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Removal of Heavy Metals from Sewage Sludge Using Sugarcane Waste Extract

O. T. Okareh[1*] and O. D. Enesi[1]

[1]Department of Environmental Health Sciences, Faculty of Public Health, University of Ibadan, Ibadan, Nigeria.

Authors' contributions

This work was carried out in collaboration between the two authors. Author OTO designed the study, wrote the protocol, and wrote the final draft of the manuscript. He is also the corresponding author. Author ODE managed the literature searches, analyses of the study performed the spectroscopy analysis and managed the experimental process. The two authors read and approved the final manuscript.

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ABSTRACT

Introduction: The disposal of Sewage Sludge (SS) or its application on farmlands is of public health concern, owing to the potentials of Heavy Metals (HMs) in SS to deteriorate soil, ground water quality and bioaccumulate in food chains. Conventional inorganic chelating agents used for removing HMs are mostly expensive and have negative environmental impacts.
Aim: This study, therefore, determined the efficacy of fermentation extracts from Sugarcane Wastes (SWs) in removing HMs from sewage sludge.
Methodology: An experimental design was adopted. Crude Fermentation Extract (CFE) and Fungus-specific Fermentation Extract (FFE) were used to remove Copper, Zinc, Chromium, Nickel, Cadmium and Lead from SS, and Commercial-grade Citric Acid (CCA) used as control. The experiment was carried out by adding 20 ml of the treatment (extracts and control) at various pH (3 – 6) to 1g of SS each. The mixture was centrifuged after a contact time of 1-5 days at 1000 rpm for 1hour. The filtrate was analysed for Heavy Metals Concentrations (HMCs) and compared with National Environmental Standards and Regulations Enforcement Agency (NESREA) permissible

**Corresponding author: Email: dapsy2001@yahoo.co.uk;*

limits. Data were analyzed using descriptive statistics and ANOVA at *P*=0.05.
Results: The HMCs (mg/Kg) in the SS were Cu (311.4±4.8), Zn (2081.0±30.0), Cr (10.8±1.3), Ni (31.5±1.4), Cd (2.5±0.1) and Pb (167.5±9.4). The concentrations were below the permissible limits (mg/Kg) set by NESREA for Cr (100.0), Ni (70.0) and Cd (3.0) but higher for Cu (100.0), Zn (421.0) and Pb (164.0). Optimum HMR was achieved on day 5 at pH 3 for Cu, Cr, Cd and Pb by CFE, FFE and CCA; and at varying pH (3-4) for Zn and Ni. The concentration of Cr, Ni and Pb removed by CFE was significantly higher than FFE, but showed no significant difference for Cu and Cd. Both extracts showed higher HMR compared with control, except for Cu and Pb; and reduced the concentrations of Zn and Pb to acceptable levels.
Conclusion: Crude fermentation extract of sugarcane wastes was most effective in removing the heavy metals except Copper from sewage sludge. Therefore, its use could be adopted and promoted for removing these heavy metals from sewage sludge to achieve safe disposal.

Keywords: Crude fermentation extract; sugarcane waste; sewage sludge; fungus-specific fermentation extract.

1. INTRODUCTION

Sewage sludge is the solid, semi-solid or liquid residue generated during the treatment of domestic sewage carried out in treatment works [1]. The increase in urbanization and industrialization has resulted in a drastic increase in the volume of wastewater and sludge generated worldwide [2]. Sewage sludge is often considered for use in agriculture due to the abundance of organic matter and nutrients [3]. This is however limited by the presence of potentially hazardous constituents which include pathogenic organisms, heavy metals, soluble salts and other trace constituents present in sewage sludge [4].

The need to remove these contaminants from sludge becomes imperative. A critical step in the decontamination of the dewatered sludge is to remove the toxic heavy metals because they are not degradable (biologically and physico-chemically) and thus, once released into the soil environments, they have high potential to deteriorate soil quality and ground water supply and hence human health and safety [5].

Heavy metals such as Zn, Pb, Cu, Cr, Ni, Cd, Hg and As constitute toxic pollutants found in sewage sludge. Heavy metals can accumulate in soil and in plants when sludge is applied as fertilizer and eventually can produce harmful effects in animals and humans. Due to the high level of awareness of the negative impacts of high concentration of heavy metals to the environment, stringent guidelines and verifications have been designed to limit the application of sewage sludge to agricultural soils [6].

There is a great interest in spreading sludge on agricultural land due to the potential of recycling valuable components such as organic matter, nitrogen, phosphorus and other plant nutrients [7]. However, due to the physical and chemical processes involved in activated sludge wastewater treatment, heavy metals that are present in the wastewater tend to accumulate in the generated sludge. As a result, heavy metal levels are generally higher in the sludge than in the soil, where these elements can be retained indefinitely in cultivated soil layers. Therefore, repeated applications of sludge gradually increase the trace element content of the soil. High heavy metal content in sewage sludge limits their use as soil conditioners and organic fertilizers due to the high potential of the heavy metals to accumulate in food chain, deteriorate soil quality, ground water supply and hence, human health and safety. Inorganic chelating agents which are the most popular extracting reagents for heavy metal removal have been proved to be very efficient as they form stable complexes with most heavy metals over a broad pH range. However, their demerits which include persistence in the environment, adverse health effects and expensive cost have precluded their use.

