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Assessment Of Potentially Toxic Elements In Biochar Remediated Crude Oil Polluted Soil From Biara Community Rivers State Nigeria

Ighomuaye, M. N., Ideriah T. J. K., Boisa N., Cookey G. A.
Department Of Chemistry, Rivers State University Nkpolu Oroworukwo, Port Harcourt
Institute Of Pollution Studies, Rivers State University Nkpolu Oroworukwo, Port Harcourt

Abstract:
Rivers State in Niger Delta region is blessed with crude oil. Anthropogenic activities by man to make ends meet have led to environmental pollution which affects the environment and therefore there is need to resolve it using environmentally friendly materials. In this study biochar (adsorbent) was produced and applied in crude oil polluted and control soils. The results of Potentially Toxic Elements in crude oil polluted, treated and control soils were determined using Atomic Absorption Spectrophotometer. The mean results of toxic metals ranged from 286.458 ±3.4 ppm to 439.729±0.412 ppm for Fe, Pb 0.299±0.001 ppm to 10.259±2.003 ppm, Cu 0.081±0.025 ppm to 4.845±0.201 ppm, Cr 2.136±0.003 ppm to 9.692±4.497 ppm, Zn 2.647 ±0.082 ppm to 14.383 ±0.235 ppm, Cd 0.324±0.010 ppm to 0.960 ±0.024 ppm and As was < 0.01. In general, metals were below standard limits both in polluted and control soils, therefore the adsorbents were effective for the degradation of pollutants. Biochars are recommended for pollutant removal due to its efficacy, soil enricher and they are biodegradable.
Keywords: *Biochar, Magnetite Nanoparticle, Toxic Metals, Pyrolysis, Absorption*

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I. Introduction

Recently, worldwide there has been an adverse impact on the environment due to man's total involvement in anthropogenic activities for economic development. Soil is one of the components of the environment that is severely affected by various anthropogenic activities. Soil pollution is the build-up in the soil with toxic compounds, chemicals, salts or disease-causing agents that negatively affects plant growth and animal's health (Karbassi & Pazoki (2015) and Yuvaraj & Mahendran (2020). Soil pollution is of particular interest in most societies due to its effect on both man and the environment. When soil is polluted, in most cases it becomes almost useless for purposes of agriculture, recreation and industrial activities. Pollutants in soil usually stays longer compared with other environmental media such as air and water. Pollutants usually go down into the soil and quickly build up but may take a long time to be degraded. Soil pollutants include toxic metals, pesticides, fertilizers, herbicides, solvents, insecticides and petroleum hydrocarbons (Havugimana *et al.*, 2015; Midhat *et al.*, 2019; Minkina *et al.*, 2019; Ghazaryan *et al.*, 2020 and Sethi & Gupta (2020). The release of toxic pollutants hinders the soil environment and also affects the aquatic environment. Soil contaminated with these pollutants are of major concern, as their hydrophobic characteristics may retain them in solid phase and eventually impact on man's health through bioaccumulation, bioconcentration and food chain systems. Potentially toxic metals are metallic elements with high atomic weight and high density. Toxic metals are highly toxic and are carcinogenic even at low concentration and are not biodegradable. They cause serious threat to human life, aquatic and vegetation cover. When these metals are absorbed, they get accumulated in human body thereby, resulting to serious health diseases such as cancer, damaging of nervous system, organ damage and even death as well as retarding growth and development in living organisms. Examples of heavy metals are Pb, Zn, Cr, Cd and Hg. They get to us through body contact, inhalation and ingestion. Lead is a highly toxic metal causing environment degradation and many health issues. On exposure, it may cause damaging of kidney, damaging of brain in new born babies. The excess intake of lead leads to loss of appetite. Zinc is supplement but over dosage of this supplement is extremely dangerous and this should be avoided. Generally, consumption of zinc may cause paralysis and neurological problems, dizziness, breathing problems and chest pain. Chromium is another heavy toxic metal, excess of it troubles many biological functions of plants and causes nausea, headache, vomiting, diarrhea. Cadmium is the commonly used heavy metal but when absorbed, it accumulate inside the body throughout the life time. It is also very carcinogenic and often leads to failure of kidney It is therefore necessary to explore biochar and magnetite nanoparticle together in remediating pollutants in soil to establish their potentiality, similarities and differences in using one of the remediating material.

