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

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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 magnetite nanoparticle (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 444.771±2.647 ppm for Fe, Pb 2.533±1.211 ppm to 9.103±0.346 ppm, Cu 0.081 ppm to 3.088±0.090 ppm, Cr 0.191 ±0.073 ppm to 7.692±0.314 ppm, Zn 3.990±0.253 ppm to 9.126 ppm±0.171 ppm, Cd 0.502±0.016 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. These adsorbents are recommended for pollutant removal due to its efficacy, soil enricher and they are biodegradable.

Keywords: *Magnetite Nanoparticles, Toxic Metals, Pyrolysis, Absorption, Crude oil, Rivers State*

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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 a 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 in human. 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.

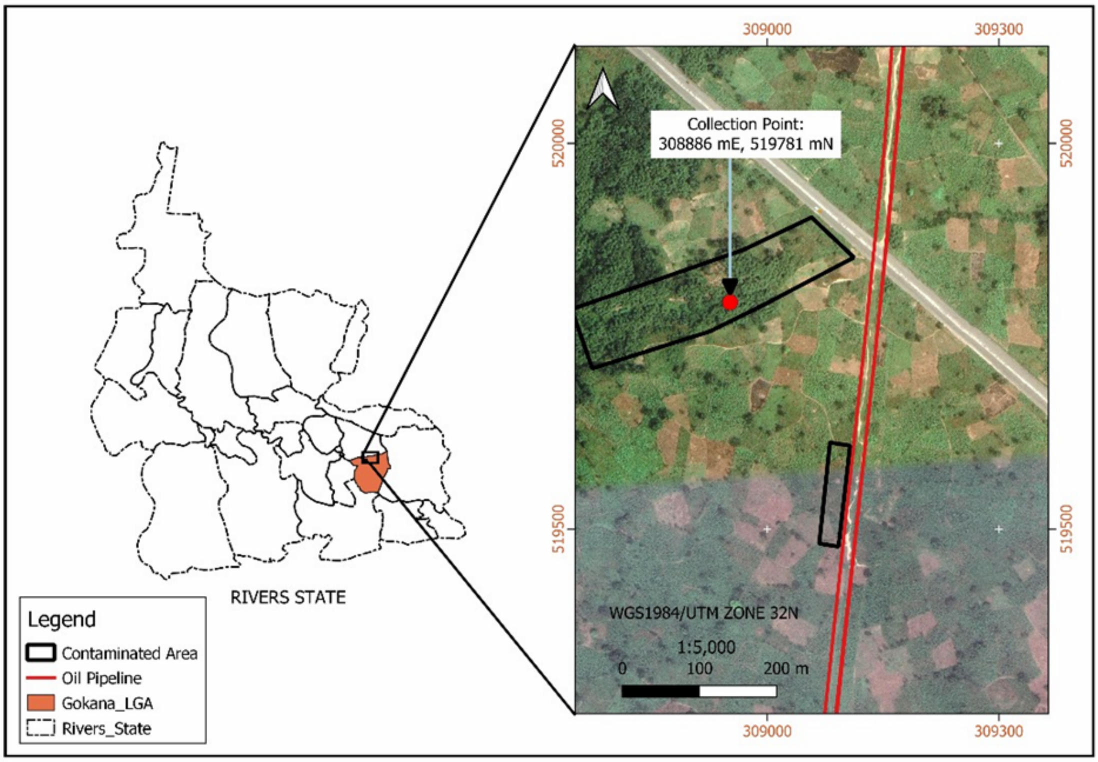

Figure1: Rivers State Map showing the Sampling Point

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 filtered magnetite nanoparticle on polluted soil (FMPS) and decanted magnetite nanoparticle on polluted soil (DMPS). 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 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 control soil was weighed into two plastic reactors labelled filtered magnetite nanoparticle on Control soil (FMCS) and decanted magnetite nanoparticle on soil (DMCS).

Potentially Toxic Elements

Five grams of prepared soil sample was weighed into a conical flask, 3 ml of HCL and 1ml of HNO_3 were added using modified method of (Boisa & Ogbede 2016). The mixture was digested 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 result 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 444.771±2.647 ppm (DMPS wk4) and 286.458±3.40 ppm (control soil) to 422.875±2.343 ppm (FMPS wk2) respectively.

