

# Assessing the effectiveness of heavy metals adsorption from a single contaminated source using a modular leachate tower (MLT)



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Aneke Frank Ikechukwu<sup>1\*</sup>

\* Corresponding Author: [AnekeF@ukzn.ac.za](mailto:AnekeF@ukzn.ac.za)

## ABSTRACT

The natural environment most often is exposed to severe threats due to the discharges from active mines in the form of acid mine drainage (AMD). This study investigates the applicability of adsorbing heavy metals (HM) from single source contamination using a modular leachate tower (MLT). The nano-slag composite liner (NSCL) was prepared using 10%, 20%, 30% 40%, and 50% to the combined masses of soil and nanosized slag. The MLT equipment was set up in a framework that contained AMD in the reservoir and the statically compacted nano-geocomposite liner in the attenuation chamber. The MLT setup was allowed for 120 minutes of equilibrium time before the application of 50 kPa, 100 kPa, 150 kPa, and 200 kPa equivalent pressure from the mounted hydraulic jack at the side of the MLT. The collected effluents were subjected to inductive coupled plasma mass spectrometry (ICP-MS) tests to evaluate the percentages of adsorbed HMs using a pseudo-first-order adsorption model. Scanning electron microscopy (SEM) tests were also used to determine the changes in the nano-geocomposite liner microstructure due to the interaction with the AMD. The results revealed that the removal of 100%Pb, 97.3%Cd, 96.4%Zn, 92.3%Cu, 89.1%Fe, 87.3%Ni, 15.13%As, 98%Co, and 59.5%Hg of HMs was achieved with the 50:50 ratio of soil: NBFS dosage even as the pressure levels increases. The results further revealed that the effluent harvested from the natural soil liner failed to comply with the Department of Water Affairs and Forestry (DWARF) standards. Whereas the residual quantities of available HMs ions in effluents complied with the standard at all pressure levels due to the formation of aluminosilicate structure and pozzolanic-soil ratio.

## RÉSUMÉ

Le milieu naturel est le plus souvent exposé à des menaces sévères dues aux rejets des mines actives sous forme de drainage minier acide (DMA). Cette étude examine l'applicabilité de l'adsorption des métaux lourds (HM) provenant d'une source unique de contamination à l'aide d'une tour de lixiviation modulaire (MLT). Le revêtement composite nano-scories (NSCL) a été préparé en utilisant 10 %, 20 %, 30 %, 40 % et 50 % des masses combinées de sol et de laitier nanométrique. L'équipement MLT a été installé dans un cadre qui contenait AMD dans le réservoir et le revêtement nano-géocomposite compacté statiquement dans la chambre d'atténuation. La configuration du MLT a été autorisée pendant 120 minutes de temps d'équilibre avant l'application d'une pression équivalente de 50 kPa, 100 kPa, 150 kPa et 200 kPa à partir du vérin hydraulique monté sur le côté du MLT. Les effluents collectés ont été soumis à des tests de spectrométrie de masse à plasma couplé inductif (ICP-MS) pour évaluer les pourcentages de HM adsorbés à l'aide d'un modèle d'adsorption de pseudo-premier ordre. Des tests de microscopie électronique à balayage (SEM) ont également été utilisés pour déterminer les changements dans la microstructure du revêtement nano-géocomposite dus à l'interaction avec l'AMD. Les résultats ont révélé que l'élimination de 100 % Pb, 97,3 % Cd, 96,4 % Zn, 92,3 % Cu, 89,1 % Fe, 87,3 % Ni, 15,13 % As, 98 % Co et 59,5 % Hg de HM a été obtenue avec le 50: 50 ratio de sol: dosage NBFS même lorsque les niveaux de pression augmentent. Les résultats ont en outre révélé que les effluents récoltés à partir du revêtement de sol naturel n'étaient pas conformes aux normes du Département des eaux et forêts (DWARF). Alors que les quantités résiduelles d'ions HMs disponibles dans les effluents sont conformes à la norme à tous les niveaux de pression en raison de la formation de structure aluminosilicate et du rapport pouzzolanique-sol.

## 1 INTRODUCTION

The AMD contributes to over 50% of environmental contamination, this percentage continues to increase due to the increased mining activities (Ahmaruzzaman, 2011). Other sources of HM contamination are also confirmed to come from the battery, pigment, and textile industries (Iloms et al. 2020). Thus, little exposure to HMs at micro levels could trigger health issues in humans and animals (WHO, 2006). The high toxicity of AMD can be identified at

a very low concentration, from single or multiple sources of contamination causing accumulation in the food chain.