II. Materials And Methods

Study Area

Biara is a town in Gokana Local Government Area of Rivers State in the South South geopolitical zone of Nigeria. It is located in the Northeast region of Gokana on latitude 519781 and longitude 308886. Biara is 34 km / 21 miles away from Rivers State Capital, Port Harcourt. It is situated between Bela and Nwabia communities. The People of Biara speaks Gokana language Papamie (2019). Biara people are traditionally farmers; farming a variety of crops such as plantain, oil palm, cassava, okra, melon, and banana fishermen, making of fishing nets, construction of canoes and traders (www.mindat.org). Biara is a community bless with crude oil but due to anthropogenic activities, oil have released contaminants thereby causing reduction in farmland fertility and aquactic organisms. Their climate is tropical.

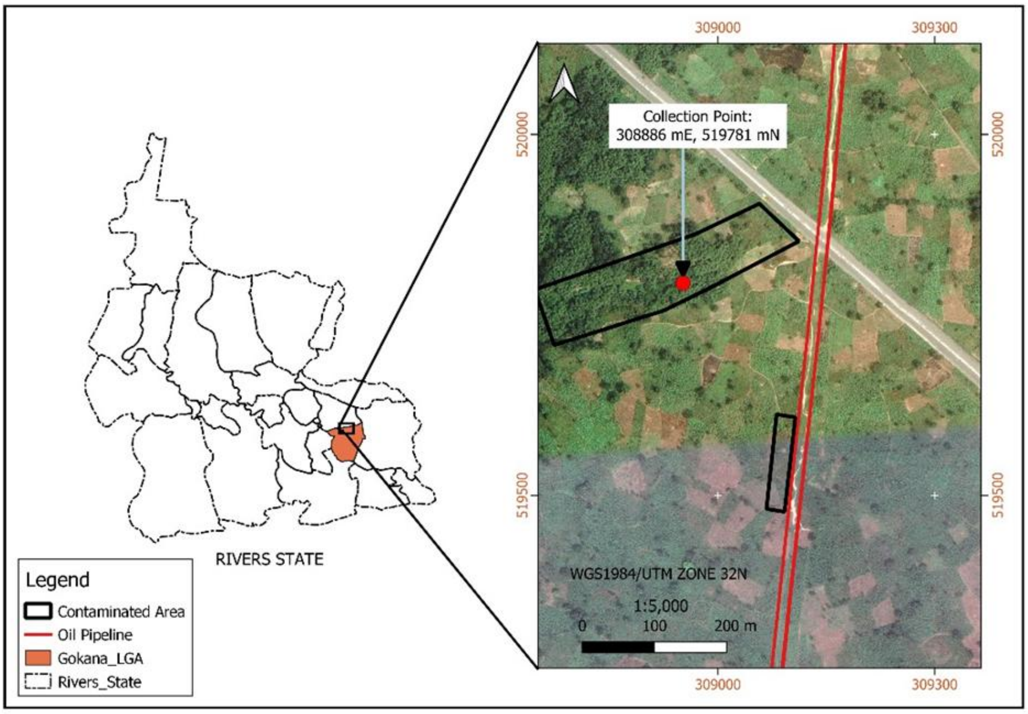

Figure1: Rivers State Map showing the Sampling Point

Sample Collection, Preparation and Analyses

Polluted and control soil samples were collected from Biara, Gokana local government area in Rivers State. 1kg of polluted soil was weighed into two plastic reactors labelled Gros Michel biochar on polluted soil (GBPS) and Cavendish biochar on polluted soil (CBPS). The samples were left for three days for acclimatization and treated by applying 10g each of the produced magnetite nanoparticles or biochar or composite of both in the polluted soil samples reactor using modified method of (Adeniyi *et al*., 2020).

Each of the soil samples was monitored within the period of one month (zero, week one, week two, week three and week four). The soil samples collected from each plastic reactor, were air – dried, grounded, sieved with 2 mm mesh and stored in labelled polythene bags under room temperature ready for extraction, digestion and analysis. Then soil samples after treatment were collected for determination of potentially toxic elements. Also the polluted and control soil samples collected were used to determine potentially toxic elements of the soil samples to ascertain their initial concentrations. These procedure was repeated using control soil sample, 1kg of polluted soil was weighed into two plastic reactors labelled Gros Michel biochar on Control soil (GBCS) and Cavendish biochar on Control soil (CBCS).