Table 1 Mean Concentrations (ppm) of Potentially Toxic Elements in Polluted Soil at Biara Decanted Magnetite Nanoparticle

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
DMPS 0	392.375±1.324	9.103±0.346	2.132±0.158	5.709±0.740	7.798±0.158	0.542±0.016	BDL
DMPS wk1	426.688±2.424	4.974±1.745	1.744±0.053	5.550±0.474	9.126±0.171	0.549±0.014	BDL
DMPS wk2	361.187±3.299	3.846±0.392	1.163±0.025	0.191±0.073	7.916±0.033	0.858±0.170	BDL
DMPS wk3	360.021±3.135	3.231±0.332	0.310±0.015	3.504±0.238	6.197±0.045	0.798±0.025	BDL
DMPS wk4	444.771±2.647	4.836±2.213	3.088±0.090	2.769±0.226	6.334±0.087	0.811±0.081	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 2 Mean Concentrations (ppm) of Potentially Toxic Elements in Polluted Soil at Biara Treated Filtered Magnetite Nanoparticle

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
FMPS 0	355.000±1.091	3.384±0.188	0.403±0.022	8.667±0.750	6.667±0,055	0.827±0.068	BDL
FMPS wk1	415.667±5.815	5.026±0.297	1.601±0.378	3.282±0.238	4.696±0.164	0.871±0.022	BDL
FMPS wk2	422.875±2.343	5.615±2.828	1.147±0.270	5.513±0.523	7.412±0.197	0.818±0.025	BDL
FMPS wk3	382.292±0.446	4.282±1.996	1.217±0.214	6.872±0.692	4.876±0.125	0.918±0.049	BDL
FMPS wk4	331.854±3.185	4.256±0.316	0.229±0.080	4.744±0.542	7.068±0.145	0.853±0.052	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

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 427.855±7.013 ppm (DMCS 0) and 286.458±3.40 ppm (control soil) to 408.521±2.868 ppm (FMCS wk3) respectively.

Table 3 Mean Concentrations (ppm) of Potentially Toxic Elements in Control Soil at Biara Treated Decanted Magnetite Nanoparticle

Sample ID/(ppm)	Fe	Pb	Cu	Cr	Zn	Cd	As
DMCS 0	427.855±7.013	7.025±0.428	2.395±0.044	5.615±0.700	8.764±0.123	0.502±0.016	BDL
DMCS wk1	359.896±1.328	5.923±0.288	0.868±0.069	7.692±0.314	8.955±0.098	0.655±0.014	BDL
DMCS wk2	330.188±1.692	5.8976±0.418	0.333±0.128	5.561±0.096	3.990±0.053	0.691±0.021	BDL
DMCS wk3	372.167±4.642	4.077±1.995	0.752±0.067	4.077±0.350	4.514±0.075	0.607±0.099	BDL
DMCS wk4	410.188±2.383	4.154±1.859	1.341±0.114	4.974±0.504	5.522±0.095	0.596±0.008	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

Table 4 Mean Concentrations (ppm) of Potentially Toxic Elements in Control Soil at Biara Treated Filtered Magnetite Nanoparticle

Sample ID/(ppm)	Fe	Pb	Cu	Cr	Zn	Cd	As
FMCS 0	296.562±1.902	1.587±0.7801	0.322±0.111	4.538±0.440	3.433±0.080	0.745±0.025	BDL
FMCS wk1	323.708±1.966	1.075±0.491	1.407±0.135	3.744±0.219	4.433±0.070	0.702±0.007	BDL
FMCS wk2	338.646±1.649	0.544±0.261	0.341±0.085	4.231±0.226	6.339±0.019	0.747±0.15	BDL
FMCS wk3	408.521±2.868	0.600±1.052	0.543±0.029	3.667±0.202	4.052±0.099	0.627±0,064	BDL
FMCS wk4	344.547±2.565	1.513±0.000	0.953±0.107	5.846±0.166	5.612±0.199	0.784±0.049	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 9.103±0.346 ppm (DMPS 0) and 2.533±1.211 ppm (control soil) to 5.615±2.828 ppm for (FMPS wk2) respectively.