A great variety of extraction schemes have been developed to remove heavy metals from sewage sludge [7]. Sludge management methods include composting, thermal and acid treatment methods for the removal and/or stabilization of heavy metal content [3]. Due to the complex matrix of sewage sludge and tight bonding of heavy metals to the minerals and organic solids, these metals can only be satisfactorily solubilised under extreme acidic conditions achieved at high redox-potential conditions and with the application of acidification techniques such as chemical leaching or bioleaching [2].

The use of organic acids (such as oxalic and citric acids) in the chemical extraction of sludge have gained prominence due to environmental concerns of using inorganic chelating agents to achieve such extractions. Citric acid, a tricarboxylic acid, has been produced from a variety of raw organic materials that were abandoned or simply residues generated from a process that were considered wastes. These wastes include orange peels, pineapple peels, bagasse, wheat bran, molasses, corn cob, beet pulp, soy residues, areca husk, apple pomace, grape pomace etc [8,9].

This study focuses on the use of sugar cane bagasse; chewed sugarcane stalks often considered as waste.

The use of inorganic and synthetic chelating agents for heavy metal removal leads to decreased soil productivity and adverse changes in the chemical and physical structure of soils due to mineral dissolution. These compounds are very stable and could remain adsorbed in the soil after extraction, this can make the soil unfit for further use [10].

In chemical extraction of heavy metals from sewage sludge, organic acids (citric and oxalic) are more promising than inorganic chelating agents since extraction can be at mildly acidic condition (pH 3 – 4) and are biodegradable, hence low environmental impact. Therefore, the study of effective methods for heavy metal removal from sludge is very important in order to minimize prospective health risk during application [11].

The use of natural compounds such as low molecular weight organic acids which are the better option for heavy metal solubilisation from sewage sludge have been found by several authors to have low effectiveness compared to the synthetic chelates [12,13,14].

With the aforementioned problems in mind, the search is on for environmentally-friendly extractant, which has additional advantages of being readily available, non-toxic and relatively low in cost for efficient heavy metal removal [10].

Therefore, the utilization of sugar cane bagasse wastes as a source of citric acid to remove heavy metals from sewage sludge can be one alternative. This study aims to determine the efficacy of fermentation extracts of sugarcane wastes in removing heavy metals from sewage sludge.

2. MATERIALS AND METHODS

2.1Sewage Slugde

Composite sewage sludge sample was collected from the University College Hospital (UCH) Sewage Treatment Plant, Ibadan. About 6-10 individual dewatered sewage sludge samples were collected, mixed together and one average sample was compiled for analysis. The collected material was prepared by drying and grinding to pass through a 0.2 mm stainless steel sieve. The sewage sludge were then analysed for basic physico-chemical properties using standard procedures.

The heavy metal content was determined using an Atomic Absorption Spectophotometer. This was done following the Nitric-Perchloric acid digestion procedure [15].

One gram of sample was placed in a 250 ml digestion tube and 10 ml of concentrated HNO_3 was added. The mixture was boiled gently for 30–45 minutes to oxidize all easily oxidizable matter. After cooling, 5 ml of 70% $HClO_4$ was added and the mixture was boiled gently until dense white fumes appeared. After cooling, 20 ml of distilled water was added and the mixture was boiled further to release any fumes. The solution was cooled, further filtered through Whatman No. 42 filter paper and <0.45 µm Millipore filter paper and transferred quantitatively to a 25 ml volumetric flask by adding distilled water.

The concentrations of Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb) and Zinc (Zn) in the final solutions were determined by an Atomic Absorption Spectrometer (AAS).

2.2 Leaching Agent or Extractant

Extracts from two fermentation groups, crude fermentation extract and *Aspergillus niger* fermentation extract were used for heavy metal removal/extraction from sewage sludge. Commercial citric acid served as the control.

2.3 Heavy Metal Removal Experiments

The heavy metal removal experiments were carried out at various pH levels and contact time for all the extractants used.

For each extractant, extraction of samples of dried sewage sludge carried out in 25 ml centrifuge tubes were conducted at various pH levels (3, 3.5, 4, 4.5, 5, 5.5 and 6). Each tube containing 1 g of sieved sewage sludge sample was filled with 20 ml of the extractant, of which the pH has been adjusted appropriately with 1M NaOH or 1M HCl. The tubes were stirred continuously on a rotary shaker at 150 rpm.

Each extraction was carried out at contact time of 1 day, 2 days and 5 days for each extractant at a given pH level.

Each tube was centrifuged at 1000 rpm for 1 hour. The supernatant was decanted and filtered through a filter paper. The filtrate was then analysed with an AAS for concentration of heavy metals. The residue is the decontaminated sludge of interest for agricultural purposes.

The analyses of heavy metals were carried out in triplicate and all the reported results are their averages. The obtained data were subjected to statistical analysis to evaluate statistically significant effects.

The mean heavy metal concentrations removed by the extracts (and the control) were expressed as a percentage of the initial heavy metal concentrations in the sewage sludge. Comparisons were made by subjecting the mean heavy metal concentrations removed from the sewage sludge collected during the leaching experiments to Analysis of Variance (ANOVA) at 0.05 α-level using LSD and Duncan tests.

3. RESULTS

3.1 Physico-chemical Properties of Sewage Sludge

The physicochemical properties of the composite sewage sludge sample are reported in Table 1. Preliminary visual inspection showed that the sewage sludge was clumped and dark brown in colour. The pH of the sewage sludge sample was 6.12, the organic matter content was 63.51% and the total heavy metal content of copper, zinc, chromium, nickel, cadmium and lead are presented in mg/Kg in Table 1.

