OPTIMIZATION OF THE LEACHING OF ZINC, IRON AND MANGANESE FROMS ELECTED SOLID WASTES IN ZARIA, KADUNA STATE USING RESPONSE SURFACE METHODOLOGY

Comment [Z1]: Review Title. Suggestion: *optimization of the leaching recovery of zinc, iron and manganese from selected solid wastes ashes in Zaria, Kaduna State, Nigeria*

Abstract

Comment [Z2]: Too long. Review it

The efficient extraction of valuable metals from solid waste has gained significant attention due to environmental concerns and the increasing demand for sustainable resource utilization. This study focuses on the optimization of the leaching recovery of zinc, iron and manganese from selected solid wastes ashes in Zaria, Kaduna State, Nigeria, using Response Surface Methodology. The objective is to determine the optimal process conditions that maximize the leaching yield of these metals while minimizing resource and energy consumption. The solid waste ash samples were collected from two dump-sites tagged burnt tyre (BT) and contraband drug ash(AS), and analyzed for their zinc, iron and manganese contents using atomic absorption spectroscopy (AAS). The X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses confirmed the occurrence of the desired heavy metals in the ashes, with BT containing 18.54 wt.% of zinc and AS containing 2.203 wt.% of iron. Subsequent studies on the leaching behaviour of these metals from the two samples revealed that mineral acids, particularly, HCl exhibited superior leaching efficiency for zinc (25433.00 ± 733.77 mg/kg), iron (98.10 ± 2.21 mg/kg) and manganese (45.22 ± 0.58 mg/kg) from the BT ash sample and 38.68 ± 0.63 mg/kg zinc, 616.68 ± 53.82 mg/kg iron and 86.81 ± 2.57 mg/kg from the AS ash sample. Experimental design based on central composite design (CCD) method was used to design leaching experiments, considering three factors: leaching time, temperature and acid concentration. Hydrochloric acid was used as the leaching agent. The concentrations of zinc, iron and manganese in the leachate were analyzed using atomic absorption spectroscopy. Response surface methodology was utilized to develop a mathematical model that describes the relationship between the leaching parameters and metal recovery. The results indicated that all three factors significantly influenced the leaching recovery of zinc, iron and manganese. The optimal conditions for maximizing the leaching recovery from BT were determined as: acid concentration 2.968 mol/l, leaching time 97.703 min and temperature 68.852^{o}C; resulting in recovery of 32009.203 mg/kg for zinc, 4552.704 mg/kg for iron and 137.096 mg/kg for manganese with a desirability of 84.5%. For AS, the optimal leaching conditions were acid concentration of 2.831 mol/l, leaching time of 97.703 min and temperature of 68.852^{o}C; leading to the recovery of 70.554 mg/kg zinc, 5770.716 mg/kg iron and 676.416 mg/kg manganese, with an impressive desirability of 98.5%. The validity of the developed mathematical model was confirmed through a verification experiment. The experimental results closely matched the predicted values, indicating the accuracy and reliability of the model. This study contributes to the understanding of the leaching behaviour of zinc, iron and manganese from solid waste ash and provides valuable insights into the application of response surface methodology for process optimization. The finding can guide future efforts to develop sustainable and efficient methods *for metal recovery from solid waste ash, contributing to the circular economy and reducing the environmental burden associated with waste disposal.*

1.0 Introduction

The steady increase in garbage around the world is one of the most pressing concerns confronting modern society, as it is linked to global pollution (Singh and Singh 2017; Ebadi *et al.,* 2020). Environmental pollution has been regarded as one of the major global challenges in recent times (Silpa *et al*., 2018). The idea of converting one of humanity's biggest challenges (pollutant) into a useful resource to address yet another challenge, the energy crisis and the shortage of economic heavy metals, is mind blowing (Funari *et al*., 2015; Imran *et al*., 2020).

Ultra-rapid industrialization, urban migration and rapid population growth have been accused of being the factors responsible for this scenario of global polluted/potentially polluted environments. This is more or less true; however, the major cause of an unhealthy environment today is simply the attitude towards it. In many developing nations, the failure to address the issue of proper waste disposal, which is the major cause of environmental pollution, has been traced to factors such as unhealthy socio-cultural practices, poor environmental sanitation habits, lack of awareness, low literacy level, bad governance, disregard to the rule of law and other forms of indiscipline (Sylvester&Ikudayisi, 2021). In addition, illicit drugs seized by the National Drug Law Enforcement Agency (NDLEA) have reportedly been burned alongside other solid waste materials, as shown in the Plate1. In the statement released, "Over 560,068.31414 kilogramme of assorted illicit drugs were on Thursday 4th August 2022 set ablaze by the National Drug Law Enforcement Agency, NDLEA, the largest to be destroyed in the 32-years history of the anti-narcotic agency" (NDLEA, 2022).

Plate 1: Solid waste dump site (a), seized illicit drug (b) burning ground (c) generation of fly ash from seized products (Source; NDLEA, 2022)

Comment [Z3]: Label the pictures accordingly. (a), (b) and (c)

As a consequence of poorly managed waste, it pollutes water bodies, blocks drainages, causes flooding, transmits diseases through breeding of vectors, contaminates agricultural farmlands and crops, and pollutes the air through airborne particles from burning of the waste, among several other issues (Silpa *et al.*, 2018).

1.1 Statement of Research Problem

Comment [Z4]: Should be part of Abstract

Solid waste incineration has undoubtedly presented a great relief to the challenge of solid waste management, as it leads to about 70 – 90 % waste reduction in mass and volume (wang *et al*., 2019). However, the end product of incineration has introduced another challenge, which is the production of toxic heavy metal-concentrated ash, which could become another source of toxic metal pollution to the environment, when the metals leach out into aquifer or air (Ishchenko, 2019). This limitation hinders the effectiveness of landfilling the incinerated ash./

In addition, there is loss of metals of high economic value such as zinc, copper, among others, which could have been harnessed. This concern is prompted by the evidence that tyres contain heavy metals such as Zn, Cu, Cd, Cr and Pb as reported by Adeyi and Oladoye, (2020). The issue is further aggravated by the rise in end-of-life tyres, which correlates with the increase in car registrations in Nigeria in 2004, estimated to be 5,828,900 and in 2011 estimated to be 7.0 million (Umunnakwe*et al*., 2020). The rise in numbers is also attributed to tyre-use machines like bikes, motor bikes, trucks/wheelbarrows etc.

Since there is no special management practice for end-of-life tyres in Nigeria, the practice of open burning has become common place (Valentini &Pegoretti, 2022), which is not environmentally healthy (Adebola & Peter, 2020). Further, the burning of contraband drugs or illicit drugs in the country is a norm. These drugs have recently been analyzed to contain certain heavy metal elements (Schimmel et al., 2018; Aghababaei*et al*., 2018).