The results of Pb levels in control treated soils are displayed in Tables 3 and 4. The Pb mean concentrations ranged from 2.533±1.211 ppm (control soil) to 7.025±0.428 ppm (DMCS 0) and 0.544±0.261 ppm (FMCS 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 3.088±0.090 ppm (DMPS wk4) and 0.081±0.025 ppm (polluted soil) to 1.601±0.378ppm (FMPS wk1) respectively.

The results of Cu levels in control treated samples are showed in Tables 3 and 4. The Cu mean concentrations ranged from 0.333±0.128 ppm (DMCS wk2) to 2.395±0.044 ppm (DMCS 0) and 0.322±0.111 ppm (FMCS 0) to 1.407±0.135 ppm (FMCS wk1) respectively**.**

Chromium (Cr)

The results of Cr level are showed in Tables 1 and 2. The Cr mean concentrations ranged from 0.191±0.073 ppm (DMPS wk2) to 5.709±0.740 ppm (DMPS 0) and 2.692±0.251 (polluted soil) to 8.667±0.750 ppm (FMPS 0) respectively.

The results of Cr levels in control treated samples are showed in Tables 3 and 4. The Cr mean concentrations ranged from 3.436±0.527 ppm (control soil) to 7.692±0.314 ppm (DMCS wk1) and 3.436±0.527 ppm (control soil) to 5.846±0.166 ppm (FMCS wk4) respectively.

Zinc (Zn)

The results of Zn level are displayed in Tables 1 and 2 The Zn mean concentrations ranged from 4.491±0.094 ppm (control soil) to 9.126 ppm±0.171 (DMPS wk1) and 4.491±0.094 ppm (control soil) to 7.412±0.197 ppm (FMPS wk2) respectively.

The results of Zn levels in control treated soil are displayed in Tables 3 and 4. The Zn mean concentrations ranged from 3.990±0.253 ppm (DMCS wk2) to 8.955±0.098 ppm (DMCS wk1) and 3.433±0.080 ppm (FMCS 0) to 6.339±0.019 ppm (FMCS wk2) respectively.

Cadmium (Cd)

The results of Cd level are shown in Tables 1 and 2. The Cd mean concentrations ranged from 0 0.542±0.016 ppm (DMPS 0)) to 0.960±0.024 ppm (polluted soil) and 0.818±0.025 ppm (FMPS wk2) 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 0.502±0.016 ppm (DMCS 0)) to 0.940±0.043 ppm (control soil) and 0.627±0.064 ppm (FMCS wk3) 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 11.6 (DMPS 0) in Pb, Cu 0.1213 (polluted soil) to 4.5431 (DMPS wk3), Cr 0.2644 (DMPS wk2) to 7.2749 DMPS 0), Zn 1.6136 (polluted soil) to 3.6253 (DMPS wk2), Cd 21.4442 (DMPS wk1), to 54.6910 (control soil), Pb 2.6959 (control soil) to 6.6390 (FMPS wk2), Cu 0.1213 (polluted soil) to 1.9258 (FMPS wk1), Cr 3.9478 (FMPS wk1) to 12.2070 (FMPS 0), Zn 1.6136 (polluted soil) to 3.5498 (FMPS wk4) and Cd 32.2396 (FMPS wk2), to 54.6910 (control soil) respectively.

Table 5 Enrichment Factor of Potentially Toxic Elements in Polluted Soil at Biara Treated Decanted Magnetite Nanoparticle

Sample ID	Pb	Cu	Cr	Zn	Cd
DMPS 0	11.6	2.7168	7.2749	3.3123	23.0222
DMPS wk1	5.8285	0.5437	6.5036	3.5647	21.4442
DMPS wk2	5.3240	1.6010	0.2644	3.6253	39.5917
DMPS wk3	4.4870	4.5431	4.8664	2.8688	36.9423
DMPS wk4	5.4365	3.4715	3.1128	2.3735	30.3902
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 Filtered Magnetite Nanoparticle