Table 1. Physico-chemical properties of sewage sludge

Parameter	Unit	Values
pH		6.12
Organic matter	(%)	63.51
Total carbon	(%)	36.84
Total nitrogen	(%)	3.74
Total phosphorus	(%)	1.79
Copper (Cu)	mg/Kg	311.43
Zinc (Zn)	mg/Kg	2081
Chromium (Cr)	mg/Kg	10.8
Nickel (Ni)	mg/Kg	31.5
Cadmium (Cd)	mg/Kg	2.52
Lead (Pb)	mg/Kg	167.45

The heavy metals concentrations in the sewage sludge were compared with the Maximum permissible standards for agricultural soils shown in Table 3.

3.2 Effect of pH on Heavy Metal Removal

The heavy metal removal efficiency of the fermentation extracts and the control decreased with increase in the pH values except for zinc and nickel whose removal efficiencies first increase from pH 3 to pH 3.5 or 4 and then decrease as pH increases from 4 to 6 as shown in Figs.1-3.

3.3 Effect of Contact Time on Heavy Metal Removal

Generally, the heavy metal removal efficiency of the fermentation extracts and the control increased with increase in contact time. The effects of contact time on the heavy metals are represented in Figs.4-9.

3.4 Heavy Metal Removal Efficiency

The optimum heavy metal removal of the fermentation extracts are presented in Table 2. *Aspergillus niger* fermentation extract was most effective for the removal of zinc (99.24%) and cadmium (13.49%) and least effective for the removal of copper (19.89%) and lead (14.59%) compared with other treatments. Crude fermentation extract was most effective for the removal of chromium (24.94%) and nickel (59.49%) but was not least effective for the removal of any of the heavy metals analysed compared to other treatments. Citric acid was most effective for the removal of copper (71.21%) and lead (19.32%) and least effective for the removal of zinc (35.11%), chromium (11.73%), nickel (38.33%) and cadmium (10.45%) compared to other treatments.

