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Optimum Value for Zinc Removal from Saponin-Based Soil Washing Across soils at Onyeama Dumpsite, Enugu State

Alexander Chidiebere Okoro[1], Louis Chukwuemeka Orakwe[2], Chike Pius Nwachukwu[3], Ella Ifeanyi Ugwu[4], Elijah Chibuzo Ugwu[5], Kenneth Eze[6], Chukwuemeka Obumneme Umobi[7]
[1]Nnamdi Azikiwe University, Awka, Anambra State, Nigeria, merciescds@yahoo.com
[2]Nnamdi Azikiwe University, Awka, Anambra State, Nigeria, lc.orakwe@unizik.edu.ng
[3]Nnamdi Azikiwe University, Awka, Anambra State, Nigeria, cp.nwachukwu@unizik.edu.ng
[4]University of Nigeria, Nsukka, Enugu State, Nigeria, ella.ugwu@unn.edu.ng
[5]Michael Okpara University of Agriculture, Umudike, Abia State, Nigeria, ugwu.elijah@mouau.edu.ng
[6]Enugu State University of Science and Technology, Enugu State, Nigeria, kennetheze@gmail.com
[7]Nnamdi Azikiwe University, Awka, Anambra State, Nigeria, co.umobi@unizik.edu.ng

Corresponding Author: merciescds@yahoo.com[1]

Abstract: High reduction in the size of available land for agriculture has been a major problem facing most farmers today. The adoption of available plant based surfactants is yet to gain attention in south eastern Nigeria. This study was conducted to ascertain the level of Zinc removal from heavy metal contaminated dumpsites. Soil samples (C1, C2 and C3) were collected from the dumpsite and taken to the laboratory for analytical procedure. Saponin was also extracted from siam weed to aid the process of batch experiment for the removal of Zinc from contaminated soil. The result of the study showed that the optimum value for Zinc removal with saponin for soils C1, C2 and C3 were 96%, 99% and 100% respectively. It is recommended that saponin from Siam weed be adopted for the removal of Zinc from contaminated soil.

Keyword: Remediation, Surfactant, Heavy metal, Batch experiment and Saponin

INTRODUCTION

In recent decades, anthropogenic activities like mining, smelting, electroplating, and wastewater irrigating have contributed to heavy-metal pollution of water and soils, which has become a major environmental concern worldwide (Jez and Lestan, 2016; Wang et al., 2020; Zhang et al., 2021a; Zhang et al., 2021b). Over five million locations, encompassing 20 million hectares of land, have soils tainted by different heavy metals worldwide (Liu et al., 2018; He et al., 2015). Heavy metal pollution of soil presents significant environmental risks since the metals are not biodegradable, can build up in living things, and can have long-term negative impacts on human health. Remediation of heavy metal-contaminated soils and preservation of soil environmental integrity are therefore urgently needed.

Many urban and industrial cities of developing countries still using landfills system to accommodate their waste and due to the various socio-economic activities, wastes are generated in tons. Landfills system is most adopted due to its capacity to accommodate great amount of waste over a long period of time using simple disposal method such as burning and/or decomposition. Notwithstanding these benefits, landfills are regarded as major reservoir for organic compounds and heavy metals in the environment (Vongdala et al., 2019). Hence, inefficient management of landfills waste has cause serious environmental and human impact, which has influence on the long term achievement of sustainable development (Ferronato and Torretta, 2019).

Many remediation methods have been proposed to remove heavy metals from polluted soils. These methods are based on physical, chemical, and even biological processes. Although some nutrients may be lost and secondary contamination may result, soil washing is regarded as an efficient method that may permanently remove heavy metals from soil with high remediation efficiency (Wei et al., 2016; Feng et al., 2020a). The most contaminated soil particles are separated by physical means in soil washing, and the heavy metals are then extracted chemically using certain washing chemicals to move them from the soil to solution (Saponaro et al., 2002; Dermont et al., 2008). The extraction reagents and the efficacy of soil washing in remediation are strongly connected. Numerous studies conducted in US Superfund programs have demonstrated that improper washing reagent selection can result in unsuccessful washing remediation (USEPA, 2004; 2005). Therefore, one of the hot topics in washing remediation is the study of washing reagents.