Therefore, this research is targeted to study the recovery of zinc, iron, and manganese from incinerated ash of contraband drugs and end-of-life tyres; employing acid and alkaline leaching of these metals and further optimizing the reaction conditions to ascertain the best extraction conditions for the method(Tang &Steenari, 2016).

Also, several other studies have employed the use of one factor at a time of the operating parameters for leaching of selected metals from ash which might not predict the actual scenario in true life leaching conditions .

1.2 Aim and objectives of the Research Study

Comment [Z5]: Too many/long. Summarize it as a statement and make it part of Abstract

The aim of this research is to optimize the leaching of zinc, iron and manganese from selected solid wastes in Zaria, Kaduna State using response surface methodology.

The aim of this study was achieved through the following set objectives: To

I. determine the concentrations of Zn, Fe, Mn, Cu and Pb in burnt tyre and contraband drug ashes obtained from two selected municipal ashes using AAS;
II. determine the chemical composition and morphology of the burnt tyre and contraband drugs ashes using XRF and XRD respectively;
III. leach Zn, Fe and Mn from each of the ashes of burnt tyre and contraband drugs dumpsites using HCl, HNO_3, H_2SO_4, citric acid, oxalic acid, NaOH, NH_3 and deionized water;

IV. derive a multiple linear regression model that expresses the relationship between a dependent variable and the multiple independent variables.

V. optimize the operational parameters efficient for leaching of Zn, Fe and Mn.

1.3 Response Surface Methodology

In 1951, as cited by (Djimtoingar et al., 2022) Box and Wilson pioneered Response Surface Methodology (RSM) as a strategy to improve chemical manufacturing processes, particularly within the chemical industry. Their primary focus was on optimizing chemical reactions, aiming to achieve favourable results such as increased yield and purity while simultaneously reducing costs. They pursued a structured approach, employing a series of sequential experiments that took into account various variables, including temperature, pressure, reaction time, and the proportions of reactants, as described by Dean *et al.* (2017). Response Surface Methodology (RSM) stands as a robust optimization approach extensively applied for evaluating the optimal process conditions when limited experimental data is available, as highlighted by Bayuo *et al.* in 2020. This method has garnered popularity for several compelling reasons, including its ability to obviate the need for excessive chemical usage, reduce time requirements, minimize costs, and alleviate labour-intensive efforts, as emphasized by Şahan and Öztürki (2014).

Further, RSM effectively addresses the limitations of single-factor optimization, a concern articulated by Aghaeinejad-Meybodi*et al.* (2015) and Kakelar and Ebrahimi (2016). RSM encompasses a suite of mathematical and statistical techniques centered on fitting empirical models to experimental designs. To achieve this goal, linear or quadratic polynomial functions are employed to characterize the system under investigation, allowing for the exploration and adjustment of experimental conditions until they are optimized, as elaborated by Veza*et al.* (2023). The methodology proves valuable in enhancing, designing, advancing, and refining processes in scenarios where multiple variables influence one or more responses (Ghorbannezhad*et al.*, 2016; Boateng , 2013). The term "optimization" is widely employed in analytical chemistry to denote the process of identifying the conditions that yield the most favourable response. When experimental data cannot be adequately described by linear functions, techniques for designing quadratic response surfaces, such as three-level factorial, Box-Behnken, central composite, and Doehlert designs as outlined in Sudha *et al.* (2013), are recommended for approximating a response function.

To employ RSM effectively, specific prerequisites must be satisfied. These criteria encompass:

1. Identification of the pivotal process factors: RSM relies on a prior understanding of the critical factors influencing the process. It is important to note that RSM software is typically tailored to handle a restricted number of variables, and as the number of

variables grows, the volume of experiments required by the designs escalates dramatically. Consequently, most RSM programmes are generally constrained to managing four or five variables.

2. Continual variation of factors: The factors under investigation must exhibit continuous variations within the range examined, allowing for a comprehensive assessment of their impact.

3. Existence of a mathematical relationship: A mathematical function should be available that establishes a connection between the response and the factors involved, as stated by Geiger in 2014.

2.0 Zinc

Comment [Z6]: Check numbering

2.1 Zinc ore and metal

Comment [Z7]: Check numbering

Metals are rarely found in the elemental forms in their natural occurring state in the earth’s crust, except a few such as gold. Many metals, however, are found in mineral forms, in combination with one or many others in a form called ores. Zinc element is usually found in combination with lead or copper. Sphalerite (ZnS), also known as zinc blende, is regarded as the most abundant zinc mineral (Srivastava and Tanveer, 2020).

The use of zinc ores dates back to the 20 B.C., when the Romans makes brass from it (Wei *et al*., 2022). Medically, zinc was also used for wound treatment (Bhutta *et al*., 2021) and to treat sore eyes. Historically, Indians are credited with the first production of metallic zinc, which occurred around 14th century (Craddock, 2018). Later, in the 17th century, the industry developed and moved to china, where sufficient zinc was produced and sold abroad (Chen, 2018; Fedje &Andersson, 2020). In 1743, William Champion built the first European zinc smelter in Bristol and thereafter the industry progressed to what we have today (Fedje &Andersson, 2020).

Zinc mining sites are not located arbitrarily; they are determined by the proximity to zinc mineral deposits with concentrations in the range of 50000 to 150000 mg/kg (Fedje &Andersson, 2020). The concentration of zinc in fly ash is said to be within the range mentioned, making location of the mining sites around their nearby deposits a guided and informed choice.

2.2 Iron

Comment [Z8]: Check numbering

2.2.1 Iron ores and metal

Comment [Z9]: Check numbering

Iron is the second most abundant element in the Earth’s crust, after aluminium; and fourth in abundance behind oxygen, silicon, and aluminium among the rest of the elements, making up about 5% of the Earth's crust (Geerdes *et al.,* 2020). However, it is the most abundant element in the earth as a whole, accounting for about 35%, and is relatively plentiful in the Sun and other stars.

Iron rarely exists in pure form in the crust. However, it exists as terrestrial iron (alloyed with 2–3 percent nickel) in basaltic rocks in Greenland and carbonaceous sediments in the United States (Missouri) and as low-nickel meteoric iron (5–7 percent nickel), kamacite (Encyclopaedia Britannica, 2022). Nickel-iron, a native alloy, occurs in terrestrial deposits (21–64 percent iron, 77–34 percent nickel) and in meteorites as taenite (62–75 percent iron, 37–24 percent nickel). Also, iron is found combined with other elements in hundreds of minerals of greatest importance are as iron ore, some of which include hematite (ferric oxide, Fe_2O_3), magnetite (triiron tetroxide, Fe_3O_4), limonite (hydrated ferric oxide hydroxide, $FeO(OH)\cdot nH_2O$), and siderite (ferrous carbonate, $FeCO_3$) (Encyclopaedia Britannica, 2022).