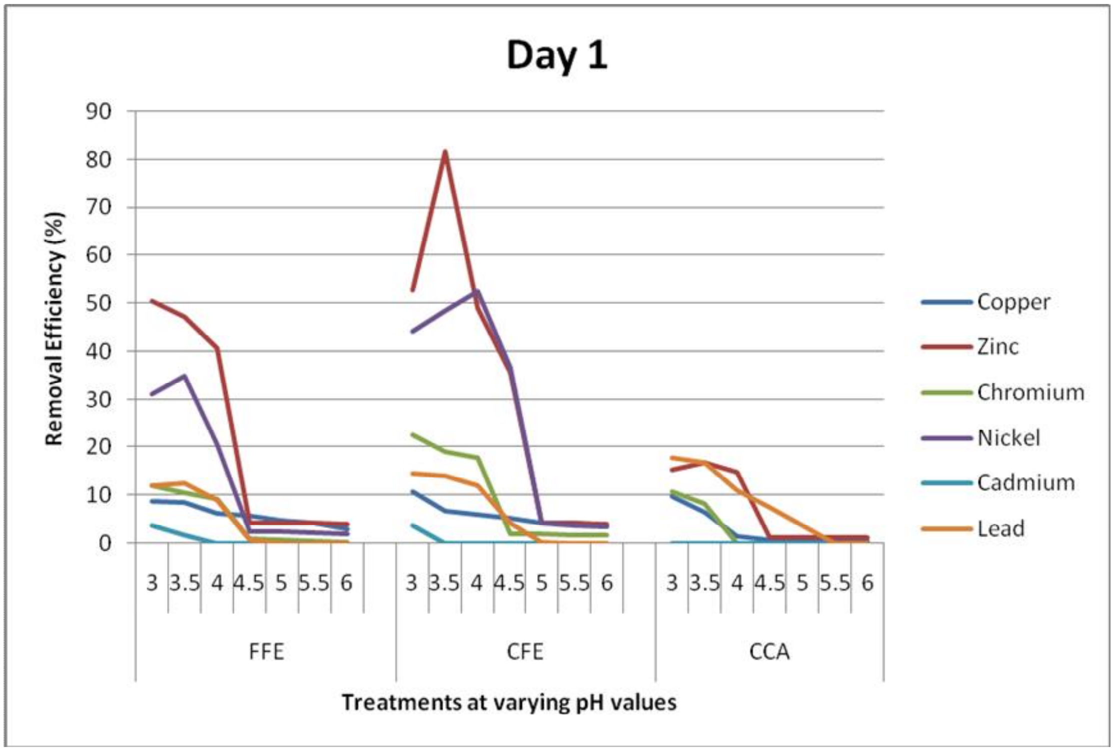

Fig. 1. Effect of pH on heavy metal removal efficiency on day 1

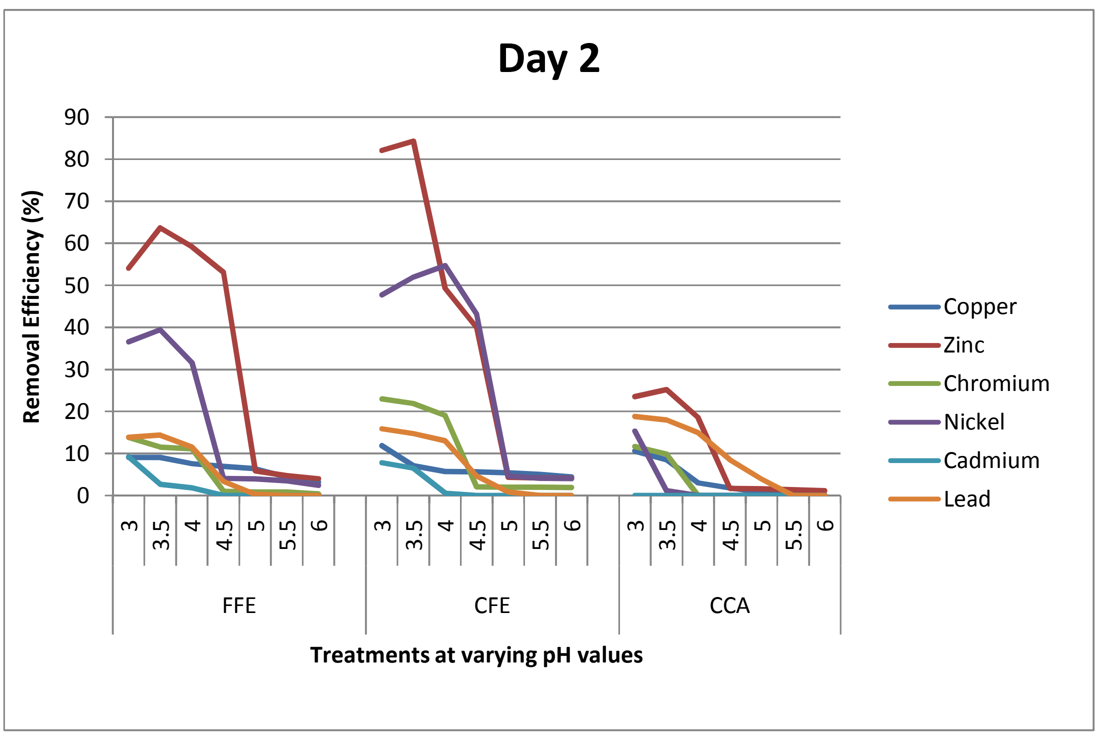

Fig. 2. Effect of pH on heavy metal removal efficiency on day 2

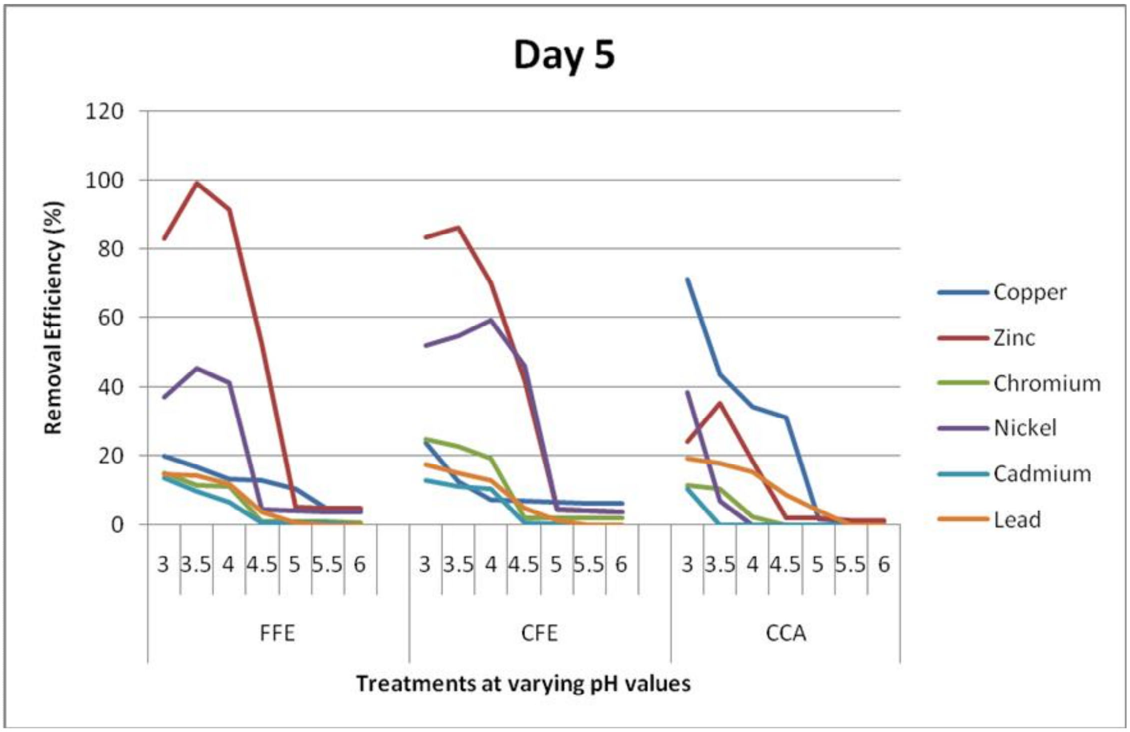

Fig. 3. Effect of pH on heavy metal removal efficiency on day 5

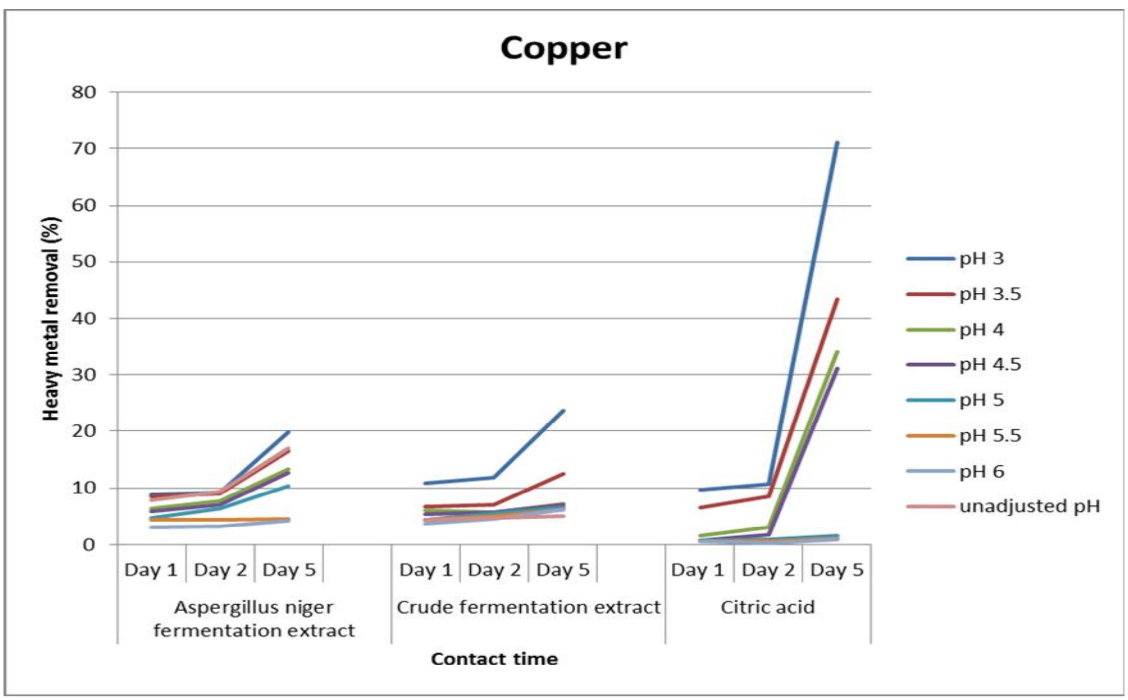

Fig. 4. Effect of contact time on copper removal

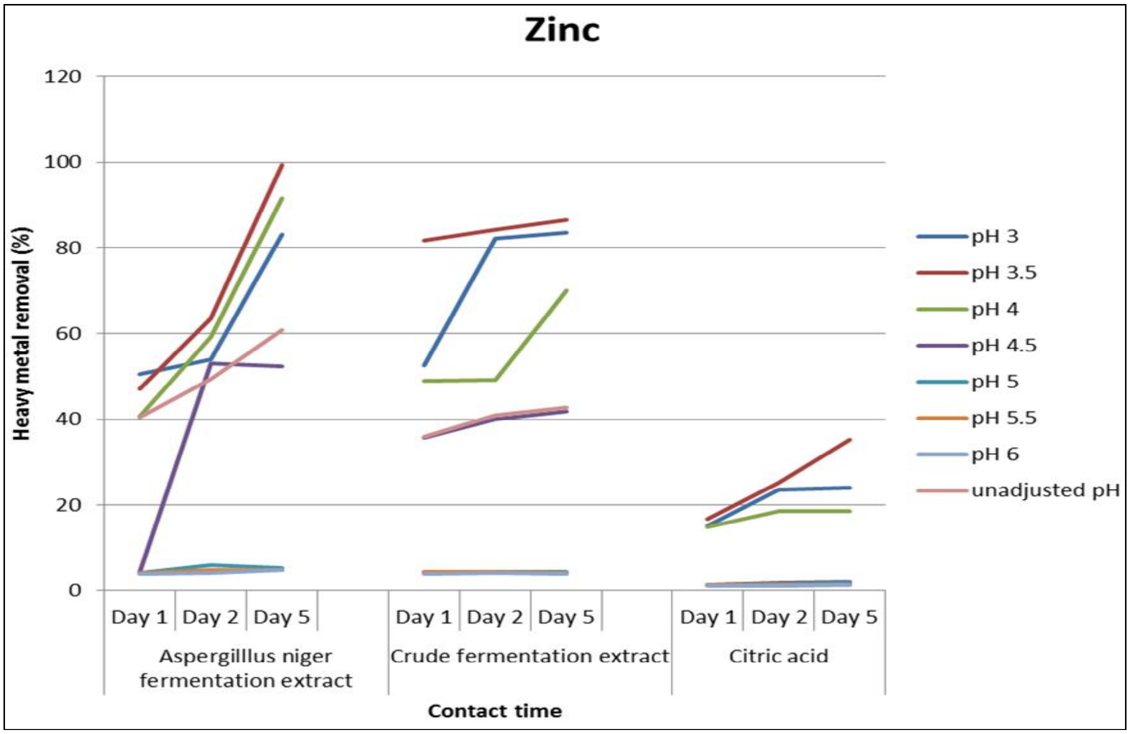

Fig. 5. Effect of contact time on zinc removal

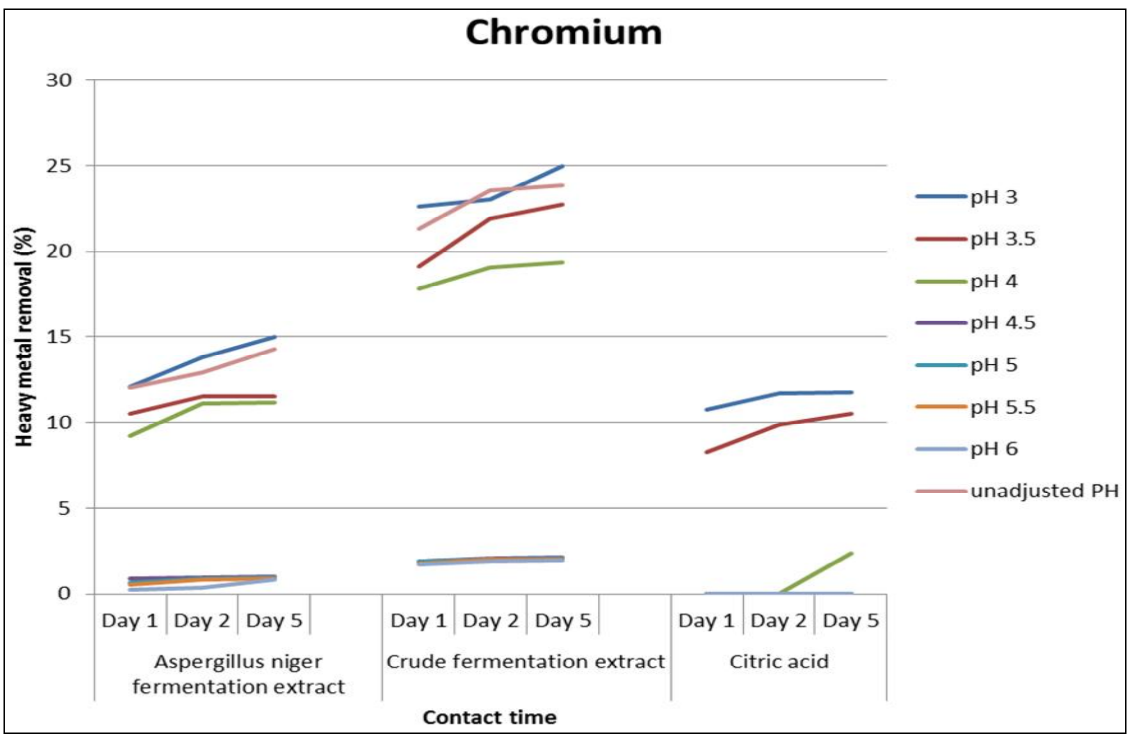

Fig. 6. Effect of contact time on chromium removal

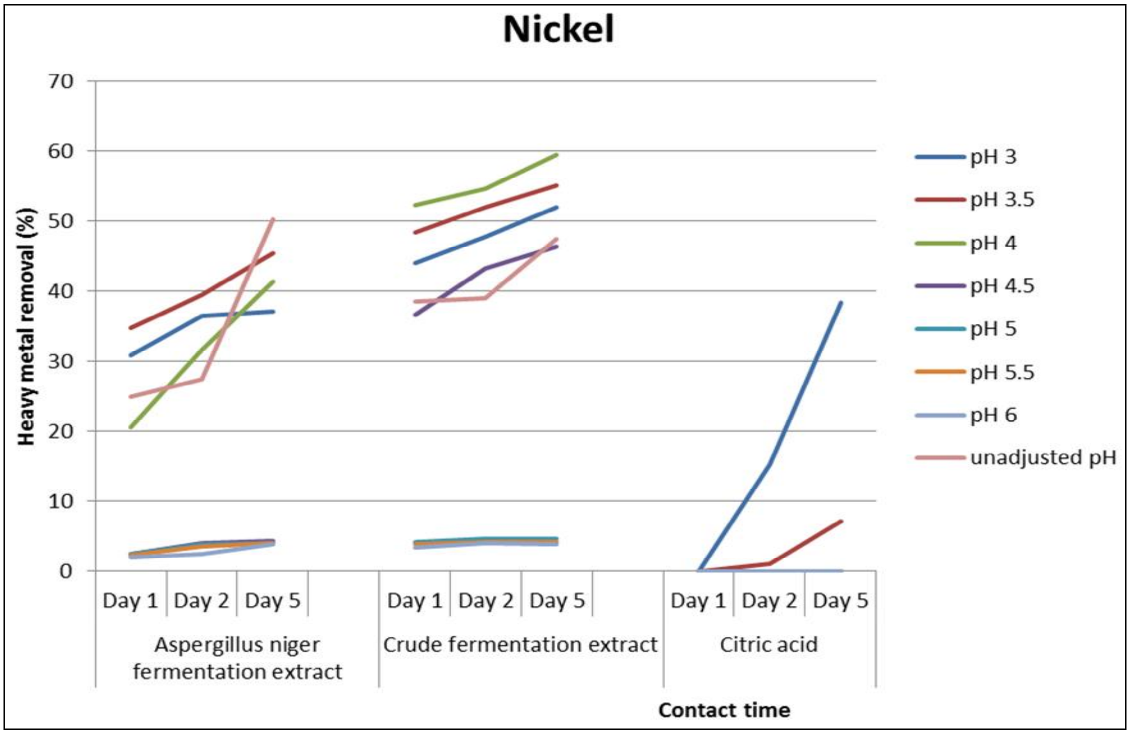

Fig. 7. Effect of contact time on nickel removal

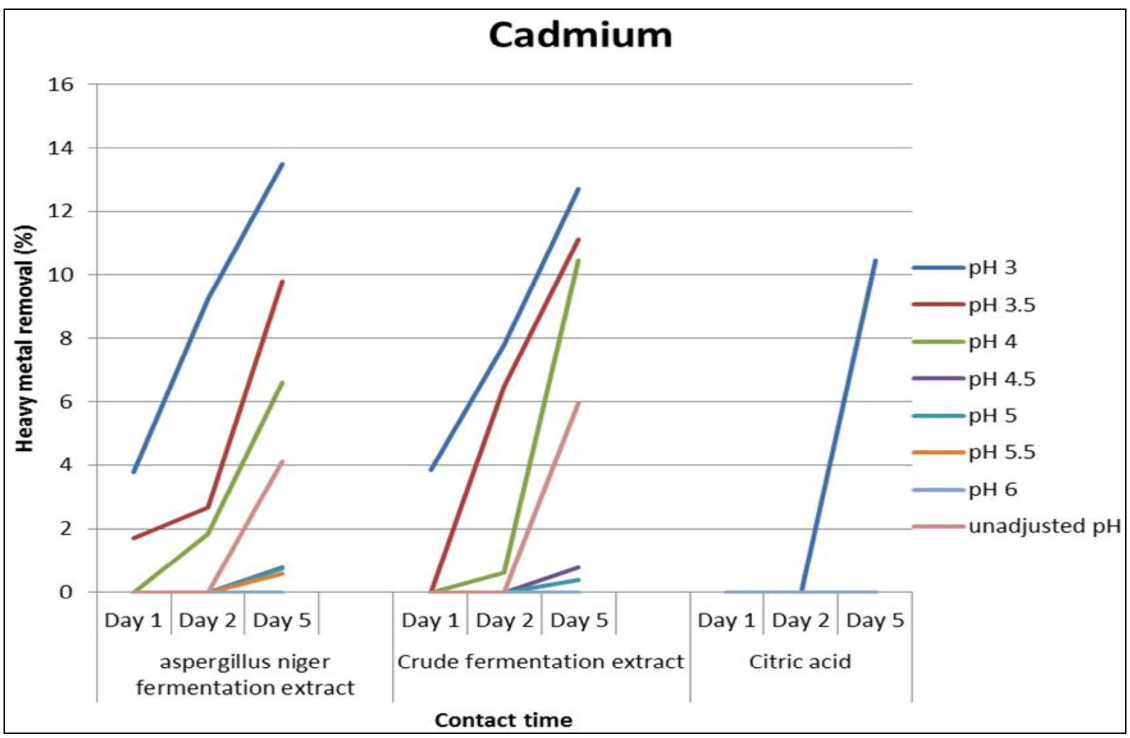

Fig. 8. Effect of contact time on cadmium removal

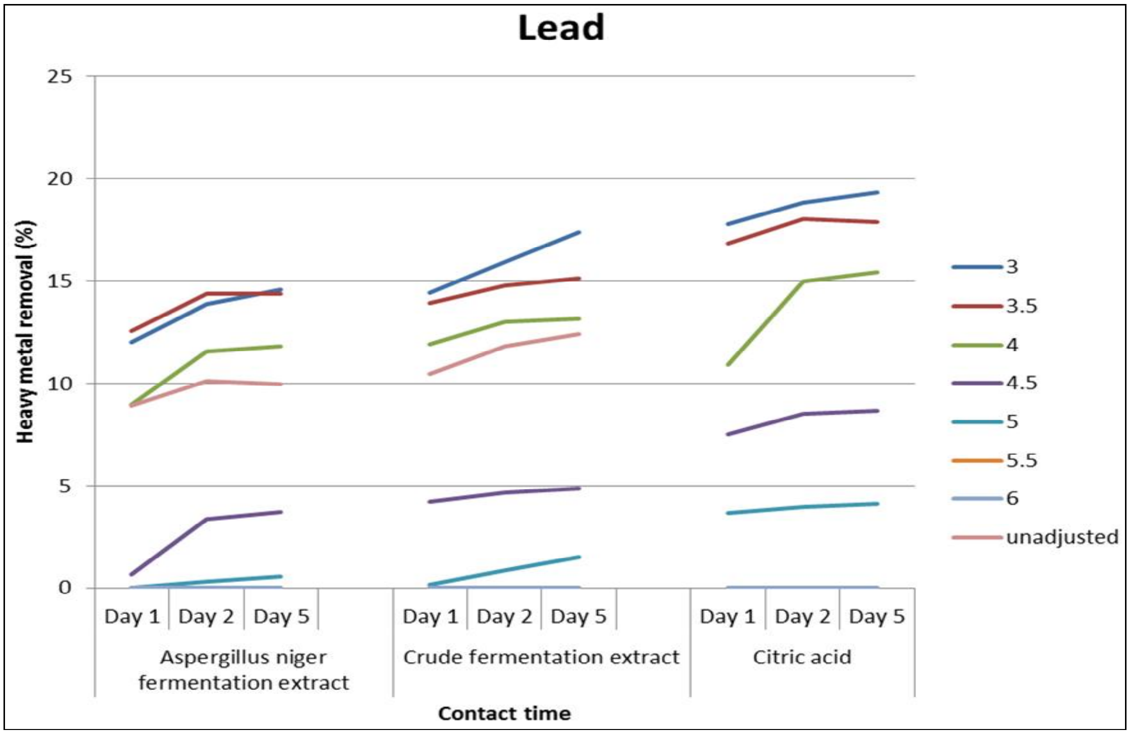

Fig. 9. Effect of contact time on lead removal

Table 2. Optimum heavy metal removal

Heavy metals		**Extractant**		
		***Aspergillus niger* fermentation extract**	**Crude fermentation extract**	**Citric acid**
Copper	Extraction Efficiency (%)	19.9	23.7	71.2
	pH	3	3	3
	Contact time	5	5	5
Zinc	Extraction Efficiency (%)	99.2	86.4	35.1
	pH	3.5	3.5	3.5
	Contact time	5	5	5
Chromium	Extraction Efficiency (%)	15.0	24.9	11.7
	pH	3	3	3
	Contact time	5	5	5