Certainly, AMD poses health challenges, due to the discharge of toxic metals such as cadmium, lead, nickel, cobalt, copper, zinc, chromium, and iron. Besides from this challenge AMD also contributes to the diminishing water eminence around the globe at an alarming rate (Wang et al. 2018; Wang et al. 2020). Also, it is a fact that water plays a vital role in the natural environment with the corresponding resolution of life on Earth (Chen et al. 2022). With this view in mind, (Markovic et al. 2020) proposed

some innovative technologies ranging from nanofiltration, ion exchange, electrodialysis, phytoremediation, and remediation utilizing fungi and bacteria, for the removal of heavy metals from AMD. These technologies include but are not limited to a nanofiltration (Pino et al. 2018), ion exchange (Robert et al. 2022), electrodialysis (Daniella et al., 2013), phytoremediation (Burgess, et al. 2018), remediation utilizing fungi and bacteria (Rambabu, et al. 2020), and adsorption on nanosized metal oxides (Taman et al. 2016). Although the processes for the removal of toxic metals were accepted, however, they had a few drawbacks, which is relatively a function of reagents cost that increases the treatment cost.

Thusly, water security is considered one of the top five global crises based on development impacts, as such, the contamination of water bodies by HMs through discharging industrial wastewater is a complex environmental issue that needs to be addressed. Therefore, this issue has motivated the quest for a green efficient technique for the removal of HMs from waste. Nanotechnology is making salient contributions to pavement geotechnics, as extensively published by (Ikechukwu et al 2021; Aneke et al. 2022). Hence, the nanotechnology application could also be seen in every civil engineering project. Zhao et al. (2016) extensively proved that nanotechnology provides cheaper and more effective techniques for HMs adsorption due to large specific surfaces, great sorption sites, diverse surface interactions, and fast adsorption rates. Mercado-Borrayo et al. (2014) confirmed that nanotechnology removes toxic metal contaminants through adsorption.

Recently, increased attention has been channeled towards nanomaterials for the removal of HMs from an aqueous system due to their large surface areas, high adsorption capacity, and fast adsorption kinetics (Yu et al. 2021). In this study, recycled wastes were used as a value-added adsorbent material for the adsorption of heavy metals from a single source contaminated system. Steel slag was selected for this purpose due to its oxides and hydroxides. In a published study, it has proven that the oxide in the slag provides adsorption sites for anions, as the surrounding system catalyzes the precipitation of dissolved heavy metal cations through the increase in pH of hydroxides (Aneke et al. 2015). Therefore, this study synthesized waste slag to a nanoscale level, and it was used to fabricate a nano-engineered composite liner from a single contaminated system at different stress loads, using a built-up laboratory Modular Leachate Tower. The choice of the adsorption techniques was due to its significant advantages towards effective resource management cost-effectiveness, convenience, reliability, and high efficiency of heavy metal adsorption.

## 2 MATERIALS AND METHODOLOGY

### 2.1 Materials

#### 2.1:1 Natural soil

The soil used for this study is natural soil (NAT-S) collected 350 km away from the mine in Mpumalanga, South Africa at a depth of 1.2 m without any form of impurities. The

particle size distribution analysis was performed following the ASTM D114 (2017) protocol; hence the soil is classified as clay of high plasticity (CH) based on the percentage of fine retained in sieve size 75  $\mu$ m according to the Unified Soil Classification System (USCS). The particle size distribution curve of the soil is presented in Figure 1.

