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Detoxification of E-waste polluted site using cashew nut shell-based activated carbon

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Abstract

This study considered the potential use of activated carbon (AC) produced from cashew nuts for remediation of electronic waste (E-waste) polluted soil sites at Agbogbloshie, Accra, Ghana. The AC supplied by Climate-Environmental Research and Technology (CLERET) Laboratory, one of the research and development (R&D) umbrellas of Explore Scientific Innovations Ltd., Ghana. It was prepared by a two-stage process involving wood-fired reactor for thermal pyrolysis at temperature ranging from 800-1000 °C, followed with activation with oxidizing gas generated by wood-fired steam boiler at 160 °C and 7.5 atm pressure for 30 minutes. The product was characterized based on bulk density, particle size, iodine number, electrical conductivity (EC), porosity, and pH. Three replicates of soil samples were scooped from at a depth of 0-15 cm using a soil auger from two randomly selected sites. The samples were digested with 10 ml of ternary solution (20 ml of HClO₄; 500 ml of HNO₃; 50 ml of H₂SO₄) on a hot plate at 90°C for 30 minutes to an hour and analyzed for selected heavy metals (Pb, Fe, Cu, Cr and Cd) using Atomic Absorption

Spectrophotometer (AAS). The cashew nut shell-based AC significantly removed the heavy metal contents of the E-waste polluted soil with removal efficiency in the order: Cd (100%) > Pb (93%) > Fe (87%) > Cu (87%) > Cr (76%) for granular and Cd (100%) > Pb (98%) > Fe (96%) > Cu (94%) > Cr (87%) for powdered activated carbons. The slopes of the linear graph of the adsorption isotherms of the tested metals which is indicative of the quality of adsorption of the metals were in the order: Pb (0.9754) > Fe (0.9093) > Cr (0.8799) > Cu (0.8176) > Cd (0.7511). These agro-based waste materials therefore have great potential for effective detoxification of E-waste polluted sites.

Keywords: E-waste Detoxification; Activated Carbon; Agro-based Waste Materials; Heavy Metals Adsorption; Agbogloshie-Ghana

1. Introduction

There is an exponential growth in the demand for electrical and electronic equipment (EEE) globally due to rapid population growth, changing lifestyle, taste and preferences [1]. This growth coupled with the speedy obsolescence of EEE as a result of consistent technological advancement, diminishing product lifetimes, lack of separate collection and disposal has led to enormous amounts of electronic wastes (E-wastes) getting into the environment. In 2014, the United Nations estimated that 20 – 50 million tons of E-wastes were generated yearly around the globe and the situation is aggravated by low global recycling rates amidst illegal trans-boundary movement from developed to developing countries who have lower capacities to manage E-wastes [2].

Like other developing nations, the influx of E-waste into Ghana has been on the rise over the years, increasing from 1,400 tons in 2004 to 10,300 tons in 2011 [3].

According to Amoyaw-Osei et al. [4], of the 215,000 tons of EEE imported into Ghana in 2009, only 30% were new products. The E-waste sector is also dominated by informal recyclers and retrievers, who are exposed to the associated high risk. Regulation of E-waste management has been challenged by the lack of legislation, even though efforts are made to curb illegal inflows [3]. E-waste produces substances that can be very injurious to the environment and humans [1, 5, 6]. They form a significant component of toxic wastes spread across contaminated sites throughout the world. Heavy metal contamination of soils is subsequently the most important environmental problem that poses significant impacts to human and ecosystem health as contaminants infiltrate and pollute groundwater as well as surface water [1, 7, 8].

The burning of cables which is a common practice in E-waste material recovery in developing countries is recognized as a practice that has the most severe impact on human health and environment. Exposure to these hazardous substances results in health challenges that affect the development of the nervous system, thyroid gland, liver, kidney and causes heart damage, eye and throat irritation [9]. Animals may suffer from reduced fertility, slower growth and development and in some cases death while plants experience phytotoxic effects. Recycling which is an emergent solution is also associated with varying degrees of hazards to workers and the environment. In incineration, orderly and total burning of E-waste is carried out in specially designed incinerators at high temperatures ranging from 900 – 1000 °C. Though incineration has the advantages of waste reduction and the utilization of the energy content of the combustible materials, the emission of hazardous substances into air poses a threat [6, 9].

The most common biological technique for treating soil and groundwater contamination is bioremediation [6, 10]. An important factor limiting the efficiency of

soil bioremediation is the high toxin levels of chemical contaminants to soil micro and macro organisms including plants used in phytoremediation. This often limits utilization of this approach for treating contaminated soils [11].

An effective heavy metal removal technique is required in detoxification of the environment from E-waste pollution. The potential of activated carbon (AC) in reducing the toxicity of heavily contaminated soils has been demonstrated by previous studies [10-12]. AC is useful in the ousting of volatile organic compounds and polychlorinated biphenyls such as chlorine-based solvents for the adsorption of contaminants from groundwater as part of the bioremediation process. The detoxification potential of AC on contaminated soils has also been studied significantly. AC can be developed from many sources, such as palm husks, coconut shells and almond husk. The use of agricultural by-products to replace wood as the carbon source helps in utilizing biomass residues in a proper and efficient way thereby reducing ecological impacts. The increasing generation and demands for proper disposal of agricultural waste make their use as AC a promising bioresource. This study therefore investigates the potential of AC produced from cashew nuts for remediation of soil from E-waste polluted sites.

2. Materials and methods

2.1. Study area

This study was conducted at the Agbogbloshie E-waste dumpsite, also known as the Agbogbloshie Scrap Market in Accra, Ghana (Fig. 1). This site has for decades remained a dumping ground for waste products of imported EEE goods mainly from Western Europe [13]. Reports in 2013 indicate that 75% of electronic goods arriving at the main port of Ghana, Tema end up at Agbogbloshie and about 129,000 tons of

E-waste is generated at the site annually [14]. Agbogbloshie has one of Accra's largest food markets and about 40,000 residents live in the wider locality of Sodom and Gomorrah, one of the main areas in Agbogbloshie [14]. This location in Agbogbloshie is purely slum and home to many scrap dealers and informal recyclers of E-wastes. The site is the main center for large scale recovery of materials from E-wastes and has been regarded as one of the largest and most polluted in the world [13, 15]. The main mode of operation at the site includes manual disassembly of obsolete electrical and electronic products to retrieve metals which include copper and aluminum. Brigden et al. [13] estimated that 40,000 - 250,000 people are at risk from the toxic fumes that engulf the community as a result of the burning of used electrical appliances. The fumes are known to cause major health complications. The water and soil from the site are contaminated with increased concentrations of lead, plastic softeners and dioxins which are carcinogenic.