2.3 Manganese

Comment [Z10]: Check numbering

2.3.1 Manganese ore and metal

Comment [Z11]: Check numbering

Manganese (Mn) is a naturally occurring metallic element and is the twelfth most abundant metallic element in the Earth's crust; constituting 0.1% of the earth's crust, depending on the model used for the crustal composition (Barry, 2010; Baba *et al.*, 2014). It is usually found in rock, soil and water. Manganese rarely exists in a pure form; instead, it combines with other elements in nearly 300 different minerals. It is extracted from several economically important oxide minerals, including pyrolusite (MnO_2), psilomelane ($BaMn_9O_{16}(OH)_4$), manganite ($Mn_2O_3H_2O$), and wad (Baba *et al.*, 2014).

Over 80% of the world's manganese deposits are found in South Africa and Ukraine, while other important manganese deposits are in China, Australia, Brazil, Gabon India, and Mexico. The economically mineable manganese deposits occur in the natural concentrations of 150-500 times the average crustal abundance (Baba *et al.*, 2014). Geological processes have created natural concentrations of mineable grade and sizes in various places, formed by distinct geological processes due to the mobility of the element (Baba *et al.*, 2014). The decrease in the reserves of high-grade manganese ores is making it necessary to consider the processing of lower-grade manganese ores and sources (Spooren et al., 2020).

2.4 Municipal Solid Waste Incineration (MSWI) Ash

Comment [Z12]: Check numbering

Municipal solid waste (MSW) incineration ash is basically product of the combustion of municipal solid waste combustion or its incineration, which is a high-temperature dry oxidation process, that converts flammable and organic waste to non-flammable and inorganic waste (Ako& Ma, 2022). MSW incineration ash is mainly constituted by two main forms of ash: bottom ashes (BsA) and fly ashes (FA) (Tang, 2017). As the words suggest, bottom ash is collected at the bottom of the combustion chambers and is the major constituent of combustion ash. On the other hand, fly ash is collected in the flue gas cleaning system of the combustion plant. The former contains materials like metal objects, slag, glassy silicate and minerals with high melting points.

Meanwhile, fly ash contains small dust particles of varying sizes (needle, strip and spherical), high porosity, low water content, large specific surface area, much lighter weight, and relatively low melting points (Ako& Ma, 2022). In any case, both the bottom ash and fly ash, but particularly fly ash contain varied but considerable amounts of metals, salts, organic pollutants, among other components, some of which might be very toxic (Bakalá*et al.*, 2020). Some typical fly ashes are characterized by high chloride content and significant amount of heavy metals and toxic organic compounds, especially polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs and PCDFs) (Ako& Ma, 2022). Generally speaking, fly ash is composed mainly of soluble salts such as CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O, K_2O, P_2O_5, TiO_2, MnO, CuO, ZnO, PbO, Cr_2O_3, SO_3, and by a minor fraction of other components such as Zn, Pb, Cr, Cd, Cu, Sn, Ba, Sb, Zr, As, Co, Mo, Rb, Bi, V, Ce, Ga, La, Nd, Nb, and Hg (Ako& Ma, 2022). Therefore, the leaching out of these heavy metals and their impact on human health and environmental pollution have become major concerns, making it imperative to carefully investigate and select a safe and efficient method of treating fly ash.

3.0 MATERIALS AND METHODOLOGY

Comment [Z13]: 2

3.1 Materials

Comment [Z14]: 2

3.1.1 Apparatus, Equipment and Reagents.

Comment [Z15]: 2

The following are the apparatus and equipment used for the research work: Watch glass, funnel, retort stand, thermometer, oven, magnetic stirring machine, electronic balance (Sartorius Extend ED224S, Germany), ball milling machine (PMT/500/250/HD, India), pulverizing machine (Yam 1100 Q 4, China), sieve shaker, x-ray fluorescence (XRF) machine (X-MET8000 spectrophotometer, England), x-ray diffractometer (XRD) (RikaguMiniflex, Japan), atomic absorption spectrophotometer (AAS) machine (AgilentTechnologies200 Series AA (280 FS AA), USA). Furthermore, all reagents used for this research were of analytical grades. Additionally, distilled water was used for the preparation of all solutions. The leaching reagents used for the experiments include hydrochloric acid, tetraoxosulphate (VI) acid, trioxonitrate (V) acid, citric acid, oxalic acid, ammonia, sodium hydroxide and deionized water. All the glassware was cleaned with distilled water and dried in an oven before use.

3.2 Methodology

Comment [Z16]:

3.2.1 Collection and Preparation of Ash Samples

Comment [Z17]:

The ash samples marked BT (burnt tyre ash) and AS (contraband drugs ash) were sourced based on activity on-site from two dump sites located at Dogarawa, Sabon Gari Local Government, Zaria, Kaduna, Nigeria; after an initial survey on several municipal solid waste dump sites at different locations in Zaria. BT and AS were samples of burnt tyre ash and contraband drug ash respectively. Each was collected as composite samples, obtained from five points (diagonals and the centre of each of the dump sites; 60 cm apart) at weekly intervals for four weeks and merged into bulk samples in November, 2021. From each collecting point, about 500 g of ash was collected using a clean glass beaker.

The bulk samples were prepared for analysis and experimentation with slight modifications of the method described by Baba and Adekola (2011). The sample of each ash was oven-dried at 105°C for 4 hours and ground into a fine powder using a pulverizing device. The ash of each group was then sieved into three fractions of particle size (75 µm, 150 µm and 250 µm) using the

ASTM standard sieve at the Department of Geology, Ahmadu Bello University, Zaria. Unless otherwise stated, characterization of the ashes and leaching experiments were carried out on the smallest fraction.

3.2.2 The Leaching of Metals from Ashes

Metals of economic value (Zn, Fe, and Mn) were selectively leached from each of the BT and AS samples. The procedure was carried out by using several acids and alkaline leaching agents as suggested by Kinoshita *et al.,* 2005. Hydrochloric acid (HCl), trioxonitrate(V) acid (HNO_3), tetraoxosulphate(VI) acid (H_2SO_4), citric acid, oxalic acid, sodium hydroxide (NaOH), ammonia (NH_3), and deionized water were used as leaching agents. The BT and AS samples (1.0 g each) were separately dissolved in 100 cm^3 of each leaching agent (1.0 M) in separate 250 cm^3 glass beaker with watch glass lid. The leaching process was conducted at a temperature of 80°C for 2 hours at a stirring speed of 360 rpm. Afterward, the metal concentrations in the leached liquors of each groups were measured by AAS after filtering out the solid residues. The leaching agent with the highest leaching efficiency and the corresponding metals of economic value was considered for use in the optimization study.

