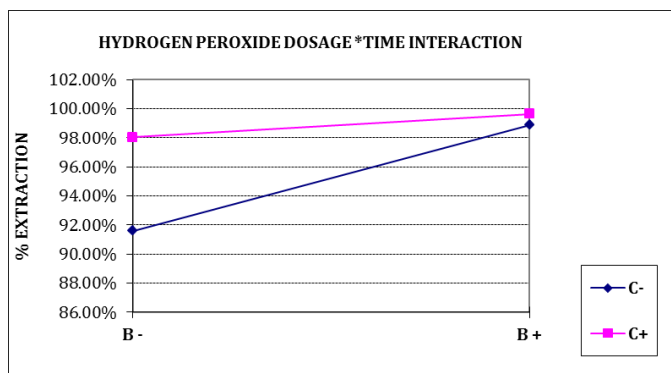


Chart 19: Effect of Hydrogen peroxide dosage *time interaction on Nickel extraction

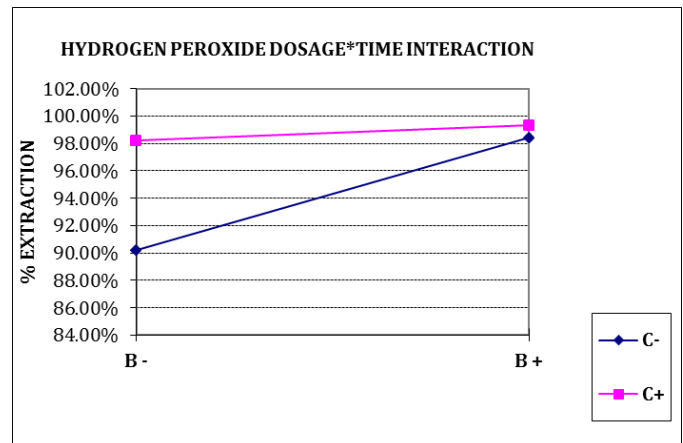


Chart 20: Effect of Hydrogen peroxide dosage *time interaction on Copper extraction

The lines are not parallel and therefore there was interaction between hydrogen peroxide dosage and time interaction on the extraction of all the heavy metals as shown on chart 17, 18, 19 and 20. This can be attributed to the fact that effect of Hydrogen peroxide dosage is dependent on the presence of Iron ions in solution and the more the extraction time the more the interaction between the ions the more the Fenton oxidation [18]. This caused the higher extraction percentage with increase with time. The highest heavy metals percentage extraction due to this interaction was Zn (99.46%), Pb (99.71%), Ni (99.62%) and Cu (99.32%). The effect of this interaction to the extraction of the heavy metals was high as shown on Pareto plot chart 2, 3, 4, and 5. This was confirmed by its t-value being higher than the t-value limit.

3.11 Final extraction models

Eliminating the insignificant effects the final heavy metals extraction model equations in terms of coded factors were as follows:

Zinc:

$$Y\% = 96.78 - 0.65A + 2.37B + 1.99C + 0.69AB - 1.68BC \dots (5)$$

Lead:

$$Y\% = 95.55 - 0.64A + 3.92B + 3.48C + 0.64AB - 3.24BC \dots (6)$$

Nickel:

$$Y\% = 97.07 - 0.67A + 2.25B + 1.76C + 0.62AB - 1.45BC \dots (7)$$

Copper:

$$Y\% = 96.56 - 0.84A + 2.36B + 2.20C + 0.86AB - 1.80BC \dots (8)$$

Where Y% is the percentage heavy metal extracted.

4. CONCLUSIONS

The results showed that the anaerobically digested sewage sludge from Kariobangi sewage treatment plant contains high amounts of Nitrogen, Phosphorous and organic matter. This implies that it can be used as an organic fertilizer and soil regenerator 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 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 efficiency. There was no significant interaction between pH and Hydrogen peroxide dosage in the extraction of heavy metals Zn, Pb, Ni and Cu under the tested conditions.

