Int. j. adv. multidisc. res. stud. 2024; 4(4):793-796

Received: 21-06-2024
Accepted: 01-08-2024

International Journal of Advanced Multidisciplinary Research and Studies

ISSN: 2583-049X

Characterizations of Untreated and Treated Automobile Workshop Polluted Soil in Enugu Metropolis

[1] Anthony U Agu, [2] Chibuikem J Ekpe, [3] Samuel O Egbuna
[1, 2, 3] Department of Chemical Engineering, Enugu State University of Science and Technology, Agbani, Nigeria

DOI: https://doi.org/10.62225/2583049X.2024.4.4.3109
Corresponding Author: **Anthony U Agu**

Abstract
The main objective of the study is to characterize the contaminated soil from car workshops both before and after treatment using methanol, ethylenediaminetetraacetic acid (EDTA), and a blend of methanol and EDTA as extractants. With the use of an X-ray fluorescence spectrometer (XRF), gas chromatography (GC), and an atomic absorption spectrophotometer (AAS), the chemical compositions, concentrations of polycyclic aromatic hydrocarbons, and heavy metals of the soil sample were determined. Numerous metallic oxide compounds were found in both treated and untreated vehicle workshop polluted soil samples, according to the XRF results. The composition of the soil was changed when it was treated with methanol, EDTA, or methanol and EDTA together as extractants. The remediating properties of the extractants are thought to be responsible for the changes and movements of the chemical compounds' mobile components and molecules during hydrothermal alteration. The untreated automobile-polluted soil has extremely high levels of polycyclic aromatic hydrocarbons, raising serious implications for public health. Anthracene, fluoranthene, and benzo(a)pyrene are the main constituents. It was shown that applying extractants to the soil significantly decreased the quantities of polycyclic aromatic hydrocarbons. High quantities of zinc and chromium are found in untreated automobile-polluted soil, according to results from an atomic absorption spectrophotometer (AAS). On the other hand, Zn and Cr concentrations were significantly reduced when methanol, EDTA, and methanol/EDTA mixed extractants were used.

Keywords: Automobile, Characterization, Soil

1. Introduction
Auto mechanics typically work out of open spaces in their workshops. Typically, a city or town will include multiple mechanic villages (Nwachukwu *et al*., 2010) [1]. For example, a well-known mechanic village in Enugu, Nigeria, is called Coal Camp Mechanic Village. It produces automotive oily wastes that may disperse polynuclear aromatic hydrocarbons to nearby environmental segments (Ogbuagu and Ogbonna, 2013) [2]. Additionally, liquid wastes like fuel and vehicle lubricants as well as solid wastes like metal scraps are frequently deposited in the soil at auto repair shops. Heavy metal-containing metal debris may seep into shallow subterranean waters.
The majority of motor oil spills into soil are made up of polycyclic aromatic hydrocarbons, or PAHs. Both PAHs and heavy metals are bad for the ecosystem. The greatest global environmental problems are caused by these contaminants (Doumett *et al*., 2008; Wuana *et al*., 2010) [3, 4]. Heavy metals and PAHs are chemical dangers that can linger in the soil environment for a very long period since they are not biodegradable. However, based on their chemical speciation in the soil, their availability to biota can vary greatly. In an ecosystem, heavy metal buildup can be harmful (D'Amore *et al*., 2005) [5]. Comparably, because PAHs are known carcinogens, Ogbuagu and Ogbonna's 2013 study has increased public health awareness.
More than 80% of used engine and transmission oil in Nigeria may have been improperly disposed of by mechanics on the ground; this used engine oil contains various additives, contaminants, and combustion-related residues (Ogbuagu and Ogbonna, 2013) [2]. Some of these, such as polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs), are toxic or carcinogenic.
The presence of natural or chemical materials in the soil has disrupted its natural equilibrium, leading to the observation of soil pollution. Innovative and long-lasting approaches to polluted land cleanup are the focus of an increasing amount of study. Co-solvents and chelating solutions, such as ethylenediaminetetraacetic acid, or EDTA, are examples of possible extractants. As

an aminopolycarboxylic acid, ethylenediaminetetraacetic acid (EDTA) is different from co-solvents, which are organic chemicals that are water-miscible due to their polar structure, such as methanol and ethanol. To ascertain whether the soil has returned to its original state, it is crucial to characterize the soil sample both before and after the treatment.