Potentially Toxic Elements

Five grams of prepared soil sample was weighed into a conical flask and 3 ml of HCL and 1ml of HNO_3 were added using modified method of (Boisa & Ogbede 2016). The mixture was d igested and allowed to cool. Filtered the mixture with whatman No. 42 filter paper into 50 ml volumetric flask and add distilled water to the 50 ml mark level. The concentrations of elements were analysed using an Atomic Absorption Spectrophotometer by Agilent Technologies.

III. Results

Potentially Toxic Elements

Toxic elements analyses results of soil at the study areas are shown in Tables 1-4.

Iron (Fe)

The results of Fe level are showed in Tables 1 and 2. The Fe mean concentrations ranged from 286.458±3.40 ppm (control soil) to 439.729±0.412 ppm (GBPS wk2) and 286.458±3.40 ppm (control soil) to 368.896±4.140 ppm (CBPS wk3) respectively.

Table 1 Mean Concentrations (ppm) of Potentially Toxic Elements in Polluted Soil at Biara treated Gros Michel Biochar

Sample ID/(ppm)	Fe	Pb	Cu	Cr	Zn	Cd	As
Polluted	333.854±4.887	3.795±0.238	0.081±0.025	2.692±0.251	4.536±0.017	0.960±0.024	BDL
GBPS 0	330.666±2.500	5.672±2.683	0.136±0.095	9.692±4.497	14.383±0.235	0.771±0.045	BDL
GBPS wk1	297.376±2.285	2.889±1.487	0.089±0.063	6.082±0.602	5.248±0.177	0.925±0.431	BDL
GBPS wk2	439.729±0.412	7.205±0.998	3.109±0.045	3.231±0.109	4.019±0.082	0.482±0.022	BDL
GBPS wk3	314.312±3.831	4.782±2.303	0.283±0.138	8.205±0.346	9.483±0.342	0.738±0.023	BDL
GBPS wk4	366.021±0.977	5.872±0.472	1.449±0.103	4.128±0.418	2.646±0.119	0.582±0.018	BDL
Control	286.458±3.400	2.533±1.211	0.644±0.043	3.436±0.527	4.491±0.092	0.940±0.043	BDL

BDL: Below detection limit

Table 2 Mean Concentrations (ppm) of Potentially Toxic Elements in Polluted Soil at Biara treated Cavendish Biochar

Sample ID/(ppm)	Fe	Pb	Cu	Cr	Zn	Cd	As
Polluted	333.854±4.887	3.795±0.238	0.081±0.025	2.692±0.251	4.536±0.017	0.960±0.024	BDL
CBPS 0	324.167±4.080	0.692±0.332	0.345±0.079	7.718±0.322	2.647±0.082	0.871±0.028	BDL
CBPS wk1	353.104±4.717	0.646±0.366	0.783±0.063	4.000±0.189	3.751±0.093	0.644±0.033	BDL
CBPS wk2	305.792±2.528	0.466±0.182	0.221±0.057	5.616±0.379	3.081±0.036	0.747±0.044	BDL
CBPS wk3	368.896±4.140	0.846±0.063	1.004±0.090	4.513±0.220	5.300±0.150	0.633±0.028	BDL
CBPS wk4	340.854±3.542	1.777±0.870	0.806±0.180	5.539±0.274	5.333±0.2077	0.573±0.048	BDL
Control	286.458±3.4000	2.533±1.211	0.644±0.043	3.436±0.527	4.491±0.092	0.940±0.043	BDL

The results of Fe levels in control treated soils are showed in Tables 3 and 4. The Fe mean concentrations ranged from 286.458±3.40 ppm (control soil) to 406.107±1.320 ppm (GBCS wk3) and 286.458±3.40 ppm (control soil) to 419.625±1.631 ppm (CBCS wk2) respectively.