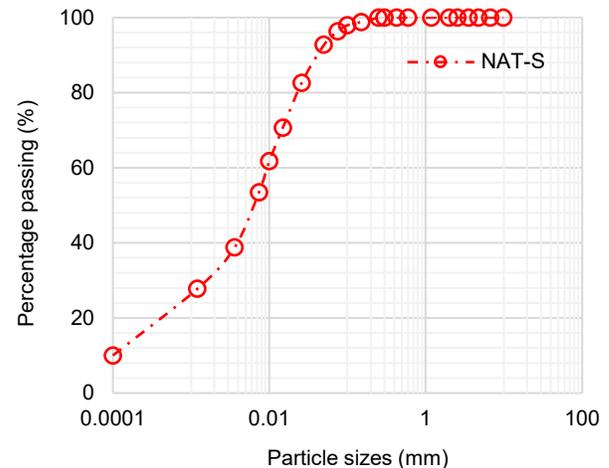


Figure 1. Soil gradation curve

#### 2.1:2 Nano-blast furnace slag (NBFS)

A fresh basic-oxygen-furnace (BOF) slag has been supplied from Fry' Metals South African Iron and Steel Company, with a nominal particle size of 1.0 mm, having more than 70% of CaO + MgO + MnO + FeO oxides. This confirms that the supplied slag is produced through the process of basic oxygen-furnace (BOF) slag (Der-Hsien et al.2009). The slag particles were scaled down to 32  $\mu$ m using different grinding steps. Followed by a milling process using a stainless-steel milling machine with a corresponding ball-to-powder ratio of 10:1. The milling process lasted for 6 h with 0.5 h intervals at a rotation of 500rpm. Toluene and anionic surface-active chemical agents were added at each interval to cool the inner chamber of the mill and eliminate any form of agglomerations that might be formed by the slag nanoparticles. These conditions were repeated for each run until the surface area of the nano-slag particles increased from 0.02 m<sup>2</sup>/gm to 23.40 m<sup>2</sup>/gm. according to the high-resolution transmission electron microscopy (HRTEM) analysis. Following the milling process, slag particle sizes were significantly transformed into nano-slag particles.

The chemical compositions of the NAT-S and NBFS were analyzed using through X-ray fluorescence (XRF) test and the results are presented in Table 1. To determine the total negative charge of the NAT-S, the cation exchange capacity (CEC) tests were performed following Indian Standard, 2720 (1976), using an ammonium chloride solution of 485 $\pm$ 3 ppm content equivalent to NH<sub>4</sub><sup>+</sup> concentration. The result showed that the NAT-S contained fine particles greater than >65%. This indicates that the NAT-S has a positive surface charge for cation exchange with a corresponding CEC value of 48.37 meq/100 g.

Table 1 chemical composition

Oxides (%)	NAT-S	NBFS
SiO <sub>2</sub>	56.59	17.41
Al <sub>2</sub> O <sub>3</sub>	18.41	5.21
Fe <sub>2</sub> O <sub>3</sub>	10.09	28.24
CaO	6.62	38.68
K <sub>2</sub> O	0.95	1.40
MgO	1.40	6.3
Others	4.94	2.77
CEC (meq/100 g)	75	298

### 2.1:3 Acid mine drainage (AMD)

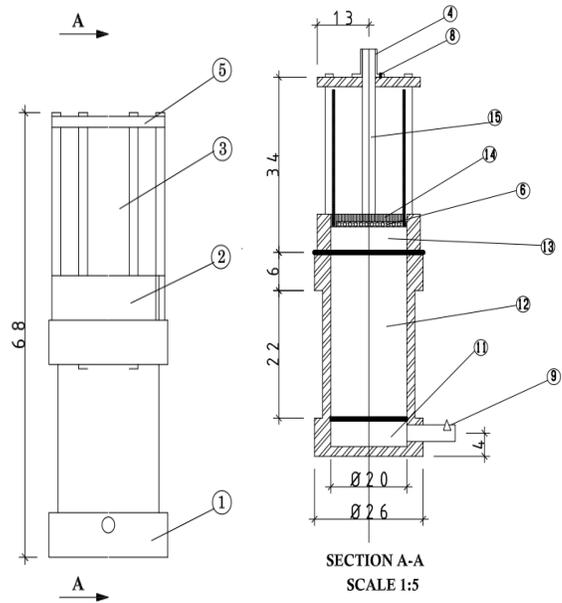
Samples of AMD were collected from a recently abounded coal mine in Mpumalanga, South Africa, from a single contaminated source. The collected AMD samples were subjected to chemical composition and concentration evaluation tests using ICP-MS. The test results confirmed that the investigated AMD rendered a pH value of 2.5, had high electrical conductivity, and contained elevated levels of sulfate and dissolved heavy metals. The concentration limits specified by DWARF (1996) for livestock watering and irrigation/construction use are summarized in Table 2 alongside the HMs concentration in AMD. The sampled AMD is acidic, revealing various heavy metals like As, Cr, Hg, Fe, Pb, Cu, Cd, and Ni with concentrations above the permitted limits for agricultural and irrigation/construction purposes. The major water contaminants are arsenic, cadmium, chromium, copper, lead, nickel, and zinc (Jaishankar et al. 2014).