2. Materials and Methods

2.1 Equipment and Raw materials

Chelation solution, ethylenediaminetetraacetic acid (EDTA) ($C_{10}H_{16}N_{208}$), co-solvent (methanol), X-Ray florescence (Supreme 8000, Oxford Instrument), and Atomic Absorption Spectrophotometer (AAS) model AA320 are among the materials, chemicals, and equipment used in this study. Gas chromatography (furnished with an on-column, automatic injector, flame ionization detector, and HP 88 capillary column (100 m, 0.25 m film thickness) CA, USA), soxhlet extractor, condenser, thermometer, beakers, stop watch, pH meter, weighing balance, sieve, and water bath with thermostat are also utilized.

2.2 Experiment Method

2.2.1 Sample Preparation

The soil sample was taken from the coal camp's automobile workshop in a damp, aggregated state that made it unfit for analysis. It was then allowed to air dry for 48 hours, ground using a mortar and pestle, and then sieved using a 1 mm pore size sieve. Three series of extraction procedures were carried out in order to evaluate the impact of various solutions. These comprised the use of methanol, EDTA, and methanol and EDTA combination extractants.

2.2.2 Characterization of the untreated and treated polluted soil samples

- Determination of Chemical Composition using XRF

The Oxford Instruments Supreme 8000 X-Ray Florescence (XRF) was utilized to ascertain the soil sample's chemical composition. High energy x-rays were used to irradiate each sample using a controlled x-ray tube. Live results were shown following the initial few seconds of measurements, facilitating a quick evaluation of the product's quality. Right up until the conclusion of the experimental measurements, the results were updated continuously.

- Determination of Zn and Cr concentrations using AAS

The contents of zinc and copper in the soil samples were measured using an atomic absorption spectrophotometer (AAS). First, the earth had to be broken down. With the use of a digital weighing balance, 2 grams of the sample were weighed into a crucible, covered, and placed inside a muffle furnace set at 5500C for three hours. After cooling, the sample was mixed and digested on a hot plate at 800C for ten minutes. The sample was then filtered through Whatman No. 4 filter paper, and the volume was brought to 50 milliliters using distilled water and placed in a reagent bottle for mineral analysis.

- Determination of polycyclic aromatic hydrocarbons of the soil samples

Florisil cleanup for polycyclic aromatic hydrocarbon: Florisil heated in an oven at 130^0C overnight (about 15hrs) were transferred to a 250ml size beaker and placed in a desiccator.

3. Results

3.1 XRF results of the soil samples

Table 1: XRF results of the soil samples

Component	Concentration (%)			
	Untreated polluted soil	Polluted soil treated with methanol	Polluted soil treated with EDTA	Polluted soil treated with methanol and EDTA
SiO_2	54.573	57.526	55.612	60.959
V_2O_5	0.100	0.094	0.109	0.083
Cr_2O_3	0.066	0.057	0.063	0.079
MnO	0.063	0.068	0.051	0.054
Fe_2O_3	17.153	15.559	16.783	14.642
CO_3O_4	0.085	0.077	0.081	0.076
NiO	0.000	0.006	0.005	0.001
CuO	0.72	0.063	0.084	0.072
Nb_2O_3	0.16	0.010	0.019	0.016
MoO_3	0.002	0.005	0.000	0.003
WO_3	0.000	0.000	0.000	0.000
P_2O_5	0.118	0.132	0.275	0.080
SO_3	1.459	0.865	1.124	0.956
CaO	4.493	3.811	3.863	3.014
MgO	0.341	0.000	0.000	0.000
K_2O	0.983	0.935	0.931	0.846
BaO	0.108	0.089	0.270	0.154
Al_2O_3	17.168	17.758	17.497	16.246
Ta_20_5	0.019	0.029	0.033	0.011
TiO_2	2.189	2.059	2.092	1.847
ZnO	0.134	0.107	0.067	0.055
Ag_2O	0.032	0.037	0.031	0.026
Cl	0.614	0.551	0.777	0.582
ZrO_2	0.211	0.163	0.235	0.198
SnO_2	0.000	0.000	0.000	0.000