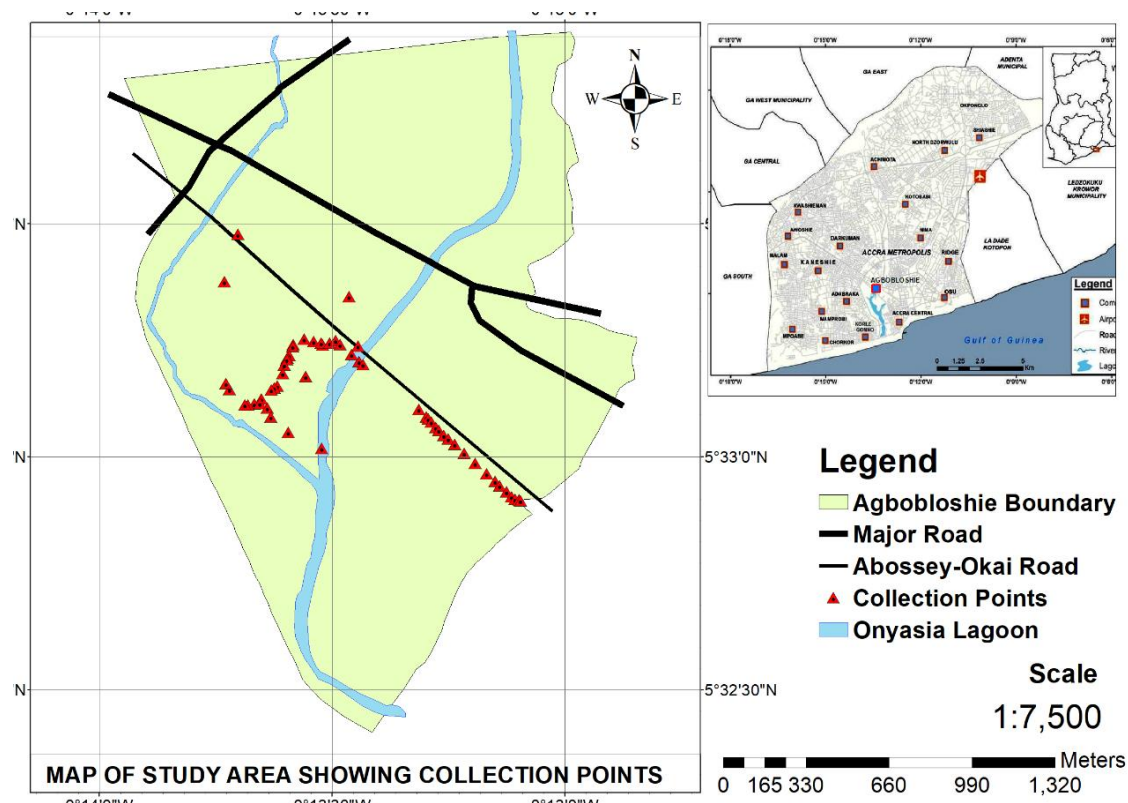


Fig. 1 Map of the study area showing sampling sites

2.2. Experimental process

The experimental process followed three main steps: (i) Determination of the physico-chemical properties of the AC, (ii) Determination of Adsorption property of the AC, and (iii) Application to samples from the polluted E-waste site.

2.2.1. Source of activated carbon

The cashew nut shell-based AC is one of the several ACs produced at the Climate-Environmental Research and Technology (CLERET) Laboratory, which is one of the research and development (R&D) umbrellas of Explore Scientific Innovations Limited, Ghana. CLERET Laboratory primarily focuses on developing AC cleaner production technologies. The products are generated based on optimization techniques appropriate for climate/environmental remediation and other science research, as well as several industrial applications. CLERET Laboratory is also a climate geoengineering setup aimed at developing technologies to mitigate greenhouse gas forcing of climate emanating primarily from industrial emissions.

In brief, the cashew nut shell-based AC was produced using physical activation, which essentially consisted of two main stages [16]: (i) Thermal pyrolysis (carbonization) of the raw material to elemental carbon in one ton stainless steel capacity reactor, with the inner and outer jackets lagged with fiber glass to minimize heat escape from the reactor. The wood-fired reactor for the pyrolytic process was carried out between 800-1000 °C, monitored by a digital temperature probe and a pyrometer, which measure core temperatures up to 1,500 °C; and (ii) oxidizing gas generated by wood-fired steam boiler, monitored by an analog temperature gage at 160 °C under 7.5 atmospheres operating conditions with an analog pressure gage

reading to a maximum of 25 atmospheres. The activation temperature by the reactor operated between 500-600 °C. The high pressure gradient established between the steam boiler and the reactor, which expelled the steam from the former to the latter. The carbon was activated for 30 minutes, after which the activation pressure became exhausted, dropping below one atmosphere. To be consistent with experimental design and to ensure production quality, three replications were made for the two-stage process. For each replicate, 50 kg of the raw material were used.

2.2.2. Polluted samples collection

The soil samples for the experiment were scooped from marked spots of selected sites at a depth of 0-15 cm using a soil auger. The collected samples were put together to form a composite sample. Three replicates were taken from each site making a total of six soil samples from the study site. The samples were put into transparent zip-locked plastic bags, labelled and transported to the laboratory for analysis. The samples were air-dried for four days, grinded into fine powder and sieved with a 2 mm sieve to remove coarse components. The resultant soil was sub-sampled for the heavy metal analysis.

2.2.3. Physico-chemical properties of the activated carbon based on particle size-powdered activated carbon (PAC) and granular activated carbon (GAC)

pH, electrical conductivity and temperature

The pH was determined with the standard method ASTM 3838-80. The ASTM standard determination of pH is based on chemical reactions between the constituents of the AC and its non-carbonaceous constituents and the adsorbate containing fluid. Ten grams of the AC were weighed into a beaker and 50 ml of distilled water were

added. The mixture was stirred for 10 minutes to ensure proper dissolution of the sample, left for one hour for the suspended particles to settle and later filtered. The pH meter was first calibrated with standard buffer solution of pH 4.0 and 7.0. The electrode was then immersed into the solution and the pH and electrical conductivity readings were taken and recorded. The temperature of the solution was also recorded.

Bulk density

A graduated cylinder was calibrated and used for the estimation of the bulk density. The cylinder was packed with the sample and compacted. The density was calculated using Eq. (1) as indicated by Meteku [17].

$$\text{Bulk density (gcm}^3\text{)} = \frac{\text{Mass (g)}}{\text{Volume (cm}^3\text{)}} \quad (1)$$

Particle size determination

By general purpose classification and based on physical properties, two types of activated carbons, i.e. powdered activated carbon (PAC) and granulated activated carbon (GAC) were produced for the study. The GAC was generated using a high-powered roller mill / hammer mill with specific mesh size. The GAC was approximately 2.0 – 4.0 mm in size corresponding to standard sieves [12, 18]. The PAC was obtained by grinding the GAC into powder using the crusher. The powdered AC was categorized into size ranges using sieves. Twenty grams of the PAC were weighed and placed on top of a set of six sieves with mesh sizes ranging from 2 mm to 71 μm . The sieves were shaken using an aggregate stability machine for 3 minutes to allow the particles to separate into the various sieves according to their sizes. The weights of active carbon retained on each of the sieves and the bottom pan were

determined using ASTM STP 447B. Using the Eq. (2), the percentage weight of each category of particles retained in each sieve were computed [17].

$$P(\%) = \frac{(S-R)}{S} \times 100 \quad (2)$$

Where P = percent of sample passing through the test sieve, R = weight of sample remaining on test sieve (g), and S = weight of sample used (g).

Filtration rate determination

After the treatment process with the digested sample and a known amount of activated carbon, the content was poured into a funnel with filter paper inserted. The filtration process was timed, that is, the time taken for all the liquid to drain through the filter paper. The filtration rate was determined using Eq. (3) [19]. After the filtrate rate determination, a vacuum filter was used in filtering in order to obtain a clear solution for further analysis.

$$\text{Filtration rate}(m/s) = \frac{\text{Volume of liquid (ml)}}{\text{Time taken to drain}} \quad (3)$$

2.3. Iodine number determination

The porous structure or character of the AC produced was examined by the iodine number. The adsorption of aqueous iodine, a quick methodology for assessing the surface area of AC associated with pores greater than 1 nm was adopted in the characterization of the activated carbon produced [12, 20]. In determining the iodine number, 0.2 g of the AC was weighed into a dry flask and 40 ml of 0.1 N Iodine solution added. The mixture was swirled vigorously for 10 minutes and filtered using a Whatman No. 42 filter paper into a conical flask. Ten milliliters of the clear filtrate were taken into a conical flask; 2 ml of freshly prepared starch solution was added to the solution as an indicator and titrated with 0.05 N Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$)

until the pale yellow color of the iodine solution became colorless. The iodine number was determined using the Eq. (4) [12].

$$\text{Iodine value (mg/g)} = \frac{(B-A) \text{ ml} \times 12.69 \times N}{\text{Weightt of sample (g)}} \quad (4)$$

Where B = titration of blank, A = titration of sample and N = normality of iodine (0.1 N).