Nickel	Extraction Efficiency (%)	45.5	59.5	38.3
	pH	3.5	4	3
	Contact time	5	5	5
Cadmium	Extraction Efficiency (%)	13.5	12.7	10.5
	pH	3	3	3
	Contact time	5	5	5
Lead	Extraction Efficiency (%)	14.6	17.4	19.3
	pH	3	3	3
	Contact time	5	5	5

Table 3. Heavy metal permissible standard limit for sewage sludge applied on agricultural soils

Heavy metals	Maximum permissible standards for agricultural soils		
	U.S.EPA-40 CFR 503.13 (mg/Kg DM)	EU Commission (mg/Kg DM)	NESREA (mg/Kg DM)
Copper (Cu)	1500	1000 – 1750	100
Zinc (Zn)	2800	2500 – 4000	421
Chromium (Cr)	–	1000 – 1750	100
Nickel (Ni)	420	300 – 400	70
Cadmium (Cd)	39	20 – 40	3
Lead (Pb)	300	750 – 1200	164

4. DISCUSSION

4.1 Physico-chemical Characteristics of the Sewage Sludge

The mean pH was 6.12 which indicate that the sludge was slightly acidic. This slightly acidic state of the sludge is within the range of agricultural soils [16].

The sewage sludge sample has a high percentage of organic matter which may be present in the ammonium, nitrate and organic forms. The clump nature and dark colour of the sewage sludge is consistent with its high organic matter content. According to a research finding [17], dissolved organic chemicals act to 'glue' soil particles together, enhancing aggregation and increasing overall soil aeration, water