In an attempt to address soil contamination issues at waste dump sites, it is important to assess a suitable surfactant that is a plant-based metal remover with low toxicity, high removal efficiency and manageable destruction of soil characteristics. Besides, making a choice of the right plant based surfactant that is adapted to south eastern Nigeria is of paramount importance. This paper is therefore targeted at ascertaining the optimum value for zinc removal from saponin-based soil washing across soils at Onyeama dumpsite, Enugu State

METHOD

1. Study Area Description

This research location is located at the Onyeama dumpsite in Ngwo, Udi Local Government Area of Enugu State (figure 2.1). It is situated in the heart of a Nigerian coalfield and in the state of Enugu. The city is home to gas work stations, a cement industry, and a steel rolling mill. The city lies between 6°21'N and 7°26'E in southeast Nigeria. The city is located in a tropical rain forest zone with derived savannah, and its population was 722,664 according to the most recent National Population Census (2006) (Sanni, 2007). The humid climate of Enugu State peaks between March and November (https://en.wikipedia.org/wiki/Enugu). According to Sani (2007), Enugu State experiences an average daily temperature of 26.7°C (80.1°F).

Figure I. A pictorial representation of Onyeama Waste Dumpsite

2. Soil Sample Collection Method

Sampling of soil was taken randomly using soil core samplers from Onyeama dumpsite in Enugu State. The sampling areas at Onyeama dumpsite were divided into three major collection points, each of the major collection points had Three (3) soil samples were taken from it, which gave a total of nine (9) soil samples. The sampling was done at 30cm depth and 10meters away from each other. Three soil samples -soil 1(C1), soil; 2 (C2) and soil 3 (C3) with the highest contamination level, each from the major collection points were chosen for remediation (Figure 2.2) after physiochemical analysis. After the three samples were brought to the laboratory, the analytical process commenced instantly. The coordinates of the sampling points for the selected soil for remediation were also taken with a Global Positioning System (GPS) (Table 2.1). Three (3) soil samples were gathered in total for analysis as was experimentally designed. The soil samples collection targeted the top soil of the dumpsite at thirty centimeter (30cm) depth using soil auger from where a composite sample was collected.

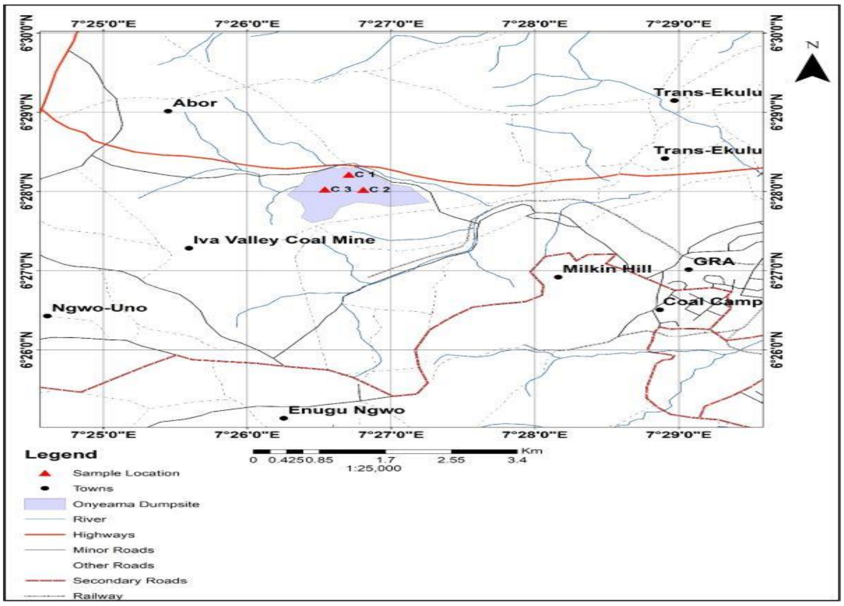

Figure 2. Enugu State's map displaying the soil sample collection points at Onyeama Waste Dumpsite