2.4. Preparation and analyses of soil samples

A 1.0 g of each of the soil samples from the study site was measured into a digestion tube and digested with 10 ml of Ternary Solution (20 ml of HClO_4 ; 500 ml of HNO_3 ; 50 ml of H_2SO_4) on a hot plate at 90 °C for 30 minutes to an hour until white fumes appeared. The digestion tube was removed from the hot plate and allowed to cool for some time and filtered into a 100 ml volumetric flask using a Whatman No. 42 filter paper. Distilled water was then added to the filtrate to make it to the 100 ml mark of the volumetric flask. PINAAcle 900T Perkin Elmer AAS was used to analyze the soil samples.

2.5. Application of activated carbon to samples from the polluted E-waste site

Incremental weights (1 g, 2 g, 3 g, 4 g and 5 g) of the AC were applied to 50 ml leachates prepared from the polluted soil samples, with known initial concentrations of the metals (Cu, Pb, Cr, Cd and Fe) being investigated and kept for 24 hours. The adsorption of the metals from the leachates by the AC was determined after the 24 hours; 20 ml of the samples (containing AC and leachates) were diluted to 100 ml and the respective metal contents after the treatment measured using AAS and the adsorption efficiency estimated using the Freundlich Adsorption Theorem [21] as indicated in Eq. (5).

$$\text{Log } q_e = \text{log } k + (1/n) \text{ log } C_e \quad (5)$$

where;

- q_e is the amount of adsorbate (pollutant) adsorbed per AC dosage.
- C_e is the equilibrium concentration of adsorbate (pollutant) in water.
- k and $(1/n)$ are empirical constants (Freundlich parameters).
 - i. k is a value which is equal to the intercept where a larger value of k indicates good adsorption efficiency for the particular AC.
 - ii. $1/n$ is the value of slope of the plot of $\text{log } q_e$ versus $\text{log } C_e$, a larger value of $1/n$ indicates a more effective adsorption.

The Freundlich's adsorption efficiency is expressed from the graph as $X/m = K_f C_e^{1/n}$. Using the adsorbance obtained based on Beer Lambert's Law, the concentrations were calculated and the responses of the standards used to determine the exact performance of the machine and accurate values of each element. Calculations of the concentrations of heavy metals were done using Eq. (6) [17].

$$\text{Metal (mg/kg)} = \frac{\text{Conc.of analytical measurement} \times \text{Volume of extraction}}{\text{Weight of sample (g)}} \quad \text{Eq. (6)}$$

2.6. Statistical analysis

Principal Component Analysis (PCA) and the Analysis of Variance (ANOVA) were used to test the efficiency and difference of the ACs. Differences in the treatments were tested using Least Significant Difference Test (LSD). Significant differences were reported at p-values of ≤ 0.05 . Graphical representations in the forms of charts were used to illustrate results from the laboratory analysis and test results.

3. Results and discussion

3.1. Properties of the activated carbon

3.1.1. Physical properties

The temperature, pH, electrical conductivity, bulk density, iodine number and filtration rate of the activated carbons used (GAC and PAC) in the study are presented in Table 1. Temperature of the AC ranged from 26.90 to 27.30 °C with a mean of 27.10 ± 0.15 °C. Mean temperatures recorded for the GAC and PAC were 27.30 ± 0.01 °C and 27.10 ± 0.00 °C, respectively. The AC generally had alkaline properties with mean pH values of 9.60 ± 0.00 and 9.55 ± 0.07 for the GAC and PAC, respectively. The bulk density on other hand was 0.43 ± 0.01 for the GAC and 0.41 ± 0.01 for the PAC. The GAC had higher temperature, pH and bulk density than the PAC whereas the PAC had higher electrical conductivity, iodine number and filtration rate. The electrical conductivity ranged from 154.00 to 435.00 $\mu\text{S}/\text{cm}$ and mean values were 431.50 ± 0.71 and 435.00 ± 0.00 $\mu\text{S}/\text{cm}$ for GAC and PAC, respectively. The mean iodine number and filtration rate were 719.14 ± 19.43 mg/g and 0.11 ± 0.15 , respectively.

282 **Table 1** Descriptive statistics of the physical properties of the GAC and PAC

| Parameter | | N | Mean | Std. Deviation | Std. Error | 95% Confidence Interval | | Minimum | Maximum |
|---------------------------------|---------------------------------|---|--------|----------------|------------|-------------------------|-------------|---------|---------|
| | | | | | | Lower Bound | Upper Bound | | |
| Temperature (°C) | Granular activated carbon (GAC) | 3 | 27.30 | 0.0071 | 0.0050 | 27.23 | 27.36 | 27.29 | 27.30 |
| | Powdered activated carbon (PAC) | 3 | 27.10 | 0.0000 | 0.0000 | 27.10 | 27.10 | 27.10 | 27.10 |
| | Total | 6 | 27.10 | 0.1493 | 0.0528 | 26.97 | 27.22 | 26.90 | 27.30 |
| pH | Granular activated carbon (GAC) | 3 | 9.60 | 0.0000 | 0.0000 | 9.60 | 9.60 | 9.60 | 9.60 |
| | Powdered activated carbon (PAC) | 3 | 9.55 | 0.0707 | 0.0500 | 8.91 | 10.19 | 9.50 | 9.60 |
| | Total | 6 | 7.56 | 2.1520 | 0.7609 | 5.76 | 9.36 | 5.50 | 9.60 |
| Electrical conductivity (µS/cm) | Granular activated carbon (GAC) | 3 | 431.50 | 0.7071 | 0.5000 | 425.15 | 437.85 | 431.00 | 432.00 |
| | Powdered activated carbon (PAC) | 3 | 435.00 | 0.0000 | 0.0000 | 435.00 | 435.00 | 435.00 | 435.00 |
| | Total | 6 | 294.20 | 148.6599 | 52.5592 | 169.92 | 418.48 | 154.00 | 435.00 |
| Bulk density | Granular activated carbon (GAC) | 3 | 0.43 | 0.0071 | 0.0050 | 0.36 | 0.49 | 0.42 | 0.43 |
| | Powdered activated carbon (PAC) | 3 | 0.41 | 0.0071 | 0.0050 | 0.34 | 0.47 | 0.40 | 0.41 |
| | Total | 6 | 0.44 | 0.0285 | 0.0101 | 0.41 | 0.46 | 0.40 | 0.48 |
| Iodine (mg/g) | Granular activated carbon (GAC) | 3 | 730.26 | 0.0071 | 0.0050 | 730.19 | 730.32 | 730.25 | 730.26 |
| | Powdered activated carbon | 3 | 742.96 | 0.0071 | 0.0050 | 742.89 | 743.02 | 742.95 | 742.96 |

| | | | | | | | | | |
|------------|---------------------------------|---|--------|---------|--------|--------|--------|--------|--------|
| | (PAC) | | | | | | | | |
| | Total | 6 | 719.14 | 19.4284 | 6.8690 | 702.90 | 735.38 | 698.49 | 742.96 |
| Filtration | Granular activated carbon (GAC) | 3 | 0.18 | 0.2036 | 0.1440 | -1.65 | 2.01 | 0.03 | 0.32 |
| | Powdered activated carbon (PAC) | 3 | 0.20 | 0.2348 | 0.1660 | -1.91 | 2.31 | 0.04 | 0.37 |
| | Total | 6 | 0.11 | 0.1461 | 0.0517 | -.013 | 0.23 | 0.03 | 0.37 |