Table 3 Mean Concentrations (ppm) of Potentially Toxic elements in Control soil at Biara Treated Gros Michel Biochar

Sample ID/(ppm)	Fe	Pb	Cu	Cr	Zn	Cd	As
GBCS 0	331.091±1.001	1.89±0.092	0.707±0.100	4.438±0.301	6.010±0.06	0.703±0.02	BDL
GBCS wk1	342.1037±1.09	0.628±0.002	1.331±0.151	4.279±0.025	5.085±0.08	0.589±0.031	BDL
GBCS wk2	298.925±1.584	0.299±0.001	0.198±0.094	4.983±0.001	4.890±0.021	0.707±0.014	BDL
GBCS wk3	406.107±1.320	10.259±2.003	4.845±0.201	3.105±0.008	7.185±0.063	0.324±0.010	BDL
GBCS wk4	397.232±1.087	3.382±0.006	1.577±0.109	2.136±0.003	3.018±0.054	0.818±0.05	BDL
Control	286.458±3.400	2.533±1.211	0.644±0.043	3.436±0.527	4.491±0.092	0.940±0.043	BDL

Table 4 Mean Concentrations (ppm) of Potentially Toxic Elements in Control soil at Biara Treated Cavendish Biochar

Sample ID/(ppm)	Fe	Pb	Cu	Cr	Zn	Cd	As
CBCS 0	373.333±2.808	1.492±0.724	1.504±0.069	0.308±0.109	5.866±0.166	0.789±0.021	BDL
CBCS wk1	382.354±4.103	0.854±0.435	1.577±0.129	1.451±0.761	6.520±0.243	0.633±0.019	BDL
CBCS wk2	419.625±1.631	0.0713±0.036	2.842±0.017	5.846±0.618	7.677±0.081	0.655±0.058	BDL
CBCS wk3	302.417±2.102	0.649±0.000	0.613±0.049	8.436±0.446	4.664±0.069	0.818±0.028	BDL
CBCS wk4	403.646±6.073	0.488±0.218	2.124±0.055	4.487±0.584	7.764±0.196	0.573±0.031	BDL
Control	286.458±3.400	2.533±1.211	0.644±0.043	3.436±0.527	4.491±0.092	0.940±0.043	BDL

Lead (Pb)

The results of Pb level are displayed in Tables 1 and 2. The Pb mean concentrations ranged from 2.533±1.211 ppm (control soil) to 7.205±0.998 ppm (GBPS wk2) and 0.466±0.182 ppm (CBPS wk2) to 3.795±0.238 ppm (polluted soil) respectively. The results of Pb levels in control treated soils are displayed in

Tables 3 and 4. The Pb mean concentrations ranged from 0.299±0.001 ppm (GBCS wk2) to 10.259±2.003 ppm (GBCS wk3) and 0.0713±0.036 ppm (CBCS wk2) to 2.533±1.211 ppm (control soil) respectively.

Copper (Cu)

The results of Cu level are showed in Tables 1 and 2. The Cu mean concentrations ranged from 0.081±0.025 ppm (polluted soil) to 3.109±0.045 ppm (GBPS wk2) and 0.081±0.025 ppm (polluted soil) to 1.004±0.090 ppm (CBPS wk3) respectively. The results of Cu levels in control treated samples are showed in Tables 3 and 4. The Cu mean concentrations ranged from 0.198±0.094 ppm (GBCS wk2) to 4.845±0.201 ppm (GBCS wk3) and 0.613±0.049 ppm (CBCS wk3) to 2.842±0.017 ppm (CBCS wk2) respectively.

Chromium (Cr)

The results of Cr level are showed in Tables 1 and 2. The Cr mean concentrations ranged from 2.692±0.251 ppm (polluted soil) to 9.692±4.497 ppm (GBPS wk1) and 2.692±0.251 ppm (polluted soil) to 7.718±0.322 ppm (CBPS 0) respectively. The results of Cr levels in control treated samples are showed in Tables 3 and 4. The Cr mean concentrations ranged from 2.136±0.003 ppm (GBCS wk4) to 4.983±0.00 ppm (GBCS wk2) and 0.308±0.109 ppm (CBCS 0) to 8.436±0.446 ppm (CBCS wk3) respectively.