Table 2 Chemical composition of raw AMD& water standard

Element	AMD (Mgdm <sup>-3</sup> )	DWARF, (1996) standards	
		Livestock watering (Mgdm <sup>-3</sup> )	Irrigation (Mgdm <sup>-3</sup> )
Hg	14	1.0	<<
Fe	32	10	5.0
As	9.0	1.0	0.001
Zn	5.41	20	1.0
Pb	15.3	0.5	0.2
Cu	22	5.0	0.2
Cd	39.3	10	10
Ni	14.4	1.0	0.20
Cr	<0.5	1.0	0.05
SO <sub>4</sub>	1280	1000	<<
pH	2.2	6.5-8.5	6.5-8.5

### 3 EXPERIMENTAL SETUP & SAMPLE PREPARATION

In this study, a modular leachate tower (MLT) was built from scratch to test the effects of applied pressures on the AMD flowing through a clay liner treated engineered NBFS. The experimental setup and schematic diagrams of the built MLT are shown in Figure 2. Nonetheless, the tests on the natural soils as composite clay liner without any form of treatment were performed also to evaluate the adsorption capacity of the NAT-S used in this study without treatment.



NAME	PART	QTY
PRESSURE PISTON	15	1
POROUS PRESSURE PLATE	14	1
SAMPLE HOLDER	13	1
ATTENUATION CHAMBER	12	1
POROUS STONE CHAMBER	11	1
CLIP	10	1
EFFLUENT	9	1
STANDARD NUT	8	6
STANDARD NUT	7	6
GEOSYNTHETIC MATERIAL	6	1
LID	5	1
INFLUENT	4	1
LEECHATE CHAMBER	3	1
MID BLOCK	2	1
LOWER BLOCK	1	1

Figure 2. Schematic diagram of MTL

The Proctor compaction test was performed on the engineered nano-geocomposite that constitutes 50% of soil and 50% of NBFS following (ASTM D-698, 2007). This composite was selected for this study due to its elevated pH value of 13.58. The compaction test was conducted to determine the quantity of moisture required for the composite liner, as 13.42% moisture content was used to prepare the liner. The compaction procedure started by thoroughly dry mixing the NBFS with the natural soil for 20 minutes, to eliminate agglomeration. Subsequently, extra 15 minutes of thorough mixing were followed upon the addition of the water. The blends were covered for 24 h to allow for moisture equilibrium. This was followed by the compaction of the composite liner into the attenuation chamber using an automatic compaction machine distributing an average of 11 blows at every layer to a total of 5 layers and 55 blows per layer. The perforated pressure pad was placed on the attenuation chamber to aid the distribution of AMD across the circumference of the compacted nano-slag geocomposite liner. Subsequently, the AMD was placed into the reservoir following the coupling of modular leachate tower equipment. A pressure gauge was connected to the hydraulic jack and mounted on the top side of the frame load as shown in Figure 2b. Following the coupling of the modular leachate tower, the equipment was powered to maintain the internal temperature of 40°C with the help of a heat ring embedded around the attenuation chamber. The method was chosen based on the study by (Dubey et al. 2016) to maintain a constant temperature of 50°C hence this temperature plays a key role in the adsorption process of composites. Additionally, the equilibrium adsorption capacity of nanomaterials is expected to alter by changing the temperature of the adsorbent phase. As this will mobilize the redox reaction rate.

After the setup of the Modular Leachate Tower equipment, the first trial pressure of 50 kPa was applied as the outlet was closed to prevent the effluent from leaching out. The AMD was retained in the attenuation chamber for 6 hours, this is to allow the adsorption of HMs ions to reach the adsorption equilibrium. After the equilibrium period was attained, the outlet was opened, and effluent was collected using a graduated cylinder, following another inductive coupled plasma mass spectrometry (ICP-MS) tests to measure the concentration of heavy metal ions on the effluent. The quantities of heavy metals ions adsorbed per gram of adsorbent,  $Q$  ( $\text{mg}\cdot\text{g}^{-1}$ ), were calculated using Eq 1.

$$Q = \frac{(C_0 - C_e)}{W} \times V \quad (1)$$

where  $Q$  is the amount of adsorbed metal ion at equilibrium conditions (metal ion (mg)/adsorbent (g)),  $V$  is the solution volume (L), and  $W$  is the sorbent mass (g).  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of metal ions in solution ( $\text{mg}\cdot\text{L}^{-1}$ ), which are determined by the ICP-MS. It is worthy to mention that all experiments were performed in triplicate and the average value was recorded as the final test result.