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3.1.2. Particle sizes

Percentage composition of the various particle sizes of the AC produced is presented in Fig. 2. The composition of particles by size was in the order: 1 mm > 300 μm > 225 μm > 125 μm > 71 μm > (< 71 μm) > 2 mm. Particles size of 1 mm, 300 μm and 225 μm dominated (73.8%). PAC consisted of finer carbon particles of 0.177 mm mesh size (95 – 100%). GAC defined as the AC being retained on a 0.297 mm mesh size, ranged in sizes 8 \times 20, 20 \times 40 or 8 \times 30 for liquid phase applications and 4 \times 6, 4 \times 8 or 4 \times 10 for vapor phase applications. A 20 \times 40 GAC thus consists of particles capable of passing through a standard U.S Mesh Size No. 20 sieve (0.84 mm) (specified as 85% passing) but retained by a Standard Mesh Size No. 40 sieve (0.42 mm) (specified as 95% retained). Powdered or fine granules less than 1.0 mm in size with an average diameter between 0.15 and 0.25 mm are the most active carbons due to their large surface to volume ratios and small diffusion distances. GAC on the other hand has lower external surface. Diffusion of the adsorbate is therefore a key factor in the use of GAC for adsorption. GACs are commonly used for adsorption of gas and vapour as a result of their high diffusion rate.

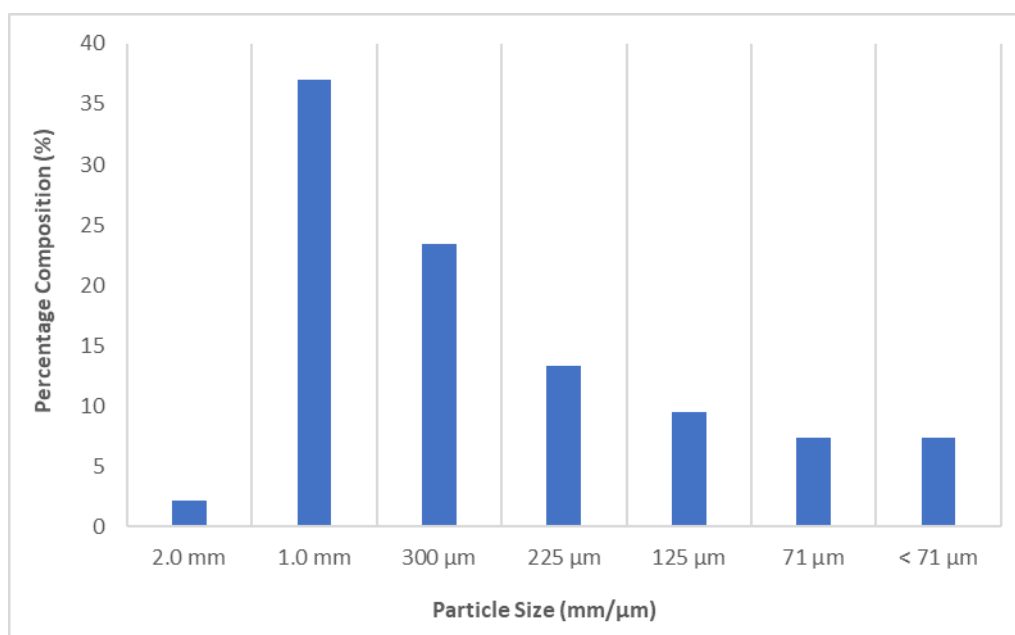


Fig. 2 Size composition of the activated carbon

3.1.3. Adsorption isotherm parameters

The adsorption isotherms for copper (Cu), iron (Fe) cadmium (Cd), chromium (Cr), and lead (Pb) are presented in Figs. 3 – 7. The occurrence of the metals adsorption from the treated samples is indicated by the straight-line plot. From the graphs, the coefficients of determination (R^2) are a good indication of the quality of adsorption of the heavy metals by the activated carbon. Higher R^2 values imply higher adsorption rates and Table 2 shows the adsorption rates obtained. Adsorption isotherm measures the amount of substance (in this case heavy metal) adsorbed per unit weight of adsorbent (AC) to adsorbent amount remaining in the sample solution [21]. Adsorption isotherm experiment was conducted to determine the feasibility and efficiency of an adsorption treatment for the removal of the heavy metals using the cashew-based AC. The quality of the adsorption of specific heavy metal by the AC which is shown by the graph of adsorption isotherm is determined by the coefficient of determination (R^2), and to a large extent the slope of the linear plot.

From the results, the R^2 for the tested metals range from the least value of 0.7511 for Cd to a maximum of 0.9754 for Pb. The values of the R^2 were in the order: Pb > Fe > Cr > Cu > Cd. The value of $1/n$ was obtained from the slope of the linear plot while the K_f were obtained by taking the antilog value of $\log C_e$. Large adsorption constant (K_f) values are indicative of greater adsorption capacity while the slope ($1/n$) measures the strength of the activated carbon used. It can therefore be concluded that all the metals (copper, iron, cadmium, chromium, lead) tested could be reduced in the samples by the cashew-based activated carbon.