3. The total quantity of metals in the soil

EPA method 3050B was employed in order to calculate the soil's overall metal content (USEPA, 1996). This approach provides ecologically accessible metals rather than complete digestion. The samples were digested by heating using a fume hood and a hotplate containing

10 milliliters of nitric acid and a representative sample of 1 gram dry weight, then refluxing the mixture for 15 minutes at 95^0C ± 5^0C (heating a solution to its boiling point and condensing the vapour back into the solution). After that, the samples were digested by repeatedly adding 5 milliliters of strong nitric acid until there was no more reaction with the nitric acid. The conclusion of nitric acid digestion is indicated by the absence of dark vapors from the solution. After that, 30% hydrogen peroxide was used to digest the material. Until the sample's appearance remained constant, hydrogen peroxide (1 ml each) was added repeatedly. Lastly, the material was digested for 15 minutes using 10 milliliters of strong hydrochloric acid. Following their digestion, the samples were filled with 100 milliliters of distilled water after being collected in a 100 milliliter volumetric flask and filtered through Whatman No. 40 filter paper. Atomic Absorption (AA) Spectrometry was used to produce and analyze the filtered sample at the appropriate dilutions (USEPA, 1996). To ensure safety, soil sample digestion was carried out in triplicate under a hood.

4. Surfactants Extraction

The plant based surfactant was extracted from Siam weed leaves (Figure 2.3) at the Project Development Institute (PRODA) labouratory in Emene Enugu State. Different species and even different portions of the same plant have varying saponin extract concentrations and compositions. Maceration method was adopted in this process (Silva *et al.*, 2017). The powdered material of dried Siam weed leaves (Figure 2.4) of a known weight was separately placed in an airtight container, to which a predetermined amount of alcohol was added, mixed for two hours, and then left to stand for twenty-four hours, then it was allowed to stand for 24 hours. The mixture of each sample was filtered using Whatman's filter paper size No. 1 after being sieved using a mucilin cloth to get a clean filtrate of the extract. To remove the water and obtain a crude plant concentrate known as "Extract," the filtrate was heated to 90°C in a hot water bath. Equation 2.1 was used to determine the plant extract % yield in the following manner:

$$\%\, yield = \frac{\text{Weight of extract}}{\text{Weight of material}} \times \frac{100}{1} \qquad 2.1.$$

Figure 3. **A picture of Siam weeds from Emene Forest**

a) Phytochemical screening

Standard phytochemical techniques described by Siddiqui and Ali (1997), Trease and Evans (1998), and Harborne (1998) were used to screen the plant extracts and fractions both quantitatively and qualitatively.

Figure 4. A pictorial representation of Siam weed undergoing drying at PRODA Enugu labouratory

b) Test for saponins (Qualitative test).

Saponin was tested using the olive oil test method (Gul *et al.*, 2017). The screening test was based on saponins' capacity to form an emulsion with oil. In a water bath, 20 mg of extract was cooked for five minutes in 20 ml of distilled water before being filtered. Five milliliters were mixed with ten milliliters of the filtrate and distilled water, and the mixture was agitated vigorously to create froth. Three drops of olive oil were combined with the foam, agitated briskly, and the formation of an emulsion was monitored.

c) Determination of Total Saponins (Quantitative test)

After being ground, 20g of each sample and 100ml of 20% ethanol in water were put to a 250ml conical flask. Over a hot water bath, the samples were continuously stirred while being cooked for 2 hours at 55°C. The residue was extracted a second time after the mixtures were filtered. 200ml more of 20% ethanol should be added. The saponin extracts were reduced to 40 milliliters using a water bath at about 90°C. The concentrate was placed in a 250 ml separating funnel, and the aqueous layer was recovered after 20 ml of diethyl ether was added and thoroughly shaken. The purifying procedure was carried out once more. Ten milliliters of 5% aqueous sodium chloride were used twice to wash the nbutanol extracts following the addition of 60 milliliters of n-butanol. The samples were dried in an oven to a consistent weight after evaporation, the saponin content was ascertained, and the remaining solution was boiled in a water bath. (Obdoni and Ochuko, 2001).

$$\%\,Saponin = \frac{W2 - W1}{W.T} \times \frac{100}{1} \qquad 2.2$$

W1 = weight of the empty beaker
W2 = weight after drying
W.T = weight of sample.

d) Fractionation for saponins isolation using column chromatography.