## 4. RESULTS & DISCUSSION

### 4.1 Adsorption capacity of the natural soil

The quantity of adsorbed heavy metal ions was first tested on the untreated soil. The buffering results of the natural soil interaction with AMD showed that the natural soil through ion exchange and adsorption mechanisms slightly removed the cations and anions after buffering at 120 days. The typical cations and anions determined on the soil surface are  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ . These ions are exchanged with the HMs ions without affecting the microstructure of the clay liner. The effluent obtained from the modular leachate tower after equilibrium time showed that the natural soil possessed medium adsorption capacity, hence major quantities of Cd, Pb, and Hg were removed by adsorption as the concentrations of the HMs ions decreased. The adsorption hierarchy of the natural soil is in the order of 72.2% Cd > 75% Pb > 70.31% Hg. Whereas there is no absorption order recorded on the rest of the HMs ions. This could be attributed to the percentage of free aluminum phyllosilicate minerals available in the clay. Thus, the specific surface area, chemical, and mechanical stability, double-layered structure, and low cation exchange capacity (CEC) contributed to the adsorption capacity of the natural soil used herein. The result obtained in this study agrees with the investigation by (Bhattacharyya et al., 2008) which stated that soil with Smectite clay minerals could decrease the AMD concentration by 28 to 30% depending on the Ph value of the AMD. The trend indicates that there is a great proportionality between the soil's buffering capacity and the percentage of free aluminum phyllosilicate mineral available in the soil.

Certainly, the applied pressures have significant effects on the effluent, hence effective adsorption of HMs was recorded at 50 kPa. Contrary to these results, the effluents obtained upon 150 kPa and 200 kPa applied pressure are the same when compared to the initial ions concentration of HMs prior to buffering process. This result was expected because the HMs were adsorbed onto the specific pores of the soil at the outer surface, therefore upon the completion of the equilibrium period 50 kPa and 100 kPa equivalent pressures failed to push the AMD fluid through the soil voids. However, upon an increase in applied pressure from 150 kPa and 200 kPa, the HMs traveled with the AMD through the soil voids leaving the AMD with the same concentrations of HMs as determined initially. The degree of concentration evaluated from the effluent for heavy metals is higher compared to the standard stipulated by (DWARF, 1996 and WHO). Whereas, Cd, Pb, and Hg metals were evaluated below the standards at a stress level of 50 kPa, beyond which the HMs become higher than standard values stipulated by (DWARF, 1996 and WHO).

### 4.2 Adsorption capacity of NSCL

The adsorption capacity of nano-slag clay composite liner prepared using 50% of soil and 50% of NBFS with equivalent adsorbed quantities of HMs is discussed in this section. The result showed that NSCL portrayed the

adsorption order of Cd>, Cu>, Zn>, As>, Hg>, Pb>, Ni> Fe>, and Cr> ions. These HMs were adsorbed with a high reduction of SO<sub>4</sub> according to the ICP-MS test performed on the harvested effluents under different applied pressures. The HMs adsorption was possible due to the increase in pH value triggered by the addition of NBFS. Upon the addition of 50% NBFS, the pH value of the AMD increased from 2.5 to 13.58, thus, mobilizing the precipitation of HM ions at elevated temperatures. Certainly, the NSCL was observed to transform the acidity of AMD to alkalinity during the interaction between the AMD and NSCL in the attenuation chamber at 120 days. At the stage when adsorption equilibrium was reached, the interaction between the AMD and NSCL triggered metal hydroxides insolubility forming a precipitate within the pores of the liner. This trend agrees with the report published elsewhere by (Anjum et al. 2019). Their report stated that at an increased pH, a higher percentage of HMs ions precipitation occurs, fostering the adsorption of interacted HMs ions in the influent. The application of engineered nanomaterial, in this study contributes to extraordinary adsorption capacity and reactivity of the HMs ions, both of which are favorable for the removal of heavy metal ions. Also, the nano-slag composite liner used herein is believed to contribute to the efficient adsorption of HMs ions which are mobilized by surface effect, small particle size effect, quantum effect, and macro quantum tunnel effect (Yang et al. 2019).