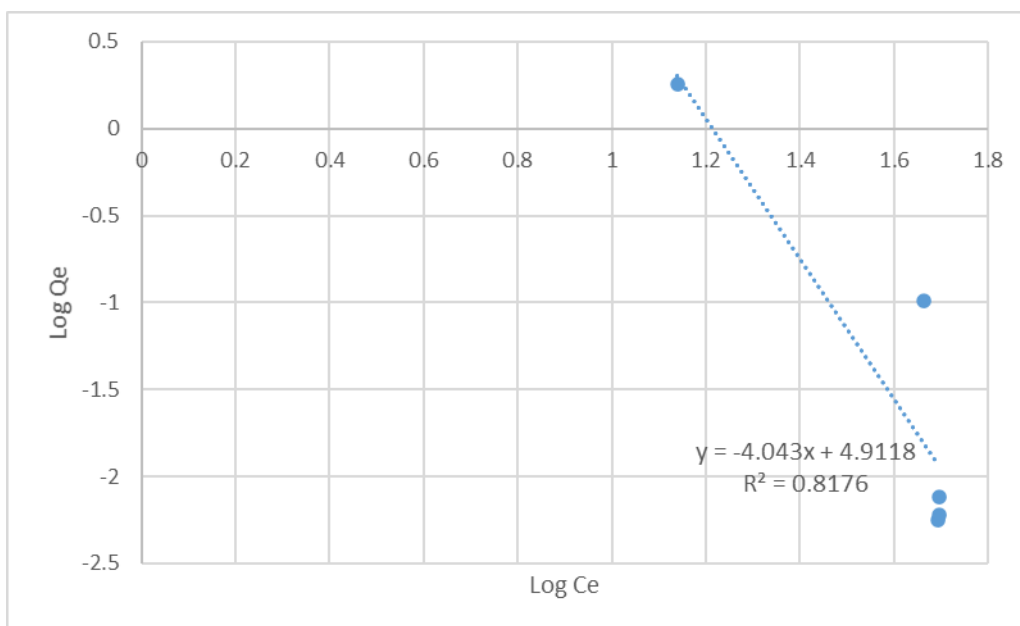


Fig. 3 Adsorption isotherm for copper

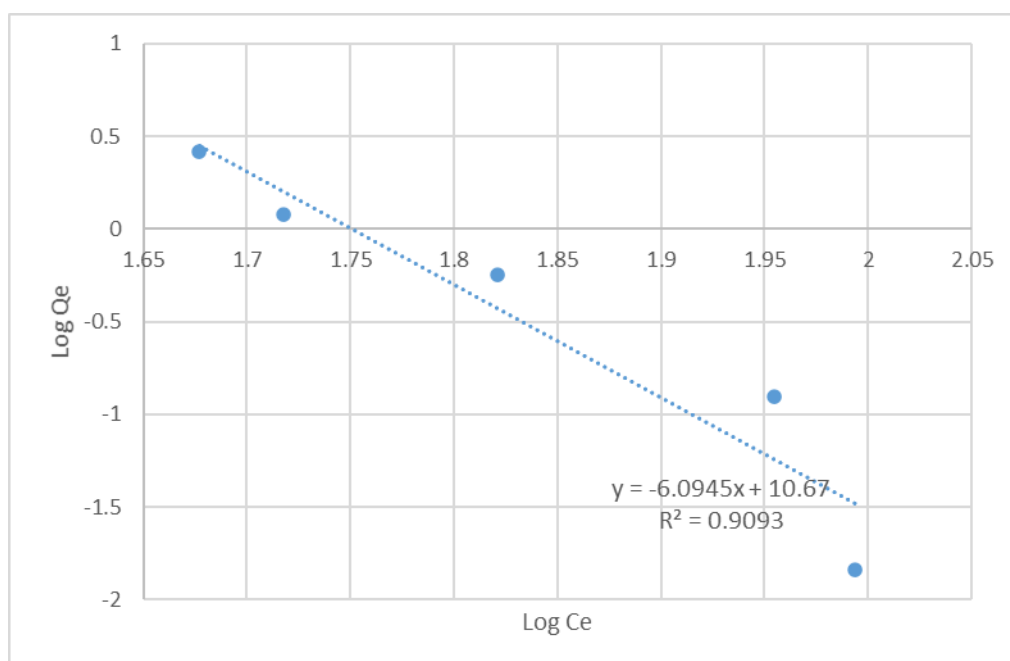


Fig. 4 Adsorption isotherm for iron

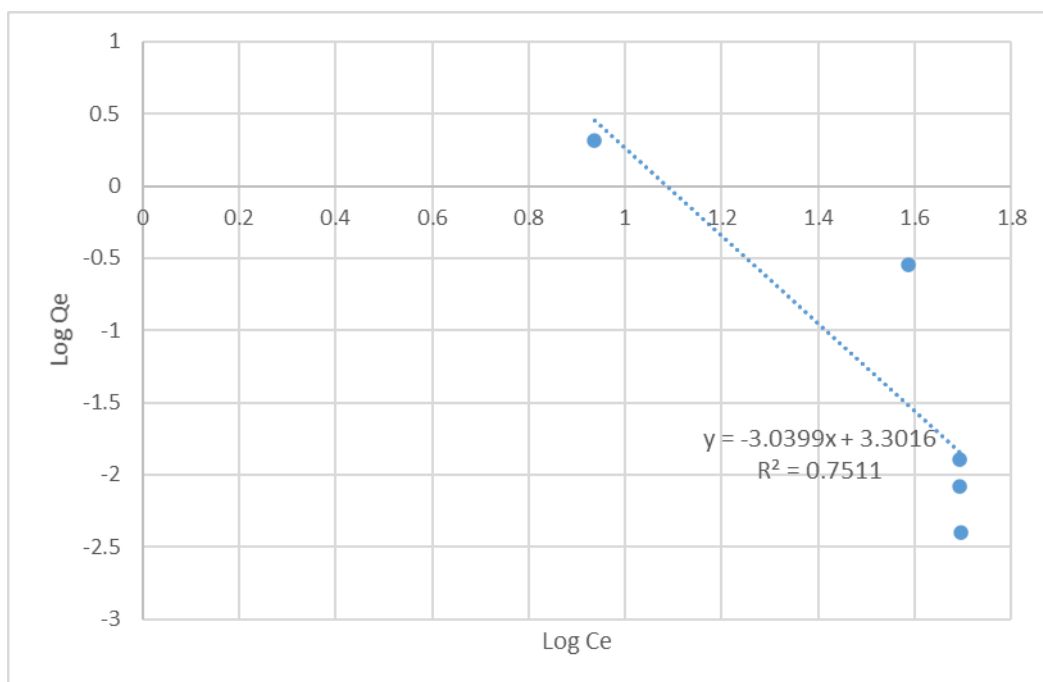


Fig. 5 Adsorption isotherm for cadmium

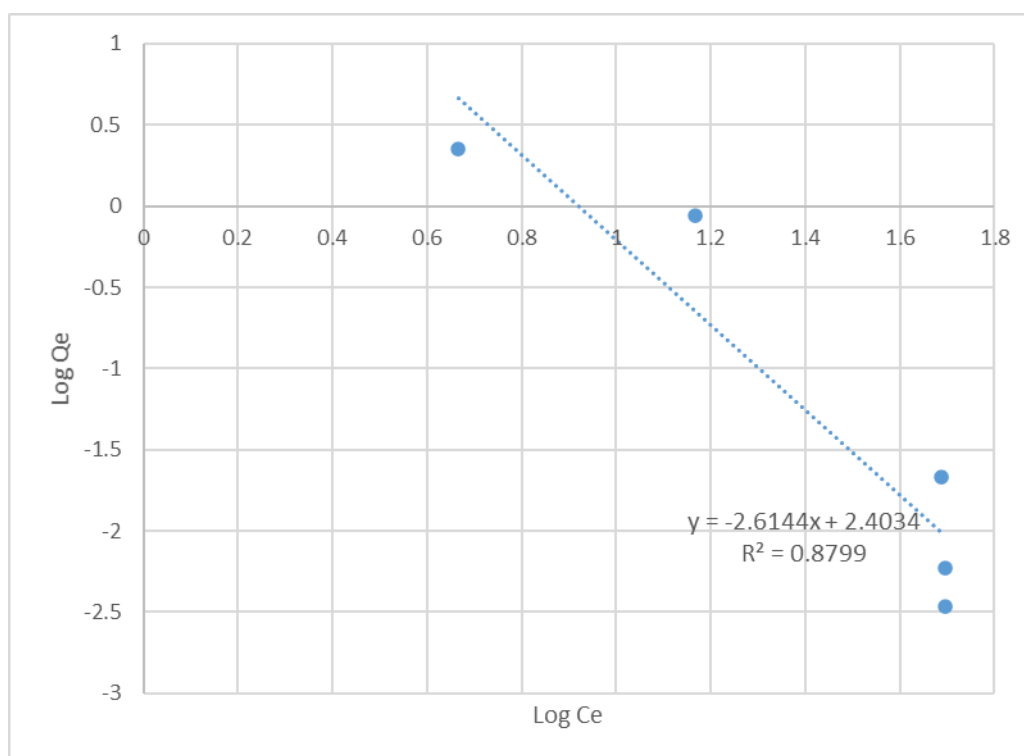


Fig. 6 Adsorption isotherm for chromium

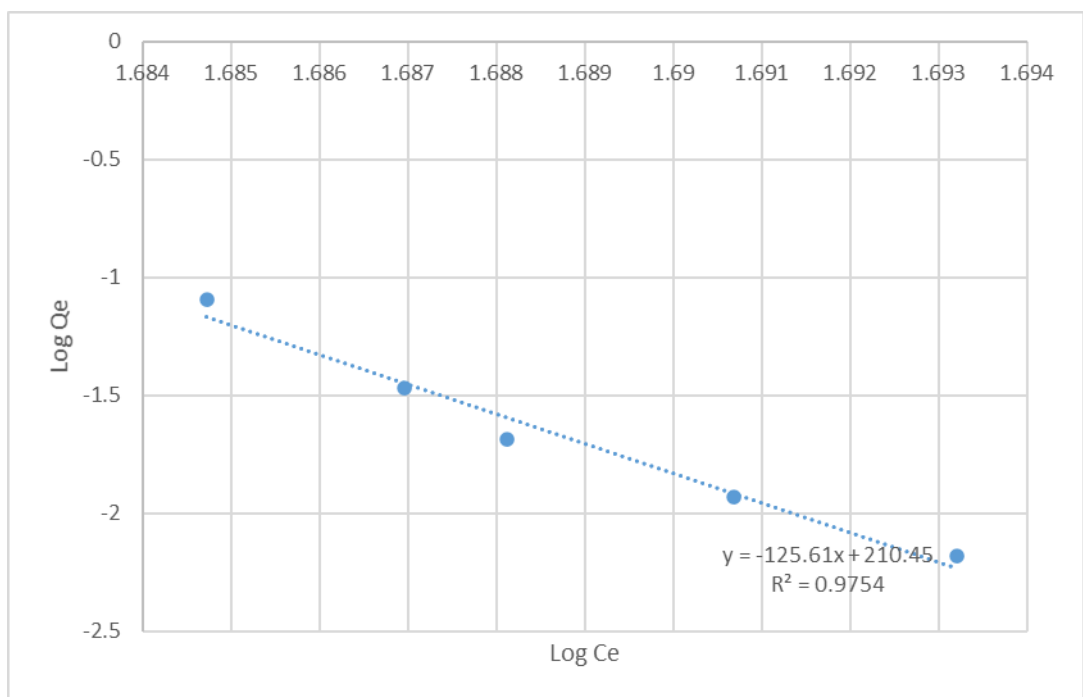


Fig. 7 Adsorption isotherm for lead

Table 2 Summary of the adsorption isotherms for the metals considered

| Type of adsorbent | Slope | Intercept (K_f) | R^2 | Equation |
|-------------------|--------|---------------------|--------|---------------------------------|
| Copper | 4.043 | 81620.6 | 0.8176 | $X/m = 81620.6 Ce^{4.043}$ |
| Iron | 6.0945 | $4.67e^{10}$ | 0.9093 | $X/m = 4.67e^{10} Ce^{6.0945}$ |
| Cadmium | 3.0399 | 2002.63 | 0.7511 | $X/m = 20002.6 Ce^{3.039}$ |
| Chromium | 2.6144 | 253.16 | 0.8799 | $X/m = 253.16 Ce^{2.4034}$ |
| Lead | 125.61 | $2.82e^{210}$ | 0.9754 | $X/m = 2.82e^{210} Ce^{125.61}$ |

3.2. Levels of metals in the soil samples

3.2.1. Metal levels in untreated soil samples

Fig. 8 shows the mean metal concentrations of the soil samples before treatment with the activated carbon. Iron recorded mean concentrations of 2740 ± 1.08 and 3083.67 ± 0.45 mg/kg for plots 1 and 2, respectively. Mean Pb concentrations in the untreated soil samples

were respectively 5657.33 mg/kg and 5218.67 mg/kg for plots 1 and 2. The mean concentration of Pb at both plots 1 and 2 exceeded the WHO/FAO acceptable maximum limit of 50.00 mg/kg for soils [22]. Comparatively, these concentrations were several times higher than those reported near similar E-waste recycling sites in Ibadan, Nigeria [23] and in Guiyu, China [24]. Mean Cu levels were 33663.33 ± 5.2888 and 47313.33 ± 11.2324 mg/kg, respectively for plots 1 and 2. These concentrations also exceeded the acceptable limit of 100 mg/kg. Similarly, the mean concentrations of Cd (194.20 ± 0.09 and 97.17 ± 0.01 mg/kg) and Cr (4237.33 ± 0.59 and 2561 ± 0.33 mg/kg) for the plots 1 and 2 respectively, exceeded the WHO/FAO acceptable levels for soils [22]. These results are consistent with that of Yeboah [9] who indicated that the concentrations of heavy metals measured at Agbogbloshie were significantly higher than that of the EPA in Canada and Dutch environmental standards.