Zinc (Zn)

The results of Zn level are displayed in Tables 1 and 2 The Zn mean concentrations ranged from 2.646±0.119 ppm (GBPS wk4) to 14.383±0.235 ppm (GBPS 0) and 2.647 ±0.082ppm (CBPS 0) to 5.333±0.208 ppm (CBPS wk4) respectively. The results of Zn levels in control treated soil are displayed in Tables 3 and 4. The Zn mean concentrations ranged from 3.018±0.054 ppm (GBCS wk4) to 7.185±0.063 ppm (GBPS wk3) and 4.491±0.092 ppm (control soil) to 7.764±0.196 ppm for (CBCS wk4) respectively.

Cadmium (Cd)

The results of Cd level are shown in Tables 1 and 2. The Cd mean concentrations ranged from 0.482±0.022 ppm (GBPS wk2) to 0.960±0.024 ppm (polluted soil) and 0.573±0.048 ppm (CBPS wk4)) to 0.960±0.024 ppm (polluted soil) respectively. The results of Cd levels in control treated soils are showed in Tables 3 and 4. The Cd mean concentrations ranged from 0.324±0.010 ppm (GBCS wk3) to 0.940±0.043 ppm (control soil) and 0.573±0.031 ppm (CBCS wk4)) to 0.940±0.043 ppm (control soil) respectively.

Enrichment Factor (EF)

The EF values are displayed in Tables 5 and 6. The EF values ranged from 2.6959 (control soil) to 8.765 (GBPS 0) in Pb, Cu 0.1213 (polluted soil) to 3.5351 (GBPS wk2), Cr 3.6738 (GBPS wk2) to 14.6553 (GBPS 0), Zn 1.2049 (GBPS wk4) to 7.2495 (GBPS 0), Cd 18.2688 (GBPS wk2) to 54.6910 (control soil), Pb 0.5578 (CBPS wk1) to 3.4656 (polluted soil), Cu 0.1213 (polluted soil) to 1.3608 (CBPS wk3), Cr 4.0317 (polluted soil) to 11.9044 (CBPS 0), Zn 0.9698 (CBPS 0) to 2.6077 (CBPS wk4) and Cd 20.7381 (CBPS wk2) to 54.6910 (control soil) for Cd respectively.

Table 5 Enrichment Factor of Potentially Toxic Elements in Polluted Soil at Biara treated Gros Michel Biochar

Sample ID	Pb	Cu	Cr	Zn	Cd
GBPS 0	8.765	0.2057	14.6553	7.2495	38.8610
GBPS wk1	4.8575	0.1496	10.2261	2.9412	51.8423
GBPS wk2	8.1925	3.5351	3.6738	1.5233	18.2688
GBPS wk3	7.6070	0.4502	13.0523	5.0284	39.1331
GBPS wk4	8.0215	1.9794	5.6390	1.2049	26.5012
Polluted	3.4656	0.1213	4.0317	1.6136	47.9252
Control	2.6959	1.1241	5.9932	1.8620	54.6910

Table 6 Enrichment Factor of Potentially Toxic Elements in Polluted Soil at Biara treated Cavendish Biochar

Sample ID	Pb	Cu	Cr	Zn	Cd
CBPS 0	0.6508	0.5321	11.9044	0.9698	44.7815
CBPS wk1	0.5578	1.1087	5.6641	1.2616	30.3971
CBPS wk2	0.7620	0.3614	9.1827	1.6793	20.7381
CBPS wk3	1.1465	1.3608	6.1169	2.3946	28.5986
CBPS wk4	2.6065	1.1823	8.1252	2.6077	28.0179
Polluted	3.4656	0.1213	4.0317	1.6136	47.9252
Control	2.6959	1.1241	5.9932	1.8620	54.6910

The EF values in control treated soils are displayed in Tables 7 and 8. The EF values ranged from 0.765 (GBCS wk3) to 29.095 (GBCS 0) in Pb, Cu 0.148 (GBCS wk3) to 3.602 (GBCS wk2), Cr 0.283 (GBCS wk3) to 5.993 (control soil), Zn 1.805 (GBCS 0) to 2.305 (GBCS wk1), Cd 34.347 (GBCS wk2), to 54.691 (control soil), Pb 0.085 (CBCS wk2) to 2.696 (control soil), Cu 1.124 (control soil) to 10.135 (CBCS wk3), Cr 0.412 (CBCS 0) to 13.948 (CBCS wk3), Zn 1.862 (control soil), to 3.206 (CBCS wk4) and Cd 24.927 (CBCS wk4), to 54.691 (control soil) respectively.