Sample ID	Pb	Cu	Cr	Zn	Cd

FMPS 0	4.7660	0.5676	12.2070	3.1301	38.8263
FMPS wk1	6.0455	1.9258	3.9478	1.8829	34.9238
FMPS wk2	6.6390	1.3562	6.5185	2.9213	32.2396
FMPS wk3	5.6005	1.5917	8.9879	2.1258	40.0218
FMPS wk4	6.4125	0.3450	7.1477	3.5498	42.8401
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 2.696 (control soil) to 8.912 (DMCS wk2) in Pb, Cu 0.504 (DMCS wk2) to 5.280 (DMCS 0), Cr 5.477 (DMCS wk3) to 10.686 (DMCS wk1), Zn 1.862 (control soil) to 4.147 (DMCS wk1), Cd 24.217 (DMCS wk4) to 54.691 (control soil), Pb 0.735 (FMCS wk3) to 2.696 (control soil), Cu 0.543 (FMCS 0) to 2.173 (FMCS wk1), Cr 4.488 (FMCS wk3) to 8.484 (FMCS wk4), Zn 1.653 (FMCS wk3) to 3.120 (FMCS wk2) and Cd 25.891 (FMCS wk3) to 54.691 (control soil) respectively.

Table 7 Enrichment Factor of Potentially Toxic Elements in Control Soil at Biara Treated Decanted Magnetite Nanoparticle

Sample ID	Pb	Cu	Cr	Zn	Cd
DMCS 0	8.021	5.280	6.562	3.414	25.289
DMCS wk1	8.400	1.206	10.686	4.147	30.333
DMCS wk2	8.912	0.504	8.421	2.014	34.879
DMCS wk3	5.478	1.010	5.477	2.022	27.183
DMCS wk4	5.064	1.635	6.063	2.244	24.217
Control	2.696	1.124	5.993	1.862	54.691

Table 8 Enrichment Factor of Potentially Toxic Elements in Control Soil at Biara Treated Filtered Magnetite Nanoparticle

Sample ID	Pb	Cu	Cr	Zn	Cd
FMCS 0	2.676	0.543	7.651	1.929	41.869
FMCS Wk1	1.661	2.173	5.783	2.282	41.948
FMCS wk2	0.803	2.050	6.247	3.120	36.764
FMCS wk3	0.735	0.665	4.488	1.653	25.891
FMCS wk4	2.196	1.383	8.484	2.715	37.924
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 0.0089 (DMPS wk4) in Fe, Pb 0.0155 (control soil) to 0.0555 (DMPS 0), Cu 0.0004 (polluted soil) to 0.0154 (DMPS wk4), Cr 0.0010 (DMPS wk2) to 0.0286 DMPS 0), Zn 0.0107 (control soil) to 0.0217 (DMPS wk1), Cd 0.1807 (DMPS 0), to 0.3200 (polluted soil), Fe 0.0057 (control soil) to 0.0085 (FMPS wk2), Pb 0.0155 (control soil) to 0.0342 (FMPS wk2), Cu 0.0004 (polluted soil) to 0.0080 (FMPS wk1), Cr 0.0135 (polluted soil) to 0.0433 (FMPS 0), Zn 0.0107 (control soil) to 0.0176 (FMPS wk2) and Cd 0.2727 (FMPS wk2) to 0.3200 (polluted soil) respectively.

Table 9 Soil Metal Index of Potentially Toxic Elements in Polluted Soil at Biara Treated Decanted Magnetite Nanoparticle

Sample ID	Fe	Pb	Cu	Cr	Zn	Cd	Total SMI
DMPS 0	0.0079	0.0555	0.0107	0.0286	0.0185	0.1807	0.1030
DMPS wk1	0.0085	0.0303	0.0087	0.0278	0.0217	0.1830	0.0467
DMPS wk2	0.0072	0.0235	0.0058	0.0010	0.0188	0.2860	0.0570
DMPS wk3	0.0072	0.0197	0.0016	0.0175	0.0147	0.266	0.0545
DMPS wk4	0.0089	0.0295	0.0154	0.0139	0.0151	0.2703	0.0588
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 Filtered Magnetite Nanoparticle