3.2.3 Characterization of Sample

The elemental composition, as well as the mineralogical phase identification of the raw samples of BT and AS was determined using X-ray fluorescence spectrometry and X-ray diffractometry. The aqueous metal analysis of the BT and AS samples was carried out using Atomic Absorption Spectrophotometry (AAS) to determine the concentration of each of the metals present in the selected aqueous or leached liquor, during the leaching and optimization of the leaching experiments.

3.3 Analysis

3,3.1 Multiple linear regression model for the recovery of metals from BT and AS samples

Design Expert statistical software Version 12 (STAT-EASE Inc., Minneapolis, USA) was used for statistical calculations, modeling, and plotting. Based on the literature and initial experiments, the effects of three parameters, including concentration (0.5-12.0 Mol/dm^3), temperature (25-80°C), and time (10-120 min), on the leaching of the three selected metals of economic interest from BT and AS ashes collected from Dogarawa area in Zaria, Nigeria were considered.

The RSM method is suitable for fitting a quadratic surface and aids in the analysis of parameter interactions, as well as the optimization of process parameters with the least number of experiments (Behera *et al.,* 2018). Three responses (Zn, Fe, and Mn) were chosen to be optimized in a nonlinear optimization, where the experimental data were fitted to a second polynomial equation as shown in equation (3.2), and regression coefficients were obtained. However, the software randomizes the experimental run in order to diminish the error and the effect of uncontrolled factors (Anderson and Whitcomb, 2016).

$$\gamma = \beta_0 + \sum_{i-1}^{n} \beta_i X_i + \sum_{i-1}^{n} \beta_{ii} X_i^2 + \sum_{i-1}^{n} \sum_{j-i+1}^{n} \beta_{ij} X_i X_j + \varepsilon \quad (3.2)$$

Where γ is the predicted response; β_0 the constant coefficient;β_i the linear coefficients; β_{ii} the quadratic coefficients; β_{ij} the interaction coefficients; n the number of factors studied and optimized in the experiments; X_i and X_j are the coded values of the variable parameters for leaching process; and ε is the random error.

3.3.2 Statistical analysis

The analysis of variance (ANOVA) was performed to justify the significance and adequacy of the developed regression model. The adequacy of the response surface model was evaluated by calculating the determination coefficient (R^2) and also by testing it for the lack of fit. The significance of model terms was evaluated by the probability value (P-value) at a 95% confidence interval.

4.0 Results and Discussion of Findings

Comment [Z18]: 3

4.1 Quality Assurance

Comment [Z19]: 3

Table 1 reveals the percentage recovery of Zn, Fe and Mn from BT and AS ash samples analysed from the spiking experiment.

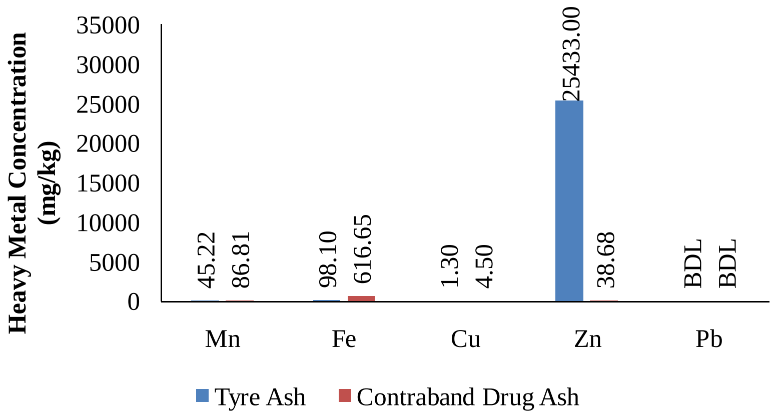
	%Recovery	
Metal	**BT Sample**	**AS Sample**
Zn	95.34	86.34
Fe	89.60	90.15
Mn	81.04	82.90

Table.1: Percent recovery of Zn, Fe and Mn from BT and AS ash samples

Comment [Z20]: Should be placed on the Table and not beneath

4.2.1 Determination of heavy metals present in ash samples

The first analysis carried out on the prepared ash samples aimed to determine the type(s) and amount of heavy metals present in the two ash samples. The five (5) heavy metals tested for, in both the BT and AS sample is presented in Figure 1.



Key: BDL = Below Detectable Limit

Figure 1: Heavy metal concentration in BT and AS

From the figure above, the concentration of Mn in burnt tyre ash was 45.22 ± 0.58 mg/kg, while those of Fe, Cu and Zn were 98.10 ± 2.21, 1.30 ± 0.02 and 25433.00 ± 733.76 mg/kg respectively. Analyses of the contraband drug ash revealed that concentration of Mn was 86.81 ± 2.56 mg/kg, while those of Fe, Cu, and Zn were 616.65 ± 53.82, 4.50 ± 0.11 and 38.68 ± 0.63

mg/kg respectively. The concentration of Pb, however, was below the detectable limit in both ash samples as presented in table 2 and 4.2.2

Table 2: Preliminary determination of heavy metals in burnt tyre ash

S/No.	Heavy metal	1st	2nd	3rd	Average	SD
1.	Mn (mg/kg)	45.43	44.42	45.80	45.22	0.58
2.	Fe (mg/kg)	95.23	100.61	98.46	98.10	2.21
3.	Cu (mg/kg)	1.30	1.27	1.33	1.30	0.02
4.	Zn (mg/kg)	24400.00	26035.00	25864.00	25433.00	733.77
5.	Pb(mg/kg)	BDL	BDL	BDL	N/A	N/A

Key: BBL: Below Detectable Limit, N/A: Not Applicable

Table 3: Preliminary determination of heavy metals in contraband drug ash

S/No.	Heavy metal	1st	2nd	3rd	Average	SD
1.	Mn (mg/kg)	83.62	89.91	86.89	86.81	2.57
2.	Fe (mg/kg)	688.62	559.2	602.13	616.65	53.82
3.	Cu (mg/kg)	4.62	4.53	4.35	4.50	0.11
4.	Zn (mg/kg)	39.43	37.89	38.72	38.68	0.63
5.	Pb (mg/kg)	BDL	BDL	BDL	N/A	N/A

Key: BBL: Below Detectable Limit, N/A: Not Applicable

From the results, it was observed that the concentration of Zn, Fe, and Mn were the highest in the two ash samples. Consequently, these heavy metals were selected for further investigation.

4.2.2 Selection of leaching reagent

Three (3) heavy metals (Zn, Fe, and Mn) were selected for further investigation. In this section, the leaching behaviour of these metals from the two selected solid waste samples, BT and AS, was investigated using eight (8) leaching agents. The result of the use of the eight reagents to leach the three heavy metals from the ash samples is presented in Figure.2.