Fractionation of the saponin extracts was carried out by column chromatography after the methods of Gupta et al., with a few changes. After packing the silica gel into the column, it was left to stand for a while. In order to separate the extract's polar and non-polar components, the concentrated extract was then placed onto the column and its contents were eluted using a range of solvents arranged by polarity (n-hexane, dichloromethane, ethyl acetate, and ethanol) (WHO, 2014). Following the concentration of the resultant fractions, the phytochemical components were analyzed, revealing that the ethanol fraction was primarily composed of saponin with trace levels of other chemicals. To determine the ideal solvent mixture for isolating saponin from other minute components, Thin Layer Chromatography (TLC) was performed in the lab. The ratios of n-butanol, methanol, and water were 1.5:1:0.5. After that, the concentrated ethanol fraction was put into a silica gel column, which was used as the stationary phase and divided between the n-butanol, methanol, and water combination. Following concentration in a water bath, the phytochemical content of the resultant effluent was examined.

After that, it was discovered that the effluent had glycosides, terpenoids, and saponins. A second TLC examination will demonstrate that saponins can be separated from other components using a methanol-chloroform mixture. The components were eluted using silica gel as the stationary phase after After being placed in the column, the concentrated n-butanol eluent was split 9:1 between methanol and chloroform. A "saponin-rich fraction of ethanoic leaf extract" is the quantity of saponin that was discovered bound to lactone and glycoside compounds following the concentration of the final efluent and an analysis of its phytochemicals. Since the saponin content was found to be low, the column was washed with 70% analytical grade ethanol to liberate the trapped saponin (figure 5).

Figure 5. A pictorial representation of extracted Saponin

5. Batch Soil Washing Studies

Research on Batch Soil Cleaning tests were used to examine how the desorption of heavy metals from contaminated soil samples is affected by pH, the ratio of surfactant soil solution, and contact time in order to liberate the trapped saponin (Ugwu, 2019). Using a rotary shaker set to approximately 200 rpm, A 125 ml conical flask was used for a number of batch tests in the laboratory. All tests were carried out at room temperature with variable contact times. Samples were then gathered and centrifuged for 15 minutes at 7000g (Luna *et al.*, 2016). The starting pH was change by the addition either sodium hydroxide or hydrochloric acid to the soil solution after collecting the supernatants on filter paper. The nitric acid droplets were used to preserve the filtrates, which were then kept for heavy metal analysis. A similar equation was used to calculate the responses, which were expressed as percentages of metals eliminated from the washing experiment (Equation. 2.3). To examine the heavy metals, an Atomic Adsorption Spectrophotometer (AAS) was employed.

$$Percentage\ metal\ removal(\%)\frac{C1-C2}{C1}\times 100 \qquad 2.3$$

Where
C1 = concentrations of metal in soil before batch experiment (mg/kg)
C2 = concentrations of metal in the soil after the batch experiment (mg/kg).

All experiments were conducted in three replicates to guarantee accuracy, and the average findings were displayed.

6. Experimental Design

The impact of pH, Soil-Solution Ratio (SSR), and contact time on the remediation of Zn from a polluted soil was assessed in this study using the Box Behnken Design (version 13). These factors' interplay and optimization were examined. Three components in three levels—coded as +1 (high), 0 (medium), and -1 (low)—were examined (Ugwu *et al.*, 2022). Ugwu *et al.* (2021a) provided the values for the three pH and time levels. Table 2.1 lists the process variables along with their levels. Eqn. 2.4 defines the number of experiments (N) in BBD (Gharibzadeh *et al*., 2018).

$$N = 2k(k-1) + Co \qquad 2.4$$

Where k is the number of factors and Co is the number of central points.