3.2 Results of the AAS analysis of the samples

Table 2: Results of the mineralogical analysis of the samples

Sample	Zinc (ppm)	Chromium (ppm)
UAPS	2.034	0.402
APS treated with methanol	0.679	0.145
APS treated with EDTA	0.491	0.116
APS treated with combine methanol and EDTA	0.389	0.098

UAPS – Untreated auto-mechanic polluted soil, APS - Auto-mechanic polluted soil, EDTA - ethylenediaminetetraacetic acid

3.3 Polycyclic aromatic hydrocarbons results

Table 3: Untreated automobile polluted soil

S. No	Component	Concentration (mg/ml)
1	Acenaphthylene	0.2051
2	Benzo(k)fluoranthene	0.1827
3	Fluoranthene	2.9061
4	Naphthalene	0.1116
5	Phenanthrene	0.1064
6	Anthracene	2.4559
7	Fluorene	0.4937
8	Xylene	0.7627
9	Acenaphthene	0.1282
10	Pyrene	0.0323
11	Benzo(a)pyrene	6.7628
12	Dibenzyl(a_h)anthracene	0.0005

Table 4: Automobile polluted soil treated with methanol

S. No	Component	Concentration (mg/ml)
1	Acenaphthylene	0.0108
2	Acenaphthylene	0.1398
3	Fluoranthene	0.9938
4	Naphthalene	0.0903
5	Anthracene	1.7793
6	Fluorene	0.4367
7	Xylene	0.7704
8	Acenaphthene	0.1218
9	Pyrene	3.6842
10	Benzo(a)pyrene	0.3319
11	Benzo(g_h_i)perylene	0.0078

Table 5: Automobile polluted soil treated with EDTA

S. No	Component	Concentration (mg/ml)
1	Acenaphthylene	0.0054
2	Acenaphthylene	0.0745
3	Fluoranthene	0.9935
4	Naphthalene	0.0902
5	Anthracene	1.5509
6	Xylene	0.8910
7	Pyrene	2.8563
8	Benzo(a)pyrene	0.2205
9	Benzo(g_h_i)perylene	0.0077
10	1-2 Benzanthracene	0.0037

Table 6: Automobile polluted soil treated with combine EDTA and Methanol

S. No	Component	Concentration (mg/ml)
1	Acenaphthylene	0.0008
2	Acenaphthylene	0.0097
3	Fluoranthene	1.1362
4	Naphthalene	0.0831
5	Anthracene	1.5013
6	Pyrene	2.2556
7	Benzo(a)pyrene	0.1783
8	Benzo(g_h_i)perylene	0.0054
9	1-2 Benzanthracene	0.0044

4. Discusion

4.1 XRF analysis of the soil samples

Table 1 displays the XRF results of samples of polluted soil that were left untreated, treated with methanol EDTA, and blended with methanol and EDTA. SiO_2, V_2O_5, Cr_2O^3, MnO, Fe_2O_3, CO_3O_4, NiO, CuO, Nb_2O_3, MoO_3, WO_3, P2O5, SO_3, CaO, MgO, K_2O, BaO, Al_2O_3, Ta_20_5, TiO_2, ZnO, Ag_2O, Cl, ZrO_2, and SnO_2 compounds were found among the compounds, according to the XRF data. But at some point, NiO, WO_3, MgO, and SnO_2 were absent. This is because the energy of these elements' fluorescent photons is too low or negligible to detect their transmission via the air (Spanó *et al*., 2009) [6]. The composition of the soil was changed by treating it with methanol, EDTA, and methanol/EDTA blend extractants. Changes and motions of the chemical compositions' mobile components and molecules are likely to be associated with hydrothermal alteration driven by the remediating abilities of the extractants.

4.2 The AAS analysis of the samples

The AAS analysis of the soil samples for untreated auto-polluted soil (UAPS), auto-polluted soil (APS) treated with methanol and EDTA, and methanol and EDTA combined is shown in Table 2 in terms of Zn and CR. High quantities of zinc and chromium were found in untreated automobile-polluted soil, according to AAS data. Plants may experience aberration and ultra-structural alterations as a result of zinc and chromium concentrations (Gonzalez *et al*., 2017) [8]. However, the amounts of Zn and Cr were significantly reduced in the extractants of methanol, EDTA, and combination methanol/EDTA. According to Mossop *et al*. (2009) [9], the therapy was highly beneficial and commensurate with the analytes released.