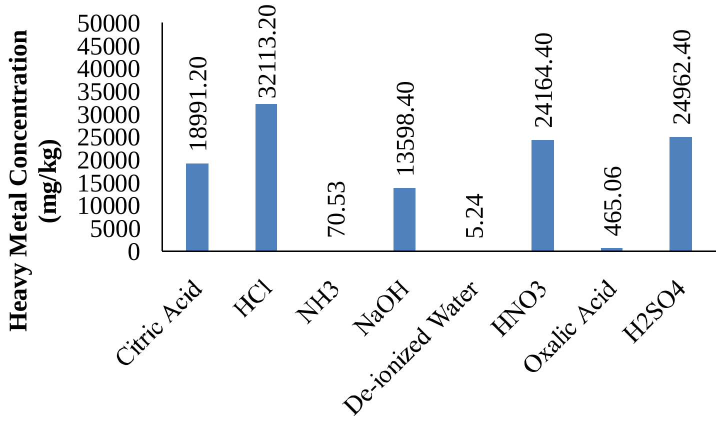


Figure 2: Concentration of Zn leached from burnt tyre ash by various reagents

From the findings, the concentration of Zn leached from the burnt tyre ash by each of the eight reagents indicated that HCl, H_2SO_4, and HNO_3 leached 32,113.20 ± 892.83, 24,962.40 ± 1507.44, and 24,164.40 ± 1308.54 mg/kg of Zn, respectively. Meanwhile, citric acid and NaOH leached 18,991.20 ± 892.83 and 13,598.40 ± 1380.65 mg/kg of Zn, respectively.

The concentration of Fe leached from the BT by the reagents is presented in Figure.3.

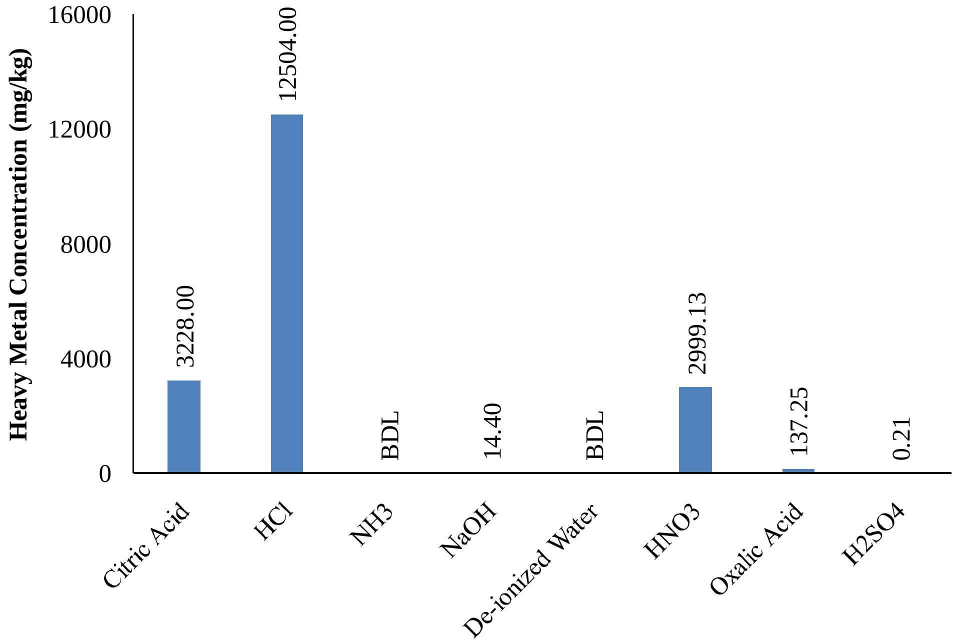


Figure 3: Concentration of Fe leached from burnt tyre ash by various reagents

The results revealed that HCl, citric acid and HNO_3 leached 12,504.00 ± 1393.03, 3,228.00 ± 206.56 and 2,999.13 ± 118.73 mg/kg of Fe respectively; while oxalic acid and NaOH leached 137.25 ± 6.14 and 14.4 ± 1.04 mg/kg of Fe respectively.

The concentration of Mn leached from BT by the reagents is presented in Figure 4.

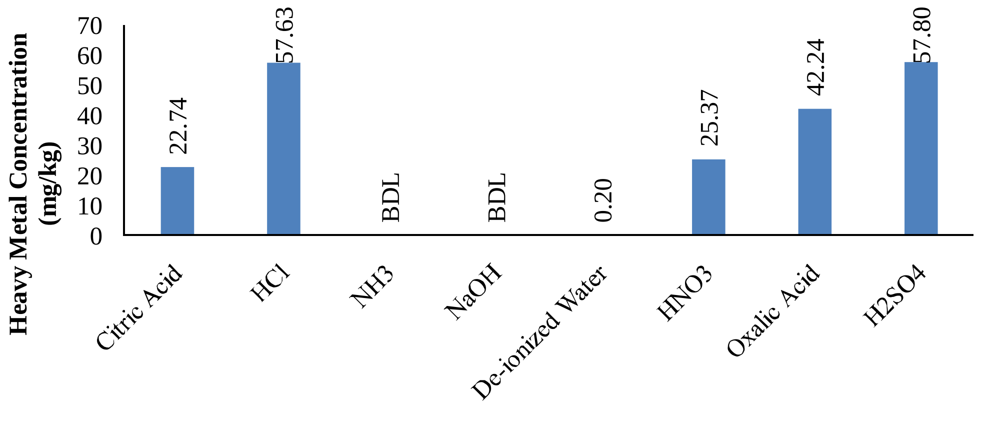


Figure 4: Concentration of Mn leached from burnt tyre ash by various reagents

The results revealed that H_2SO_4, HCl and oxalic acid leached 57.80 ± 4.26, 57.63 ± 5.18 and 42.24 ± 1.23 mg/kg of Mn respectively; while HNO_3 and citric acid leached 25.37 ± 0.33 and 22.74 ± 3.15 mg/kg of Mn, respectively as presented in table 4. and 4.2.8

Table 4.: Amount of Zn leached from burnt tyre ash by reagents

S/No.	Reagent	Reading (mg/kg)			Average	SD
		1st	2nd	3rd		
1	Citric Acid	19037.5	17875.3	20060.8	18991.20	892.83
2	HCl	32547.2	34123.8	29668.6	32113.20	1844.54
3	NH3	67.62	84.65	59.311	70.53	10.55
4	NaOH	15256.6	11876.5	13662.1	13598.40	1380.65
5	De-ionized water	4.578	5.883	5.261	5.24	0.53
6	HNO3	24659.3	25461.2	22372.7	24164.40	1308.54
7	Oxalic acid	453.26	472.85	469.07	465.06	8.49
8	H_2SO_4	26527.5	22926.3	25433.4	24962.40	1507.44