Table 7 Enrichment Factor of Potentially Toxic Elements in Control Soil at Biara Treated Gros Michel Biochar

Sample ID	Pb	Cu	Cr	Zn	Cd
GBCS 0	29.095	0.846	1.324	1.805	44.726
GBCS wk1	2.330	2.267	3.037	2.305	38.416
GBCS wk2	1.720	3.602	4.956	1.853	34.347
GBCS wk3	0.765	0.148	0.283	1.813	41.990
GBCS wk4	4.265	1.117	2.054	2.228	42.046
Control	2.696	1.124	5.9932	1.8620	54.691

Table 8 Enrichment Factor of Potentially Toxic Elements in Control Soil at Biara Treated Cavendish Biochar

Sample ID	Pb	Cu	Cr	Zn	Cd
CBCS 0	1.999	2.014	0.412	2.619	35.223
CBCS wk1	1.117	2.062	1.898	2.842	27.592
CBCS wk2	0.085	3.386	6.966	2.305	26.015
CBCS wk3	1.073	10.135	13.948	2.570	45.081
CBCS wk4	0.605	2.631	5.558	3.206	24.927
Control	2.696	1.124	5.993	1.862	54.691

Soil Metal index (SMI)

The SMI values are displayed in Tables 9 and 10. The SMI values ranged from 0.0057 (control soil) to 0.0088 (GBPS wk2) in Fe, Pb 0.0155 (control soil) to 0.0439 (GBPS wk2), Cu 0.0004 (polluted soil) to 0.0156 (GBPS wk2) , Cr 0.0135 (polluted soil) to 0.0485 (GBPS 0), Zn 0.0063 (GBPS wk4) to 0.0342 (GBPS 0), Cd 0.1607 (GBPS wk2) to 0.3200 (control soil) , Pb 0.0028 (CBPS wk2) to 0.0231 (polluted soil), Cu 0.0004 (polluted soil) to 0.0050 (CBPS wk3), Cr 0.0135 (polluted soil) to 0.0386 (CBPS 0), Zn 0.0063 (CBPS 0) to 0.0127 (CBPS wk4) and Cd 0.1910 (CBPS wk4) to 0.3200 (polluted soil) respectively.

Table 9 Soil Metal Index of Potentially Toxic Elements in Polluted Soil at Biara Treated Gros Michel Biochar

Sample ID	Fe	Pb	Cu	Cr	Zn	Cd	Total SMI
GBPS 0	0.0066	0.0346	0.0007	0.0485	0.0342	0.257	0.0636
GBPS wk1	0.0060	0.0176	0.0005	0.0304	0.0125	0.3083	0.0625
GBPS wk2	0.0088	0.0439	0.0156	0.0162	0.0096	0.1607	0.0424
GBPS wk3	0.0063	0.0292	0.0014	0.0410	0.0225	0.2460	0.0577
GBPS wk4	0.0073	0.0358	0.0073	0.0206	0.0063	0.1940	0.0452
Polluted	0.0067	0.0231	0.0004	0.0135	0.0108	0.3200	0.3745
Control	0.0057	0.0155	0.0032	0.0172	0.0107	0.3133	0.0609

Table 10 Soil Metal Index of Potentially Toxic Elements in Polluted Soil at Biara Treated Cavendish Biochar

Sample ID	Fe	Pb	Cu	Cr	Zn	Cd	Total SMI
CBPS 0	0.0065	0.0042	0.0017	0.0386	0.0063	0.2903	0.0580
CBPS wk1	0.0071	0.0039	0.0039	0.0200	0.0089	0.2147	0.0431
CBPS wk2	0.0061	0.0028	0.0011	0.0281	0.0073	0.2490	0.0491
CBPS wk3	0.0074	0.0052	0.0050	0.0226	0.0126	0.2110	0.0440
CBPS wk4	0.0068	0.0108	0.0041	0.0277	0.0127	0.1910	0.0422
Polluted	0.0067	0.0231	0.0004	0.0135	0.0108	0.3200	0.3745
Control	0.0057	0.0155	0.0032	0.0172	0.0107	0.3133	0.0609