REFERENCES

- [1] Ronald J. LeBlanc, Peter Matthews, Roland P. Richard (2008). "Global atlas of excreta, wastewater sludge, and biosolids management: moving forward the sustainable and welcome uses of a global resource". Un-habitat.
- [2] Alvarez, E. A., Mochón, M. C., Sánchez, J. C. J., and Rodríguez, M. T. (2002). "Heavy metal extractable forms in sludge from wastewater treatment plants" *Chemosphere*, 47(7), 765-775
- [3] Stephanie L. L., Lecomte, P., & Ehrhardt, J. J. (2001). Behavior of hexavalent chromium in a polluted groundwater: Redox processes and immobilization in soils. *Environmental Science & Technology*, 35(7), 1350-1357.
- [4] Baek, K., & Yang, J. W. (2004). Cross-flow micellar-enhanced ultrafiltration for removal of nitrate and chromate: competitive binding. *Journal of Hazardous Materials*, 108(1-2), 184-191.
- [5] Seleem E. Gaber, Mahmoud S. Rizk, Mohamed. M. Yehia (2011). Extraction of certain heavy metals from sewage sludge using different types of acids. 41.
- [6] Zouboulis A.I., N.K. Lazaridis, Th.D. Karapantsios and K.A. Matis. (2008). Heavy metals removal from industrial wastewaters by biosorption *Int. J. Environment and Pollution*, Inderscience Enterprises Ltd.
- [7] Ribeiro M.H.L., I.A.C. Ribeiro, Recovery of erythromycin from fermentation broth by adsorption onto neutral and ion-exchange resins, *Sep. Purif. Technol.* 45 (2005) 232-239.
- [8] Lombardi A.T. and Garcia Jr. O. (1999). An evaluation into the potential of biological processing for the removal of metals from sewage sludges. *Critical Reviews in Microbiology* 25(4): 275-288.
- [9] Badmus M.A.O. Audu T.O.K and B.U. Anyata. (2007). *African Journal of Biotechnology* Vol. 6 (3), pp. 238-242, 5 February, 2007.
- [10] Zagorodni, A. A. (2006). *Ion Exchange Materials: Properties and Applications*, p. 496. Elsevier Science & Technology Books.
- [11] Mohammadi, T., Razmi, A., and Sadrzadeh, M. Effect of operating parameters on Pb²⁺ separation from wastewater using electrodialysis. *Desalination*, 167(1-3), 379-385, 2004.
- [12] Batista, J. R. and Young, J. C. (1997). Removal of selenium from gold heap leachate by activated alumina adsorption. *Min. Met. Proc.*, 14(2), 29-37.
- [13] Byrne, W. (1995). *Reverse Osmosis, a Practical Guide for Industrial Users*, p. 636. Tall Oaks Publishing Inc.,
- [14] Marchioretto, M. M., Bruning, H., Loan, N. T., & Rulkens, W. H. (2002). Heavy metals extraction from anaerobically digested sludge. *Water Science and Technology*, 46, 1-8.
- [15] Ukiwe, L. N., & Oguzie, E. E. (2008). Effect of pH and acid on heavy metal solubilisation of domestic sewage sludge. *Terrestrial and Aquatic Environmental Toxicology*, 2, 54-58.
- [16] Ramakrishna Gottipati, (2012). Preparation and Characterization of Microporous Activated Carbon from Biomass and its Application in the Removal of Chromium (VI) from Aqueous Phase. National Institute of Technology Rourkela, Odisha.
- [17] J. Robert Okalebo, Paul L. woomeer & Kenneth W. Gathua (2002). *Laboratory methods of soil and plant analysis: A working manual*.
- [18] Erik Andersson, Vedran Malkoc, (2004). Dewatering of sludge. Lund University, SE-221 00 Lund, Sweden.
- [19] Kaara, Jane Nduta (2012). Determination of heavy metals in sewage sludge, sewage effluent, garden soils and food crops grown in ordinary and sewage -sludge amended soils.
- [20] Zivorad R. Lazic (2004). *Design of Experiments in Chemical Engineering*. Wiley-Vch Verlag GmbH & Co. KgaA., Weinheim
- [21] Nuran Bradley, (2007). *The response surface methodology*. Indiana University, South Bend