Table 5: Amount of Fe leached from burnt tyre ash by reagents

S/No.	Reagent	Reading (mg/kg)			Average	SD
		1st	2nd	3rd		
1	Citric Acid	2986.40	3491.00	3206.60	3228.00	206.56
2	HCl	12595.90	14162.30	10753.80	12504.00	1393.03
3	NH_3	0	0	0	0	0.00
4	NaOH	13.30	15.80	14.10	14.40	1.04
5	De-ionized water	0	0	0	0	0.00
6	HNO_3	2890.80	3164.40	2942.20	2999.13	118.73
7	Oxalic acid	139.34	143.50	128.91	137.25	6.14
8	H_2SO_4	0	0.42	0.21	0.21	0.17

Table 6: Amount of Mn leached from burnt tyre ash by reagents

S/No.	Reagent	Reading (mg/kg)			Average	SD
		1st	2nd	3rd		
1	Citric Acid	22.44	19.04	26.74	22.74	3.15
2	HCl	56.68	64.39	51.82	57.63	5.18
3	NH3	0	0	0	0	0.00
4	NaOH	0	0	0	0	0.00
5	De-ionized water	0.27	0	0.33	0.20	0.14
6	HNO3	25.71	25.47	24.92	25.37	0.33
7	Oxalic acid	40.82	43.81	42.09	42.24	1.23
8	H2SO4	53.39	63.56	56.45	57.80	4.26

Table 7: Amount of Zn leached from contraband drug ash by reagents

S/No.	Reagent	Reading (mg/kg)			Average	SD
		1st	2nd	3rd		
1	Citric Acid	41.04	36.15	40.06	39.08	2.11
2	HCl	63.42	53.31	57.68	58.14	4.14
3	NH3	13.66	11.21	16.53	13.80	2.17
4	NaOH	33.12	35.02	36.38	34.84	1.34
5	De-ionized water	0.00	0.00	0.00	0.00	0.00
6	HNO3	121.63	119.21	117.72	119.52	1.61
7	Oxalic aicd	49.35	46.78	47.67	47.93	1.06
8	H2SO4	40.42	36.94	38.89	38.75	1.43

Table 8: Amount of Fe leached from contraband drug ash by reagents

S/No.	Reagent	Readings			Average	SD
		1st	2nd	3rd		
1	Citric Acid	1435.60	1381.70	1157.10	1324.80	120.61
2	HCl	7834.60	7692.90	6982.60	7503.37	372.75
3	NH3	0.00	0.00	0.00	0.00	0.00
4	NaOH	7.86	6.39	7.12	7.12	0.60
5	De-ionized water	0.00	0.00	0.00	0.00	0.00

6	HNO3	7836.70	7759.40	8307.90	7968.00	242.41
7	Oxalic aicd	6836.70	7349.20	7086.50	7090.80	209.25
8	H2SO4	0.00	0.00	0.00	0.00	0.00

Table 9: Amount of Mn leached from contraband drug ash by reagents

S/No.	Reagent	Readings			Average	SD
		1st	2nd	3rd		
1	Citric Acid	47.67	39.86	41.06	42.86	3.43
2	HCl	74.84	80.34	72.15	75.78	3.41
3	NH_3	0.00	0.00	0.00	0.00	0.00
4	NaOH	0.00	0.00	0.00	0.00	0.00
5	De-ionized water	0.00	0.00	0.00	0.00	0.00
6	HNO_3	128.75	125.90	134.24	129.63	3.46
7	Oxalic aicd	4.17	6.25	4.68	5.03	0.89
8	H_2SO_4	129.84	139.48	133.52	134.28	3.97

Figure.5 presents the amount (in mg/kg) of Zn leached from AS. The results revealed that HNO_3 leached 119.52 ± 1.61 mg/kg of Zn. Further, HCl, oxalic acid, citric acid, H_2SO_4 and NaOH leached 58.14 ± 4.14, 47.93 ± 1.06, 39.08 ± 2.11, 38.75 ± 1.43, and 34.84 ± 1.34 mg/kg respectively.

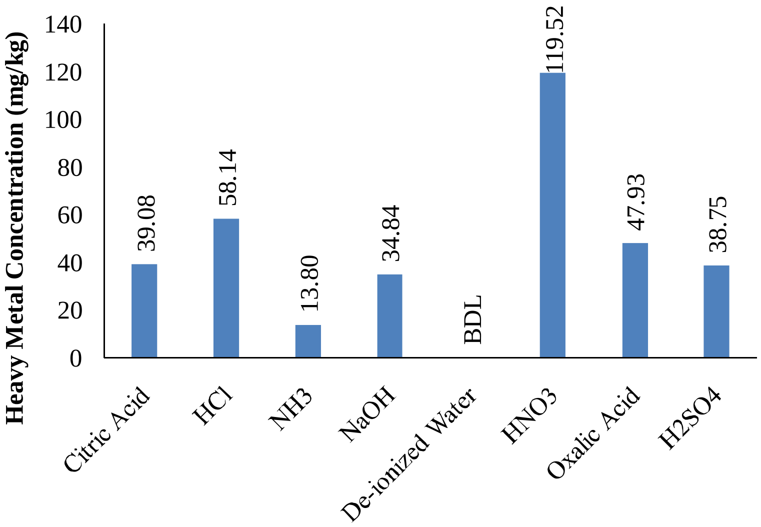


Figure 5: Concentration of Zn leached from contraband drug ash by various reagents

The amount of Fe leached by the reagents is as presented in Figure 6. HNO_3, HCl, oxalic acid and citric acid leached 7968.00 ± 242.41, 7503.37 ± 372.75, 7090.80 ± 209.25 and 1324.80 ± 120.61 respectively.

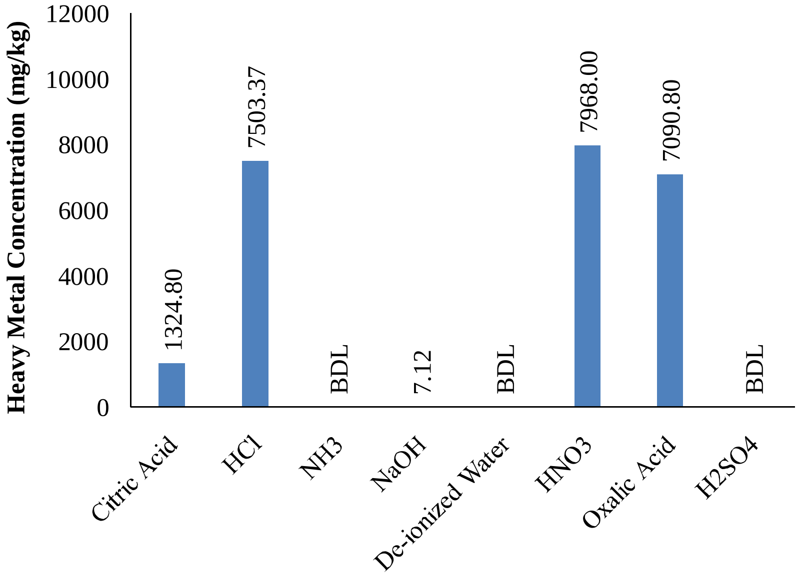


Figure.6: Concentration of Fe leached from contraband drug ash by various reagents

The concentration (in mg/kg) of Mn leached from AS is shown in Figure.7. H_2SO_4 and HNO_3 leached 134.28 ± 3.97 and 129.63 ± 3.46 mg/kg of Mn respectively; while HCl and citric acid leached 75.77 ± 3.41 and 42.86 ± 3.43 mg/kg of Mn respectively.