Copper and lead constituted the two major heavy metals in the soil samples prior to the application of the carbons. Cadmium, chromium and lead recorded comparatively higher concentrations in all the soil samples from plot 1. The concentrations of the metals in the soil samples were in the order: Cu > Pb > Cr > Fe > Cd. The increased levels of heavy metals contamination can be attributed to the burning of E-waste materials such as used computers, refrigerators, cables, batteries, among others. Using the Eigen values extracted from the PCA, nearly eighty five percent (84.6%) of the total variation in the dataset can be explained by three components, namely Pb, Fe and Cr (Table 3). Lead contributed the highest (33.9%), followed by iron (27.5%) and chromium (23.2%) with Eigen values 1.697, 1.373 and 1.159, respectively. This finding from the PCA confirms the order of metals from the adsorption isotherms using the R^2 values.

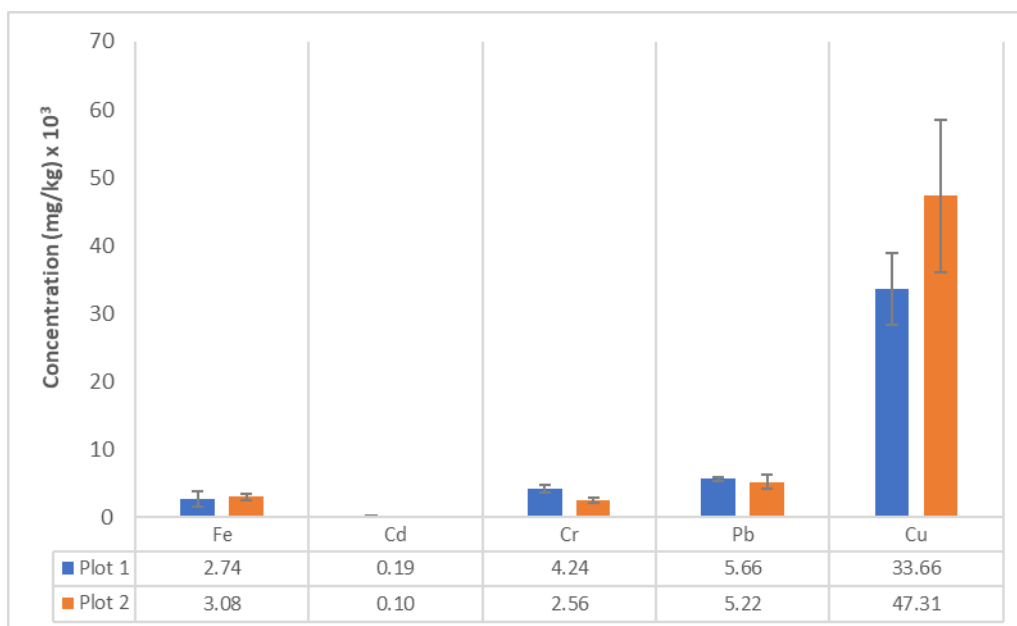


Fig. 8 Mean concentrations of metals before treatment

Table 3 Varimax rotated factor loadings and communalities of soil metals

| | PC 1 | PC 2 | PC 3 | Commonalities |
|------------------------|--------|--------|--------|---------------|
| Copper | .799 | .470 | -.122 | .874 |
| Iron | -.238 | .814* | .133 | .737 |
| Cadmium | .541 | -.622 | -.241 | .738 |
| Chromium | -.125 | -.286 | .930* | .962 |
| Lead | .833* | .143 | .451 | .917 |
| Eigen value | 1.697 | 1.373 | 1.159 | |
| Variance (%) | 33.940 | 27.454 | 23.174 | |
| Cumulative Percent (%) | 33.940 | 61.394 | 84.569 | |

* *Significant values*

3.2.2. Metal concentrations in treated samples

Figs. 9 and 10, respectively show the significant detoxification effect of the GAC on the metals considered. The results show a significant reduction in the concentrations of all the metals in the samples of both plots after treatment with GAC. The adsorption trend remains similar for the two plots 1 and 2 when PAC treatment was applied (Figs. 11 and 12).