Sample ID	Fe	Pb	Cu	Cr	Zn	Cd	Total SMI
FMPS 0	0.0071	0.0206	0.0020	0.0433	0.0158	0.2757	0.0608
FMPS wk1	0.0083	0.0307	0.0080	0.0164	0.0112	0.2903	0.0608
FMPS wk2	0.0085	0.0342	0.0057	0.0276	0.0176	0.2727	0.0611
FMPS wk3	0.0077	0.0261	0.0061	0.0344	0.0116	0.3060	0.0653
FMPS wk4	0.0066	0.0260	0.0012	0.0237	0.0168	0.2843	0.0598
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 444.771 ±2.647 ppm (DMPS wk4) as shown in Tables 1and 2. While the concentrations of Fe in control treated soils ranged from 286.458 ±3.4 ppm (control soil) to 427.855±7.013 ppm (DMCS wk3) as shown in Tables 3 and 4. This 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±1.211ppm (control soil) to 9.103±0.346 ppm (DMPS 0) as shown in Tables 1 and 2. While the concentrations of Pb in control treated soils ranged from 0.544±0.261 ppm (FMCS wk2) to 7.025±0.428 ppm (DMCS 0) as shown in Tables 3 and 4. This 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 positive correlation coefficient of 0.51443 with adsorbents. 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 3.088±0.090 ppm (DMPS wk4) as shown in Tables 1and 2. While the concentrations of Cu in control treated soils ranged from 0.322±0.111ppm (FMCS 0) to 2.395±0.044 ppm (DMCS 0) 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 of 0.79366 with adsorbents with the exception of FMCS (-0.01321). The anova showed that there is no significant within the adsorbents.

Concentrations of Cr ranged from 0.191±0.073 ppm for (DMPS wk2) to 8.667±0.750 ppm (DMPS 0) 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 3.436±0.527 ppm (control soil) to 7.692±0.314 ppm (DMCS wk1) as shown in Tables 3 and 4. The level of Cr obtained in this study were below DPR (2018) value of 380 ppm. This 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 0.28742 with adsorbents. The anova showed that there is no significant within the adsorbents.

Concentrations of Zn ranged from 4.491±0.092 ppm for (control soil) to 9.126±0.171 ppm (DMPS wk1) as shown in Tables 1and 2. While the concentrations of Zn in control treated soils ranged from 3.433±0.0800 ppm (FMCS 0) to 8.955 ±0.098 ppm (DMCS wk1) 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 of 0.68625 with adsorbents except the soil treated with FMPS. The anova showed that there is no significant within the adsorbents.

Concentrations of Cd ranged from 0.542±0.016 ppm for (DMPS 0) to 0.960 ±0.024 ppm (polluted soil) as shown in Tables 1 and 2. While the concentrations of Cd in control treated soils ranged from 0.502±0.016 ppm (DMCS 0) 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 of -0.5498 with adsorbents. The anova showed that there is significant within the adsorbents in control treated soil.

Enrichment Factor (EF)

The EF values ranged from 2.6959 (control soil) to 6.6390 (FMPS wk2) in Pb, Cu 0.1213 (polluted soil) to 4.5431 (DMPS wk3), Cr 0.2644 (DMPS wk2) to 12.2070 (FMPS 0), Zn 0. 1.6136 (polluted soil) to 3.6253 (DMPS wk2), Cd 21.4442 (DMPS wk1) to 54.691 (control soil) Tables 5 and 6. While the EF values in control treated soils ranged from 0.735 (FMCS wk3) to 8.912 (DMCS wk2) in Pb, Cu 0.504 (DMCS wk2) to

5.280 (DMCS 0), Cr 4.488 (FMCS wk3) to 10.686 (DMCS wk1), Zn 1.862 (control soil) to 4.147 (DMCS wk1), Cd 24.217 (DMCS 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 soil) to 0.0089 (DMPS wk4) in Fe, Pb 0.0155 (control soil) to 0.0555 (DMPS 0), Cu 0.0004 (polluted soil) to 0.0107 (DMPS 0), Cr 0.0010 (DMPS wk2) to 0. 0433 (FMPS 0), Zn 0.0107 (control soil) to 0.0217 (DMPS wk1), Cd 0.1807 (DMPS 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, *et al.* (2017).

V. Conclusion

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

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