4.3 Polycyclic aromatic hydrocarbons

Tables 3 display the polycyclic aromatic hydrocarbon components of the untreated vehicle-polluted soil. The constituents' values are so high that there is a serious reason for public health concerns. Anthracene, fluoranthene, and benzo(a)pyrene are among the main constituents. In both human and aquatic tissues, there is a risk of buildup. The danger is that polycyclic aromatic hydrocarbons at such high concentrations have been linked to cancer (Ogbuagu and Ogbonna, 2013) [2]. By drinking contaminated waters, humans can consume the toxic hydrocarbons. When food is prepared using the tainted water, it can also be ingested.

Tables 4, 5, and 6 show the concentrations of the constituents of polycyclic aromatic hydrocarbons in soil treated with methanol, EDTA, and combination methanol/EDTA, respectively. Overall analysis of the component concentrations revealed that the amount of pollutants in the soil was significantly decreased by using the extractants of methanol, EDTA, and combination methanol/EDTA.

5. Conclusion

From the analyses of the experimental results, the following conclusions were made:

The XRF results showed that both treated and untreated car workshops' contaminated soil samples included metallic oxide components. The composition of the soil was changed when it was treated with methanol, EDTA, or a combination of the two extractants. High quantities of zinc and chromium were found in untreated automobile-polluted soil, according to AAS data. Plants that have high amounts of zinc and chromium may exhibit aberration and ultrastructural alterations. However, the amounts of Zn and Cr were significantly reduced in the extractants of methanol, EDTA, and combination methanol/EDTA. The untreated automobile-polluted soil has extremely high levels of polycyclic aromatic hydrocarbons, raising serious implications for public health. Anthracene, fluoranthene, and benzo(a)pyrene are the main constituents. It was found that the amounts of polycyclic aromatic hydrocarbons have significantly reduced when the soil was treated by extractants.

6. References

1. Nwachukwu MA, Feng H, Alinnor J. Assessment of heavy metal pollution in soil and their implications within and around mechanic villages. Int. J. Environ. Sci. Tech. 2010; 7(2):347-358.
2. Ogbuagu DH, Ogbonna KN. Contributions to the environmentof priority polynuclear aromatic hydrocarbonsfrom the coal camp mechanic village (CCMV) in Enugu, Nigeria. Research Journal of Pharmaceutical, Biological and Chemical Sciences. 2013; 4(4):1306-1319.

3. Doumett S, Lamperi L, Checchini L, Azzarello E, Mugnai S, Mancuso S, *et al*. Heavy metal distribution between contaminated soil and Paulownia tomentosa, in a pilot-scale assisted phytoremediation study: Influence of different complexing agents. Chemosphere. 2008; 72(10):1481-1490.
4. Wuana RA, Okieimen FE, Imborvungu JA. Removal of heavy metals from a contaminated soil using chelating organic acids. Int. J. Environ. Sci. Tech. 2010; 7(3):485-496.
5. D'amore JJ, Al-abed SR, Scheckel KG, Ryan JA. Methods of speciation of metals in soils. J. Environ. Qual. 2005; 34(5):1707-1745.
6. Spanó JC, Silva RG, Guedes DF, Sousa-Neto MD, Estrela C, Pécora JD. Atomic absorption spectrometry and scanning electron microscopy evaluation of concentration of calcium ions and smear layer removal with root canal chelators. J Endod. 2009; 35:727-730.
7. Wu L, Mu Y, Deng X, Zhang S, Zhou D. Comparison of the effect of four decalcifying agents combined with 60°C 3% sodium hypochlorite on smear layer removal. J Endod. 2012; 38:381-384.
8. Gonzalez A, Gil-Diaz M, Pinilla P, Lobo MC. Impact of Cr and Zn on growth biochemical and physiological parameters and metal accumulation by wheat and barley plants. Water and air pollution. 2017; 228(11):419-425.
9. Mossop KF, Davidson CM, Ure AM, Shand C. Effect of EDTA on the fractional and uptake by taraxacum officinale of potentially toxic elements in soils from former chemical manufacturing sites. Plant and soil. 2009; 320(1):117-129.