Cadmium removal recorded the highest efficiency (100%) for both GAC and PAC treatments in the two plots while chromium removal recorded the lowest efficiencies with both treatments (75.85% for GAC and 87.19% for PAC). The order of the metal concentration in terms of their removal efficiency from the polluted soil is: Cd > Pb > Cu > Fe > Cr for GAC and Cd > Pb > Fe > Cu > Cr for PAC (Table 4). Comparatively, powdered AC recovered higher metal concentrations from the soils and had better adsorption rates than granular AC. This can be attributed to the fact the PAC have greater surface areas due to their nature which enhances adsorption of the metals considered.

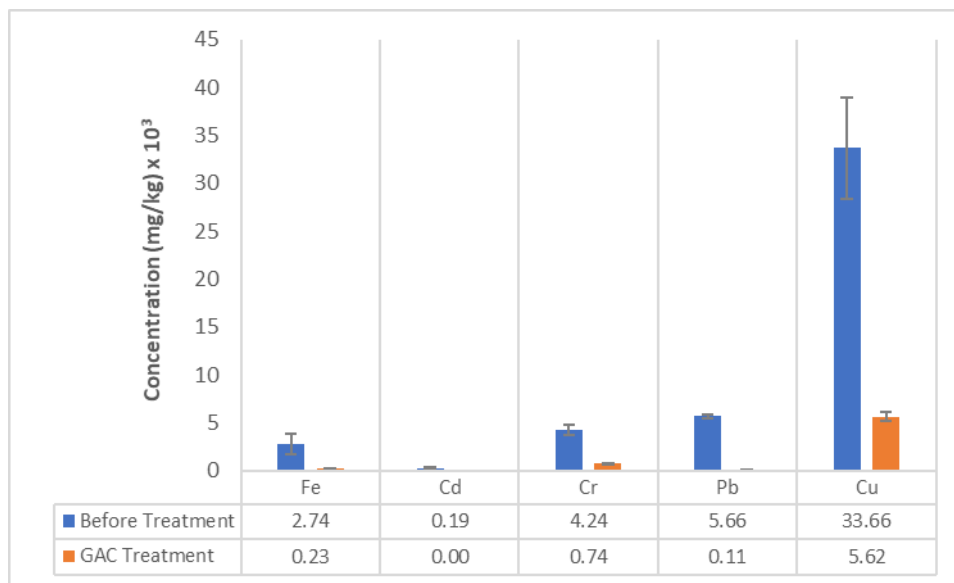


Fig. 9 Mean metal concentrations of plot 1 samples treated with GAC

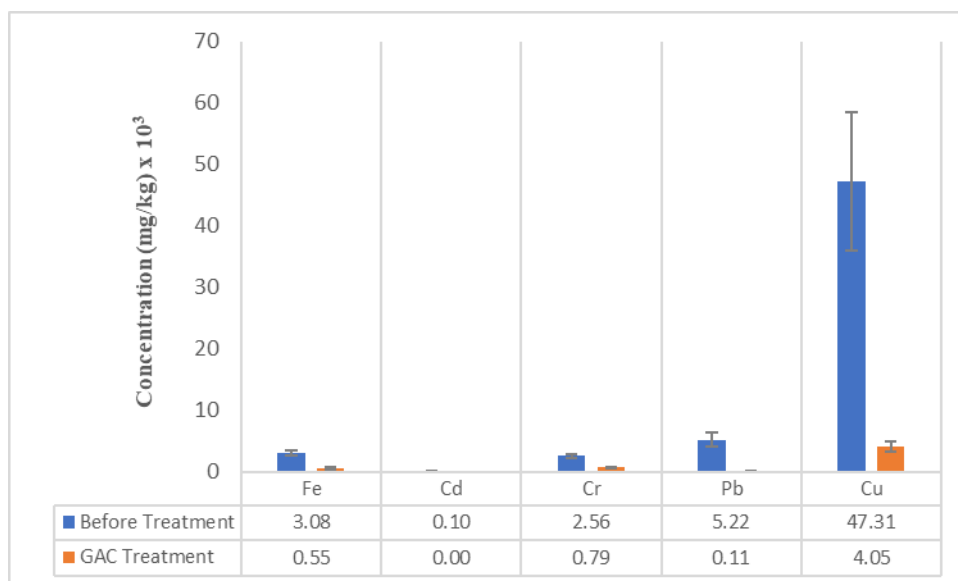


Fig. 10 Mean metal concentrations of plot 2 samples treated with GAC

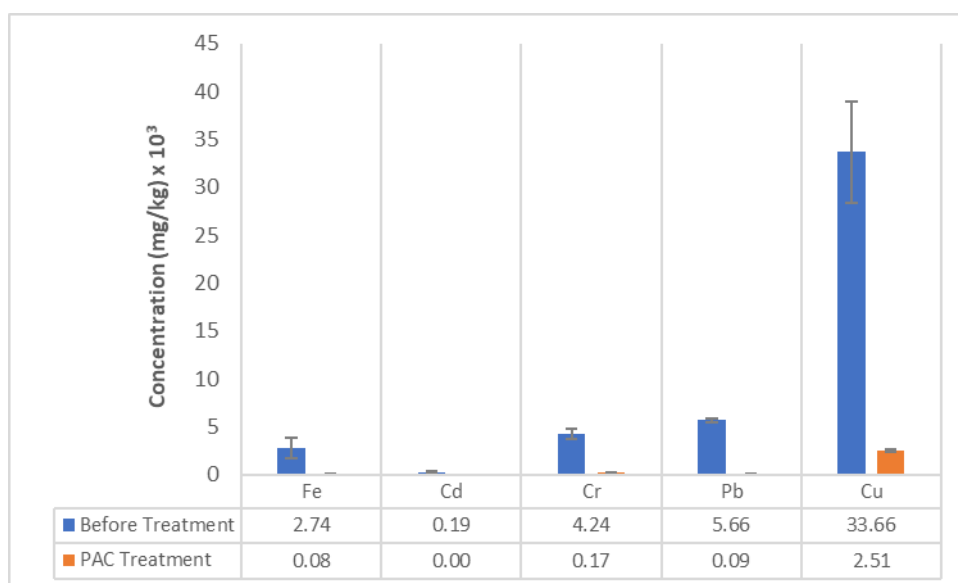


Fig. 11 Mean metal concentrations of Plot 1 samples treated with PAC

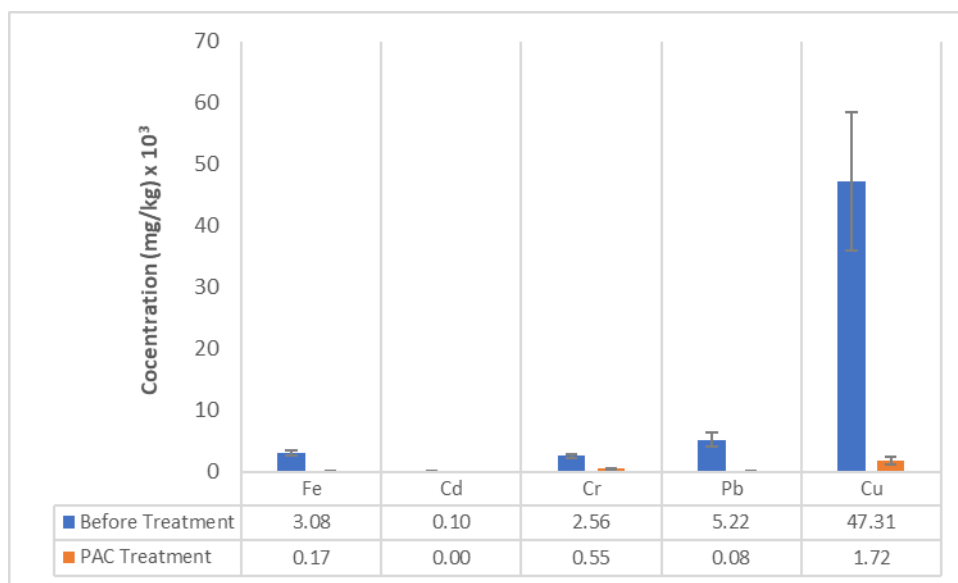


Fig. 12 Metal concentrations of Plot 2 samples treated with powdered AC

Table 4 Mean adsorption rates for the metals

| Carbon type | Adsorption rate (%) | | | | |
|----------------------|---------------------|--------|-------|-------|-------|
| | Fe | Cd | Cr | Pb | Cu |
| Granular AC (Plot 1) | 91.44 | 100.00 | 82.47 | 87.98 | 83.29 |
| Granular AC (Plot 2) | 82.11 | 100.00 | 69.22 | 97.89 | 91.45 |
| Overall rate (GAC) | 86.78 | 100.00 | 75.85 | 92.94 | 87.37 |
| Powdered AC (Plot 1) | 96.93 | 100.00 | 96.00 | 98.43 | 92.55 |
| Powdered AC (Plot 2) | 94.47 | 100.00 | 78.38 | 98.46 | 96.37 |
| Overall rate (PAC) | 95.70 | 100.00 | 87.19 | 98.45 | 94.46 |

3.3. Effects of particle size and iodine number on adsorption rates

Iodine Number is used in reference to the mass of iodine adsorbed (in milligrams) per gram of carbon at a residual iodine level of 0.02 N. It is a relative measure of the porosity, a helpful approximation of surface area for different types of AC and the fundamental parameter for determining the performance of AC [20]. Mao et al. [25] reported that the typical iodine number of high-grade AC is usually greater than 1000 mg/g. In this study, the GAC's iodine number was 730.25 mg/g while that of the powdered AC was 742.95 mg/g, indicating that the

AC was of a good quality. The iodine number of the GAC (composed of larger particles) was approximately 1.71% lower than that of PAC (composed of smaller particles). Although higher iodine numbers are indicative of higher degrees of activation, the connection between iodine number and surface area cannot be established. It differs with changes in raw material generating the carbon, processing conditions, and also pore volume distribution. Thus, there was a clear trend linking particle size and iodine number to the adsorption efficiency of both granular raw carbon and granular AC.

The PAC showed higher percentages of adsorption of all the metals (Fe, Cr, Pb, Ni, and Cu) compared to the granular form. The conversion of the carbon into the powdered form (smaller particle sizes) through grinding thus may have resulted in greater adsorption capacity through improvements in iodine number. The iodine numbers of the activated carbon increased by 2.7% from 730.25 to 742.95 mg/g after conversion from granular to powdered activated carbons. Similarly, the electrical conductivity improved slightly by 0.93% for the activated carbon being converted into powdered form. The increase in iodine numbers in the powdered carbons is as a result of improved activation reactions as smaller particles result in greater penetration by potassium hydroxide (KOH) for increased activation reactions [25]. However, the improvements in the iodine numbers did not translate into significant variations in the adsorption capacities between the granular and powdered activated carbons in this study.

3.4. Adsorption effects of the cashew nut shell-based activated carbon