Table 1: Experimental Factors and their Levels

Factors/Levels	**Level 1**	**Level 2**	**Level 3**
pH of Surfactants	3	4	5
Ratio of Soil to surfactant Concentration	1g:5mg/l	1g:10mg/l	1g:15mg/l
Contact Time	6hours	12hours	18hours

Table 2: Experimental Runs using Box Behnken Design

Std	**Run**	**Factor 1 A:Ph**	**Factor 2. B:Surfactant Concentration(mg/l)**	**Factor 3. C:Contact time(Hour)**	**Response %Zinc (Zn) Removal (soil C1)**	**Response %Zinc (Zn) Removal (soil C2)**	**Response %Zinc (Zn) Removal (soil C3)**
15	1	4	10	12			
6	2	5	10	6			
1	3	3	5	12			
11	4	4	5	18			
9	5	4	5	6			
16	6	4	10	12			
10	7	4	15	6			
2	8	5	5	12			
5	9	3	10	6			
13	10	4	10	12			
12	11	4	15	18			
3	12	3	15	12			
7	13	3	10	18			
14	14	4	10	12			
4	15	5	15	12			
17	16	4	10	12			
8	17	5	10	6			

The Box Behnken Design approach was used in the experiment's design. Every numerical factor has three levels. For each combination of the categoric factor level, the Box Behnken Design was replicated if categoric factors were introduced. It was set up as shown in table 2.2 to determine the impact of three distinct elements at three distinct levels each. In the laboratory, 17 runs, or 17 tests, were carried out for each of the three soil samples. Saponin from Siam weed was used in 51 tests in the laboratory. Every experiment was carried out three times, with a record of the average values collected. RSM based on the Box Behnken design was used for the optimization experiments.

RESULT AND DISCUSSION

Impact of Saponin-Based Soil Washing on the Zinc Removal Efficiency for Individual and Accross Soils.

The result of the percentage removal of Zinc from soil C1, C2 and C3 using saponin as a washing agent which was carried out with Box-Behnken design of the response surface methodology (RSM) is as presented in table 3.1. and the design matrix contained 17 experimental runs with three responses. Optimization analyses were carried out in Design Expert (V.13).

The optimum value was recorded in this study for soil C1 as 96% at pH, SSR and time of 5, 15 and 10.8hrs respectively. Table 3.1 shows that Zinc (Zn) removal efficiency ranges from 48.98% to 99.84%. High efficiency is observed at moderate to high pH levels, with optimal results at pH 4, SSR 10, and moderate time. The optimum value was recorded in this study for soil C2 as 99% at pH, SSR and time of 4, 13.6 and 16hrs respectively. Table 3.1 shows that Zinc (Zn) **r**emoval efficiency had a moderate to high efficiency (48.51%–98.98%). Maximum removal occurs at high SSR and longer times. The optimum value was recorded in this study for soil C3 as 100% at pH, SSR and time of 3.3, 14.4 and 18hrs respectively. Table 3.1 also shows that Zinc (Zn) removal efficiency **is h**igh (53.85%–100%), with multiple runs achieving complete removal (e.g., Run 9, 12).

Table 3. Responses to the Box-Behnken Design Matrix for Saponin Removal of Zinc from Soils

STD	Run	A: pH	B:SSR	C:Time	Soil C1	Soil C2	Soil C3
1	1	3	5	12	48.98	48.51	53.85
17	2	4	10	12	99.12	92.75	97.24
13	3	4	10	12	88.55	94.24	95.45
2	4	5	5	12	98.18	82.45	96.22
12	5	4	15	18	99.05	96.89	100
8	6	5	10	6	98.13	83.88	96.12
7	7	3	10	18	48.98	98.98	98.99
9	8	4	5	18	50.54	98.24	93.57
3	9	3	15	12	98.7	94.01	100
16	10	4	10	12	99.84	88.62	95.45
14	11	4	10	12	98.39	96.25	98.76
4	12	5	15	12	98.61	95.49	97.42
11	13	4	5	18	49.14	79.47	98.48
10	14	4	15	6	99.53	95.97	95.39
15	15	4	10	12	99.26	90.07	97.26
6	16	5	10	6	98.46	90.72	95.37
5	17	3	10	6	98.65	82.44	98.76