infiltration and retention, and resistance to erosion and crusting. The dark consistency of humus causes soils high in organic matter to be dark brown or black in colour, increasing the amount of solar radiation absorbed by the soil and thus, soil temperature [17].

The determination of heavy metal concentrations in sewage sludge is essential for interpreting their suitability for safe disposal or agricultural use.

These metals concentrations when compared with the NESREA maximum permissible guideline limits, indicated that Cr, Ni and Cd present in the sewage sludge were below the permissible limits. However, the concentrations of Cu, Zn and Pb in the sewage sludge were higher than the permissible limits. The presence of high concentrations of copper and zinc is consistent with the findings of [18] which showed that effluent from medical institutions in South Africa had high levels of zinc and copper. The presence of zinc and copper in the sewage sludge may be due to corrosion of the plumbing systems. The use of shampoos is also implicated in the high level of zinc in the sludge. The high levels of lead may be due to automobile emissions or decomposition of paints.

4.2 Effect of pH on the Heavy metals Removal

The optimum pH for *Aspergillus niger* fermentation extract lies between 3 – 3.5, which was most effective for the removal of zinc (99.24%) and least effective for the removal of cadmium (13.49%). The optimum pH for crude fermentation extract lies between 3 – 4. It was most effective for the removal of zinc (86.4%) and least effective for the removal of cadmium (12.7%).

The removal of heavy metals by progressive acidification for all the metals analysed depended on the pH. This is consistent with previous findings [19,6,2]. These studies revealed that pH is a dominant factor which influences the cation exchange capacity of the sludge, hence altering the redistribution and exchangeability of the heavy metals in the sludge.

Generally, the metal extraction efficiency seems to decrease with increase in pH. However, a closer observation shows that a small change in pH (from pH 4 to pH 5) greatly affects the metal extraction efficiency (as shown in Figs. 1 – 3). These clear pH breakpoints were similar for all the heavy metals analysed.

4.3 Effect of Contact Time on the Heavy Metals Removal

The heavy metal extraction efficiency for all treatments used and all heavy metals analyzed increased with increasing time as shown in Figs. 4 – 9. The metal extraction efficiency of day 5 was statistically significant ($p<0.05$) from those of day 1 and day 2 except for chromium and lead whose percentage extraction seem to stabilize after day 2.

This finding shows a great disparity with previous findings [11,20,3], which indicate that maximum heavy metal removal efficiency is attained in less than 24 hours. These findings, however, were made mostly from studies using synthetic inorganic chelating agents.

5. CONCLUSION

The removal of heavy metals from sewage sludge is a necessary step to achieve sustainable sludge treatment. In spite of the good heavy metal removal efficiency achieved in the inorganic acid treatment method often used, factors such as cost, environmental sustainability and technical adaptability of these methods are unattractive. This study which determined the efficacy of two fermentation extracts of sugarcane wastes in removing heavy metals from sewage sludge indicated that crude fermentation extract of sugarcane waste can remove heavy metals from sewage sludge. The extract showed acceptable heavy metal removal efficiency when compared with commercial-grade citric acid. This could therefore, be adopted in removing heavy metals from sewage sludge for improved public health status.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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