IV. Discussion

Potentially Toxic Elements

Concentrations of Fe ranged from 286.458 ±3.4 ppm (control soil) to 439.729 ±0.4127 ppm (GBPS wk2) as shown in Tables 1 and 2. While the concentrations of Fe in control treated soils ranged from 286.458 ±3.4 ppm (control soil) to 419.625 ±1.631 ppm (CBCS wk2) as shown in Tables 3 and 4. These might be due sedimentation, absorbent used, the pH, surface area, the functional group, particle size and contact period. The level of Fe obtained in this study were below DPR (2018) value of 50000 ppm. The obtained result is lower than that reported by (Mohammed & Folorunsho, 2015) but similar to that of (Ideriah, 2019). Fe had a positive correlation coefficient with adsorbents of 1. The anova showed that there is a significant within the absorbents in control treated soil

Concentrations of Pb ranged from 2.533±1.211 ppm (control soil) to 7.205±0.998 ppm (GBPS wk2) and 0.466±0.182 ppm (CBPS wk2) to 3.795±0.238 ppm (polluted soil) as shown in Tables 1and 2. While the concentrations of Pb in control treated soils ranged from 0.0713 ±0.036 ppm (CBCS wk2) to 10.259 ±2003 ppm (GBCS wk3) as shown in Tables 3 and 4. These might be due to the pH, surface area, the functional group, particle size and contact period. The level of Pb obtained in this study were below DPR (2018) value of 530 ppm. The obtained result is lower than that reported by (Mohammed & Folorunsho, 2015, Maneyahilishal *et al*., 2018 and Anegbe *et al*., 2018), but higher than the report of (Ideriah *et al*., 2020). Pb had a negative correlation coefficient with adsorbents except the soil treated with GBPS which had a positive correlation coefficient of 0.9995. The anova showed that there is significant within the adsorbents in polluted treated soil.

Concentrations of Cu ranged from 0.081 ±0.025 ppm for (polluted soil) to 3.109 ±0.045 ppm (GBPS wk2) as shown in Tables 1 and 2. While the concentrations of Cu in control treated soils ranged from 0.198 ±0.094 ppm (GBCS wk2) to 4.845 ±0.201 ppm (GBCS wk3) as shown in Tables 3 and 4. This might be due the pH, surface area, the functional group, particle size and contact period. The level of Cu obtained in this study were below maximum DPR (2018) value of 190 ppm. The obtained result is lower than that reported by (Mohammed & Folorunsho, 2015, Maneyahilishal *et al*., 2018 and Anegbe *et al*., 2018), but higher than the report of (Ideriah *et al*., 2020). Cu had a positive correlation coefficient > 0.5 with adsorbents. The anova showed that there is no significant within the adsorbents.

Concentrations of Cr ranged from 2.692 ±0.251 ppm for (polluted soil) to 9.692 ±4.497 ppm (GBPS wk1) as shown in Tables 1and 2. This might be due adsorbents used and contact period. While the concentrations of Cr in control treated soils ranged from 0.308 ±0.109 ppm (CBCS 0) to 8.436 ±0.446 ppm (CBCS wk3) as shown in Tables 3 and 4. The level of Cr obtained in this study were below DPR (2018) value of 380 ppm these might be due to the pH, surface area, the functional group, particle size and contact time of the adsorbent used. The obtained result is lower than that reported by (Mohammed & Folorunsho, 2015, Maneyahilishal *et al*., 2018 and Anegbe *et al*., 2018), but higher than the report of (Ideriah *et al*., 2020). Cr had a positive correlation coefficient of 0.64165 with GBPS. The anova showed that there is no significant within the adsorbents.

Concentrations of Zn ranged from 2.646 ±0. 119 ppm for (GBPS wk4) to 14.383 ±0.017 ppm (GBPS 0) as shown in Tables 1 and 2. While the concentrations of Zn in control treated soils ranged from 3.018 ±0.054 ppm (GBCS wk4) to 7.677 ±0.081 ppm (CBCS wk2) as shown in Tables 3 and 4. This might be due adsorbents used, sedimentation, crack, pores, the pH, surface area, the functional group, particle size and contact period. The level of Zn obtained in this study were below DPR (2018) value of 720 ppm. The obtained result is lower than that reported by (Mohammed & Folorunsho, 2015, Maneyahilishal *et al*., 2018 and Anegbe *et al*., 2018) but higher than the report of (Ideriah *et al*., 2020). Zn had both positive correlation coefficient 0.80277 with adsorbents. The anova showed that there is no significant within the adsorbents.