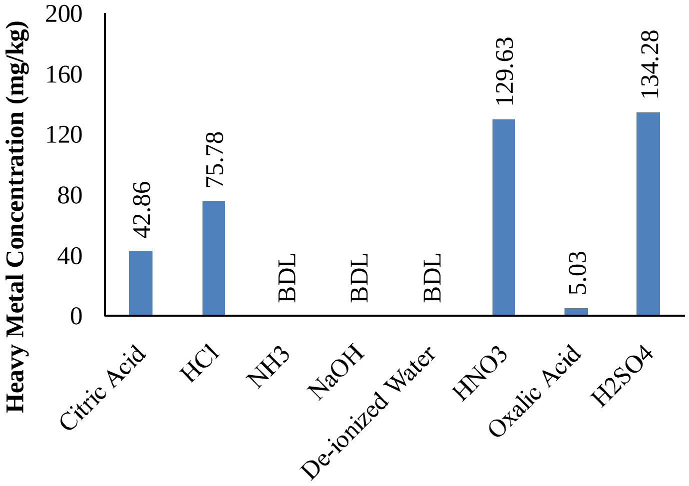


Figure.7: Concentration of Mn leached from contraband drug ash by various reagents

4.3 Design of Experiments

The experimental factor levels used in the factorial design of the Response Surface Methodology (RSM) for the leaching of BT and AS, showing the range and levels of independent variables (concentration, time, and temperature) are displayed in Table 10.

Table 10: Experimental factor levels used in factorial design

Factor	Name	Range		Coded levels	
		Min.	Max.	-1	+1
A	Concentration (mol/l)	0.50	12.00	2.83	9.67
B	Time (min.)	10.00	120.00	32.30	97.70
C	Temperature (^OC)	25.00	80.00	36.15	68.85

4.3.1 Coefficient determination values and linear correlation between the observed and predicted values for Zn, Fe and Mn responses for leaching of the Ash samples

Table 11 and Table 12 present the R-squared table, including Adequate Precision, R^2, Predicted R^2 and Adjusted R^2 for the responses of zinc, iron and manganese in the leaching of the BT and AS. Additionally, Figures 8,9 and 10 illustrate the linear correlation between the observed and predicted values for the zinc, iron and manganese responses in the leaching of BT; while Figures 11, 12 and 13 depict the same correlation for the leaching of the AS sample.

Table 11: R-square table for zinc, iron, and manganese of the BT sample

Fit Statistics	Zinc	Iron	Manganese
Std. Dev.	1452.33	282.43	13.67
Mean	19248.11	3258.14	96.66
C.V. %	7.54	8.6	14.14
R^2	0.9632	0.9494	0.9441
Adjusted R^2	0.9301	0.9039	0.8938
Predicted R^2	0.7973	0.7268	0.7021
Adeq Precision	18.7008	16.1324	18.2434

Table 12: R-square table for zinc, iron and manganese of the AS sample

Fit Statistics	Zinc	Iron	Manganese
Std. Dev.	1.48	227.92	40.46
Mean	47.55	3274.27	356.17
C.V. %	3.11	6.96	11.36
R^2	0.9893	0.9823	0.9583
Adjusted R^2	0.9797	0.9664	0.9209
Predicted R^2	0.9310	0.8902	0.7694
Adeq Precision	18.7008	39.7688	17.8763

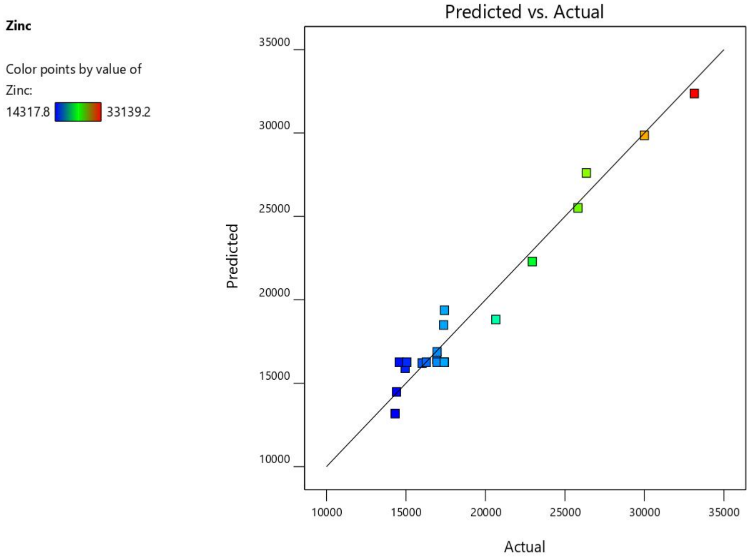


Figure 8: Linear correlation between observed and predicted value response for leaching zinc from the BT sample

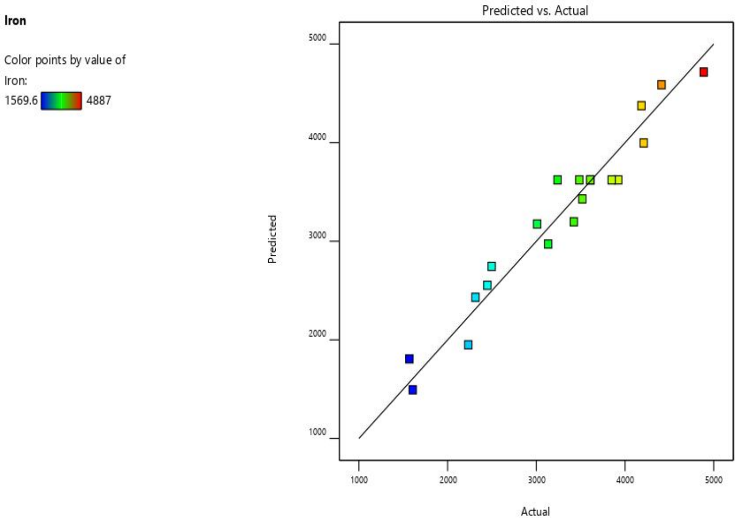


Figure 9: Linear correlation between observed and predicted value response for leaching iron from the BT sample