Soil C3 generally exhibits the highest Zn removal efficiency, with several runs achieving 100%. Soil C1 performs similarly but shows more variability. Studies by **Liu *et al.*, (2019)** reported Zn removal efficiencies of 90% using saponin, comparable to the high efficiencies observed for Soils C1 and C3 in this study. Soil C2 shows moderate to high efficiency but is slightly less consistent.

The high removal efficiencies across varying soils demonstrate the versatility of saponin for soil remediation. Soil C3 shows slightly better overall performance, likely due to favorable soil characteristics. Mukhopadhyay, (2018) observed that soapnut was more efficient than SDS due to its lower pH. Soapnut solution removed more than 73% zinc while SDS solution could only wash out up to 31% of the total zinc from the soil under similar experimental conditions.

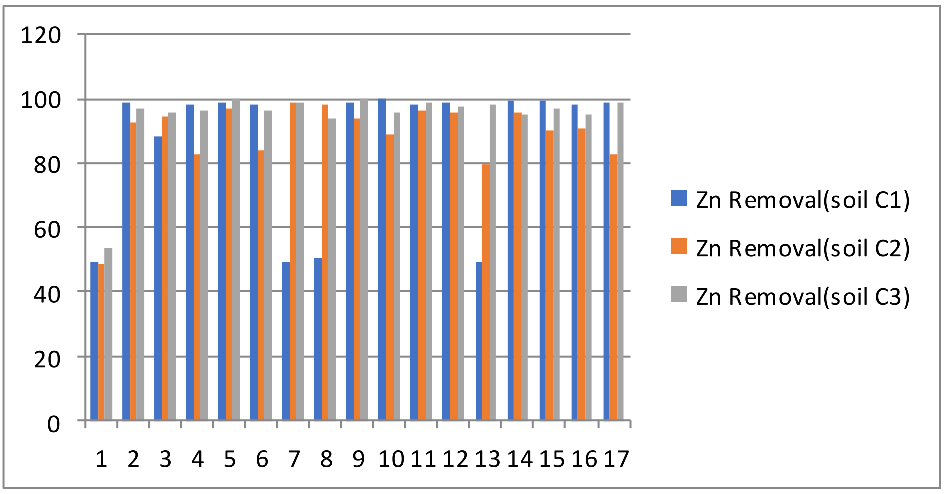

Figure 6: A graphical of runs against removal efficiency of Zinc Across soils using saponin as a washing agent.

The graph above shows the removal efficiencies of Zn across soils when washed with saponin. It could be observed that soil C1 recorded the highest removal efficiency in most cases, such as in runs 2, 4, 6, 10, 12, 14, 15 and 16 when compared to that of soil C2 and C3. Soil C3 also recorded highest removal efficiencies at runs 1, 3, 5, 9, 11 and 13 when compared to C1 and C2. C2 soil recorded its highest removal efficiency for zinc in runs 8 alone. The graph generally shows high removal efficiency for zinc when washed with saponin. According to Feng *et al*, (2020b) Zinc recorded a low removal efficiency of between 21.82–27.94% when washed with *F. esculentum*, at concentration of 50 g/L, pH 3 and contact duration of 120 min. this result is very low when compared to that of this study.

CONCLUSION

The overall results indicate that batch washing with biosurfactants showed promising results in the treatment of heavy metal contaminated soil. The study provides knowledge about performance of plant based surfactant into remediating real contaminated soil. Further studies on soil washing with biosurfactants should be extended to other metals. An assessment of the quality (in terms of fertility) of the remediated soil and the stability of retained biosurfactants is needed.

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