Generally, the effects of applied pressures were observed not to have any effects on the effluent. However, slight effects were observed upon the 200 kPa pressure equivalent. Despite these effects, no changes in the quantity of adsorbed HMs ions in the effluent were recorded. The general quality of the effluent is still acceptable in terms of quantities of residual HMs ions as stipulated by the standards (i.e., DWARF, WHO). This pressure response of the liner developed in this study, was expected due to the pozzolanic reactions that occur between free Ca<sup>2+</sup> ions from nano blast furnace slag with the corresponding dissolved Si<sup>4+</sup> and Al<sup>3+</sup> ions from the clay minerals, forming nano-calcium-silicates and nano-aluminates, which transforms into hydrates forming the cementitious matrix (viz., C-S-H, C-A-H and C-A-S-H) in the presence of adequate moisture from the acid mine drainage as supported by (Aneke et al. 2021). The quantities of HM ions were decreased by 97.31% acceptance due to the quantities of HM ions before and during the 120 days equilibrium period which allowed sufficient time for the interaction between the toxic metals and NSCL.

respectively. The study demonstrated that great proportionality exists between adsorption and pH values. The increased NBFS percentage rendered a reduction of HMs ions concentration. According to the curves, the red color indicates a high concentration of HMs with low pH values. It was observed that increasing the percentages of NBFS, caused an appreciable decrease in HMs ions concentration. This incremental increase in NBFS percentage triggered colors to change from red to orange, yellow, green, blue, and finally to purple indicating the highest level of alkalinity. The concentration quantities of the HMs ions started decreasing, as the pH values increased with the increase in NBFS percentages. The indicated color changes with the decrease in the quantities of HMs ions concentration values as shown by the curve legends. The color change from red to purple signifies the ultimate adsorption of HMs ions with the increase in pH values of effluent.

The result further revealed in the curve that the pH of the soil increased significantly upon 50% addition of NBFS due to the free CaO. Compared to the natural soil, the available CaO in NBFS triggered the increase in pH values of 13.58. Irrespective of the applied stress, the pozzolans showed up to 95% removal of HMs ions from the AMD, due to the retention time, adsorption equilibrium, and sorption which promote the formation of HMs hydroxide. The obtained results in this study agree with the investigation results published by (Saad et al. 2018) which claimed that adsorption studies of HMs ions revealed greater sorption on nanomaterials, indicating that various heavy metals were efficiently removed using nanomaterial compared to activated carbon (AC). In their study, it was confirmed that nanomaterial is characterized by significantly higher metal sorption capacity as it triggered sorption energetics due to its unique nanoporous structure.

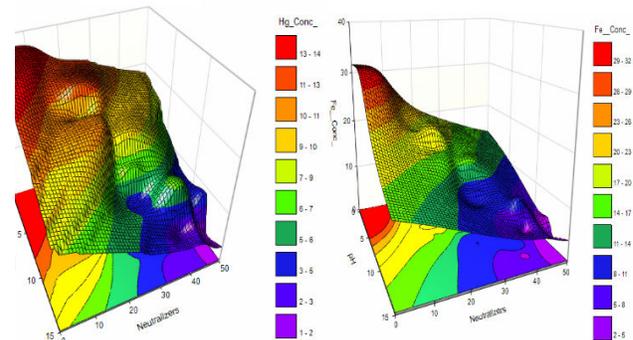


Figure 3a. Variation of NBFS and pH with Hg and Fe adsorption

#### 4.3 Variation of NBFS and pH on adsorption

The variation of NBFS and pH values with adsorption quantities are demonstrated in Figures 3a through e. In the curves, different concentration of HM ions was plotted against varying percentages of NBFS (i.e., neutralizer) and pH values. The results demonstrated that pH values increased from 2.5 to 5.53, 8.53, 10.33, and 13.58 upon 10%, 20%, 30%, 40%, and 50% addition of NBFS