Concentrations of Cd ranged from 0.378 ±0.019 ppm for (GBPS wk3) to 0.960 ±0.024 ppm (polluted) as shown in Tables 1 and 2. While the concentrations of Cd in control treated soils ranged from 0.324 ±0.010 ppm (GBCS wk3) to 0.940 ±0.043 ppm (control soil) Tables 3 and 4. This might be due adsorbents used, the pH, surface area, the functional group, particle size and contact period. The level of Cd obtained in this study were below DPR (2018) value of 12 ppm. The obtained result is lower than that reported by (Mohammed & Folorunsho, 2015, Anegbe *et al*., 2018 and Ideriah *et al*., 2020) but similar to that of (Maneyahilishal *et al*., 2018). Cd had a negative correlation coefficient with adsorbents with the exception of GBPS (0.02658). The anova showed that there is significant within the adsorbents.

Enrichment Factor (EF)

The EF values ranged from 0.5578 (CBPS wk1) to 8.765 (GBPS 0) in Pb, Cu 0.1213 (polluted) to 3.5351 (GBPS wk2), Cr 3.6738 (GBPS wk2) to 14.6553 (GBPS 0), Zn 1.2049 (GBPS wk3) to 7.2495 (GBPS wk0), Cd 18.2688 (GBPS wk2) to 54.6910 (control soil) Tables 5 and 6. While the EF values in control treated soils ranged from 0.085 for (CBCS wk2) to 29.095 (GBCS 0) in Pb, Cu 0.148 (GBCS wk3) to 10.135 (DCBCS wk3), Cr 0.283 (GBCS wk3) to 13.948 (CBCS wk3), Zn 1.805 (GBCS 0) to 3.206 (CBCS wk4), Cd 24.927 (CBCS wk4) to 54.691 (control soil) Tables 7 and 8. From the result Pb, Cu, Cr and Zn exhibits deficiently to minimal enrichment to moderate enrichment to significant enrichment moderate enrichment while Cd exhibit Significant enrichment to Very high enrichment to Extremely high enrichment. Pb, Cu, Cr and Zn is an indication of the adsorbents used while Cd could be attributed to adsorbents and the soil type. The obtained result is lower than that reported by Ideriah (2019) but similar to that of (Fadojutimi,*et al.*, 2017)

Soil Metal Index (SMI)

The SMI values ranged from 0.0057 (control) to 0.0088 (GBPS wk2) in Fe, Pb 0.0028 (CBPS wk2) to 0.0439 (GBPS wk2), Cu 0.0004 (polluted) to 0.0156 (GBPS wk2), Cr 0.0135 (polluted soil) to 0.0485 (GBPS 0), Zn 0.0063 (GBPS wk4 and CBPS 0) to 0.0342 (GBPS 0), Cd 0.257 (GBPS 0) to 0.3200 (polluted soil) as shown in Tables 9 and 10. The results of Fe, Pb, Cu, Cr, Zn and Cd were below 100. Although the soil is polluted but unpolluted with heavy metals. This is due to the adsorbents used. The obtained result is higher than that reported by Ideriah (2019) but similar to that of (Fadojutimi,*etal.*, 2017)

V. Conclusion

Cu, Zn, Cr, Cr, Fe and Cd concentrations were within DPR (2018) permissible limits. The trend of metals degradation for polluted treated soil are as follows; CBPS > GBPS > (Fe), CBPS > GBPS (Pb), CBPS > GBPS (Cu), GBPS > CBPS (Cr), GBPS > CBPS (Zn) and CBPS > GBPS (Cd). While the trend of metals degradation for control treated soil are as follows; GBCS > CBCS (Fe), CBCS > GBCS (Pb), GBCS > CBCS (Cu), GBCS > CBCS (Cr), GBCS > CBCS (Zn) and CBCS > GBCS (Cd). EF and SMI were also below limits. In conclusion these adsorbents are highly recommended for pollutant removal in whatsoever type of soil due to its efficacy, soil enricher and they are biodegradable.

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