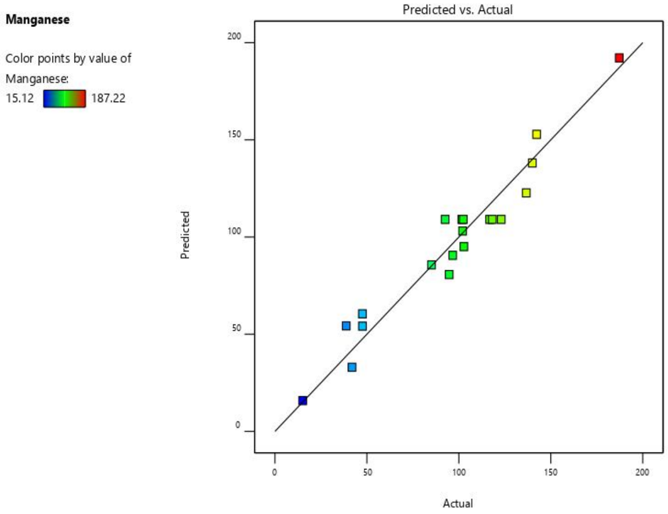


Figure 10: Linear correlation between observed and predicted value response for leaching manganese from the BT sample

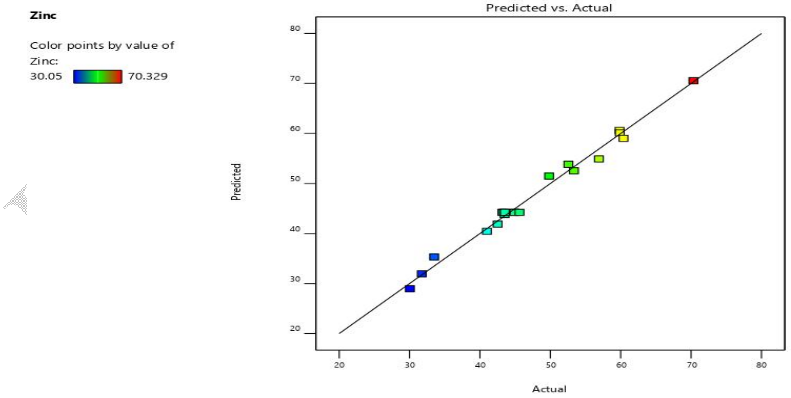


Figure 11: Linear correlation between observed and predicted value response for leaching of zinc from the AS sample

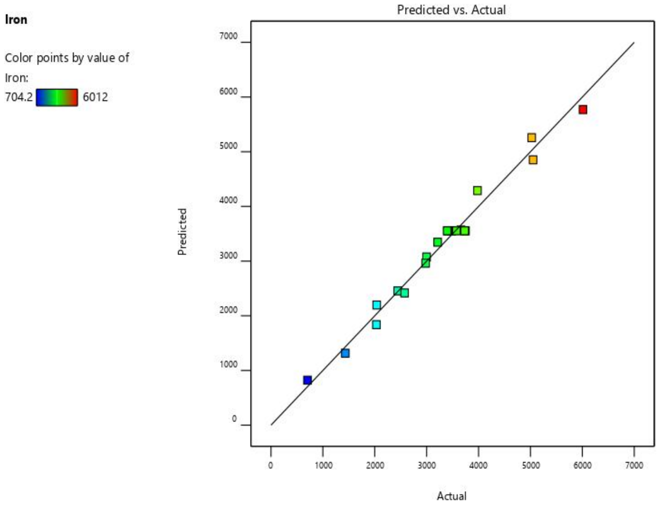


Figure 12: Linear correlation between observed and predicted value response for leaching of iron from the AS sample

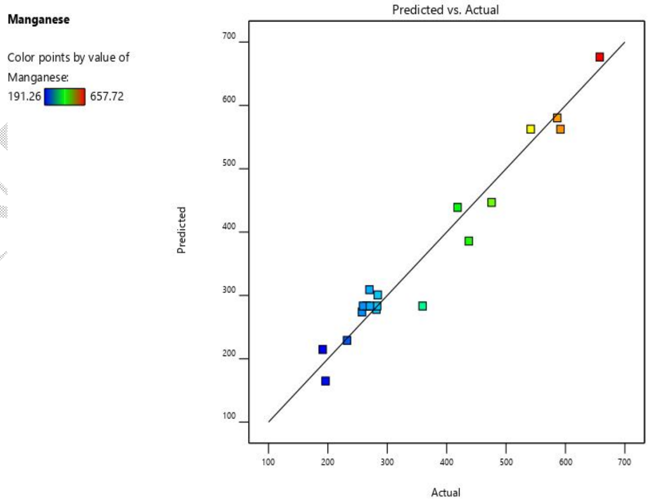


Figure 13: Linear correlation between observed and predicted value response for leaching of manganese from the AS sample

5.0 Conclusion

The successful optimization of the leaching process using response surface methodology and the identification of optimal conditions for the recovery of zinc, iron and manganese demonstrate the potential for efficient extraction of these valuable metals from solid waste. This study provides valuable insights for the development of sustainable and economically viable strategies for the utilization of waste materials and the recovery of valuable resources. Further research and application of these findings could contribute to environmental sustainability and the development of a circular economy by reducing waste generation and promoting resource recovery.

The regression model equations developed after successfully performing the experiments design through CCD of the RSM indicated that the model was statistically significant, underscoring its suitability for predicting the leaching performance (responses).

6.0 Recommendations

Based on the results and conclusions reached on this study, the following recommendations are therefore offered for future research and application.

i. Kinetic modeling of the process should be undertaken: Conducting kinetic modeling studies can help elucidate to the leaching mechanisms and provide insights into the rate-controlling steps during the leaching process. By developing mathematical models, the leaching kinetics of zinc, iron and manganese from solid wastes can be better understood, leading to improved process design.
ii. Further study to investigate the effects of impurities on the leaching process should be carried out. Understanding the role of impurities will contribute to more accurate process optimization and ensure production of high-quality metal concentrates.
iii. Further study should scale-up the work. It is essential to investigate the scalability of the optimized leaching process under large-scale conditions, simulating industrial operations. This will help determine the feasibility and potential challenges associated with implementing the optimized process on a commercial scale.
iv. A techno-economic analysis of the large-scale process should be carried out for evaluating the economic viability of the optimized leaching process. This analysis will provide a realistic assessment of the economic feasibility and potential profitability of implementing the optimized process in a commercial setting.
v. An environmental impact assessment of the large-scale leaching process should be carried out for the potential environmental implications due to the use of chemicals and generation of waste streams. This should include assessing the potential risk associated with the use and disposal of leaching agents, evaluating the waste management strategies and identifying potential mitigation measures to minimize the environmental footprint of the process.

By undertaking these further studies, researchers can enhance the understanding of the leaching process for zinc, iron and manganese recovery from solid waste, improve process efficiency and address potential challenges. The outcome of these studies will contribute to the development of sustainable and economically viable strategies for metal recovery from solid waste in Zaria, Kaduna State, Nigeria and beyond.

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