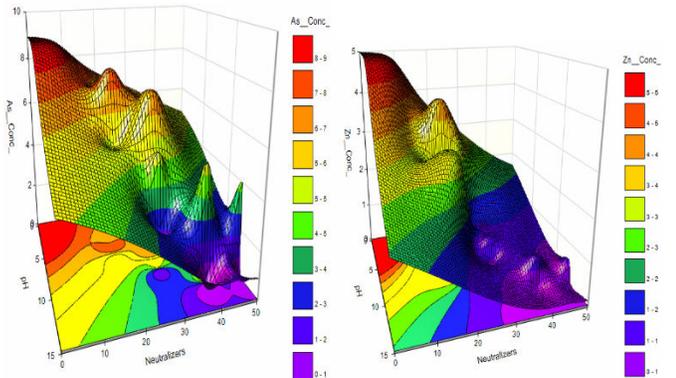


Figure 3b. Variation of NBFS and pH with As and Zn adsorption

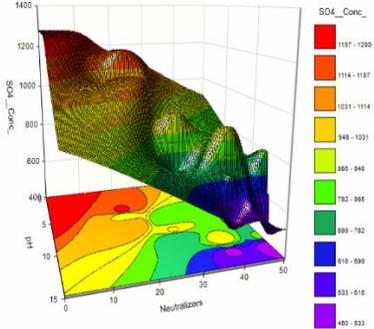


Figure 3e Variation of NBFS and pH with SO<sub>4</sub> adsorption.

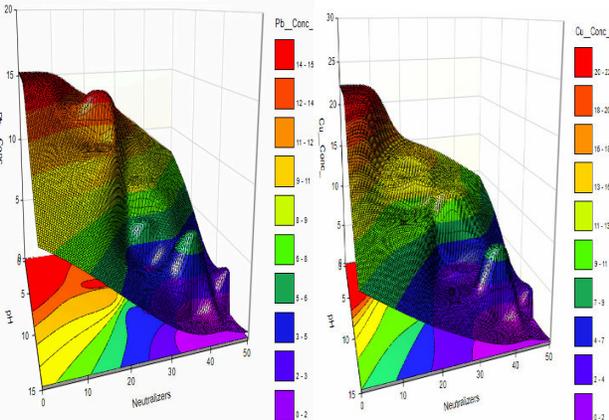


Figure 3c. Variation of NBFS and pH with Pb and Cu adsorption

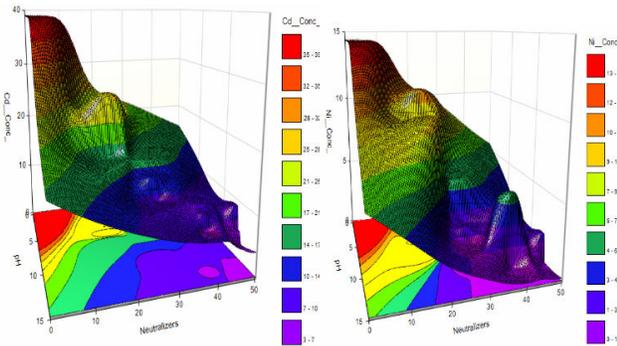


Figure 3d. Variation of NBFS and pH with Cd and Ni adsorption

5. CONCLUSION

In this study, the quantities of adsorbed HMs ions were evaluated using NSCL. The obtained quantities were compared with non-treated natural soil used herein as a liner. Based on the result presented in this paper, the conclusions were drawn as follows:

The study confirmed that the developed MLT is a reliable tool for leachate testing, due to the removal of HMs ions as the leachate attenuates with geo-media within the attenuation chamber.

The natural soil does not possess the full capacity to completely adsorb all the HMs ions at 100% capacity, however, the soil was observed to absorb HMs ions like Cd, Pb, and Hg at adsorption percentages and order of 72.2%Cd> 75%Pb> 70.31%Hg due to the diffused double layer of the soil and two silica sheets. Whereas the NSCL used in this study portrayed sufficient efficiency for the removal of HMs ions. This was confirmed because the adsorption capacities of NBFS were observed to be higher than other nanomaterials reported in the literature as well as the natural soil used herein due to the physical and chemical make-up of NBFS, it can be safely concluded that removal occurs not just through adsorption mechanism only, thus through precipitation resulting from the pozzolanic reaction.

The performance of NBFS was found to have maximum removal efficiencies in the following adsorption order and percentages 100%Pb>, 97.3%Cd>, 96.4%Zn>, 92.3%Cu>, 89.1%Fe>, 87.3%Ni>, 15.13%As>, 98%Co>, 59.5%Hg>, and 92.21SO<sub>4</sub>> in effluent below the criteria for irrigation and livestock purposes.

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