All the two AC types; GAC and PAC, showed adsorption effects on the heavy metals in the soil samples tested. The GAC and PAC were efficient in adsorbing the heavy metals from the contaminated soil samples. In all the cases, Cd was below detection limit after treatment. The combined adsorption rates/adsorption efficiencies of the heavy metal ions by the respective

ACs for all the treatments were in the order Cd > Pb > Fe > Cu > Cr. In analyzing the effects of the treatments in the adsorption of the heavy metals, the randomized completely block design (RCBD) using Analysis of Variance was adopted. The design eliminates any known source of external factors or variations that could influence the treatments. Both blocking and treatments had significant effects on the adsorption of the heavy metals (Table 5). The analyses further indicated that the treatment had a statistically significant detoxification effect at 95% confidence interval ($p \leq 0.05$) on the heavy metals in the E-waste sample. The treatment is thus responsible for the overall mean adsorption rate of 93% of the heavy metals from the E-waste sample. The Randomized Completely Block Design (RCBD) using analysis of variance was used to test the efficiency of the different ACs. The LSD showed that no significant difference existed in the adsorption capacities of the powdered and granular activated carbons though the powdered carbon had a slightly better performance in removing the heavy metals from the soil.

Table 5 Blocking and treatment effects

| Tests of Between-Subjects Effects | | | | | |
|-----------------------------------|-------------------------|----|-------------|--------|------|
| Source | Type III Sum of Squares | df | Mean Square | F | Sig. |
| Corrected Model | 18.533 ^a | 5 | 3.707 | 5.349 | .000 |
| Intercept | 67.500 | 1 | 67.500 | 97.403 | .000 |
| Treatment | 18.533 | 4 | 4.633 | 6.686 | .001 |
| Block | 24.933 | 1 | 24.933 | 6.686 | .005 |
| Error | 3.467 | 5 | .693 | | |
| Total | 46.933 | 10 | | | |
| Corrected Total | 53.456 | 11 | | | |

a. R Squared = 0.959 (Adjusted R Squared = 0.932)

4. Conclusions

The study focused on the potential use of cashew nut shell-based AC for remediation of soils from E-waste polluted site from Agbogbloshie in Accra, Ghana. The AC was produced using physical activation techniques and characterized based on bulk density, particle size, iodine number, EC, porosity, and pH. Results from the application of the AC to the polluted soil sample from Agbogbloshie indicates that the AC has significant detoxification effect on heavy metals (lead, iron, copper, chromium and cadmium) in the soil collected from the E-waste polluted area. At 95% confidence interval ($p \leq 0.05$), the AC is responsible for the overall elimination of 93% of the heavy metals.

Specifically, the GAC significantly removed the heavy metal contents of the E-waste polluted soil with percent removal efficiency in the order: Cd (100%) > Pb (93%) > Fe (87%) > Cu (87%) > Cr (76%) whereas the PAC had in this order: Cd (100%) > Pb (98%) > Fe (96%) > Cu (94%) > Cr (87%). Their adsorption isotherms depict that PAC and GAC are good adsorbents and have the potential to be used for other polluted environmental settings.

Availability of data and materials

All data generated or analyzed during this study are kept by the corresponding author and will be provided upon request.

Competing interests

The authors declare they have no competing interests.

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Authors' contributions

The first author conceived, designed the experiment, directed and supplied the activated carbon for the study. The second author performed the field and laboratory studies. All authors assisted in data analysis, interpretation and contributed to the writeup. All authors reviewed and approved the final manuscript.

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Figures

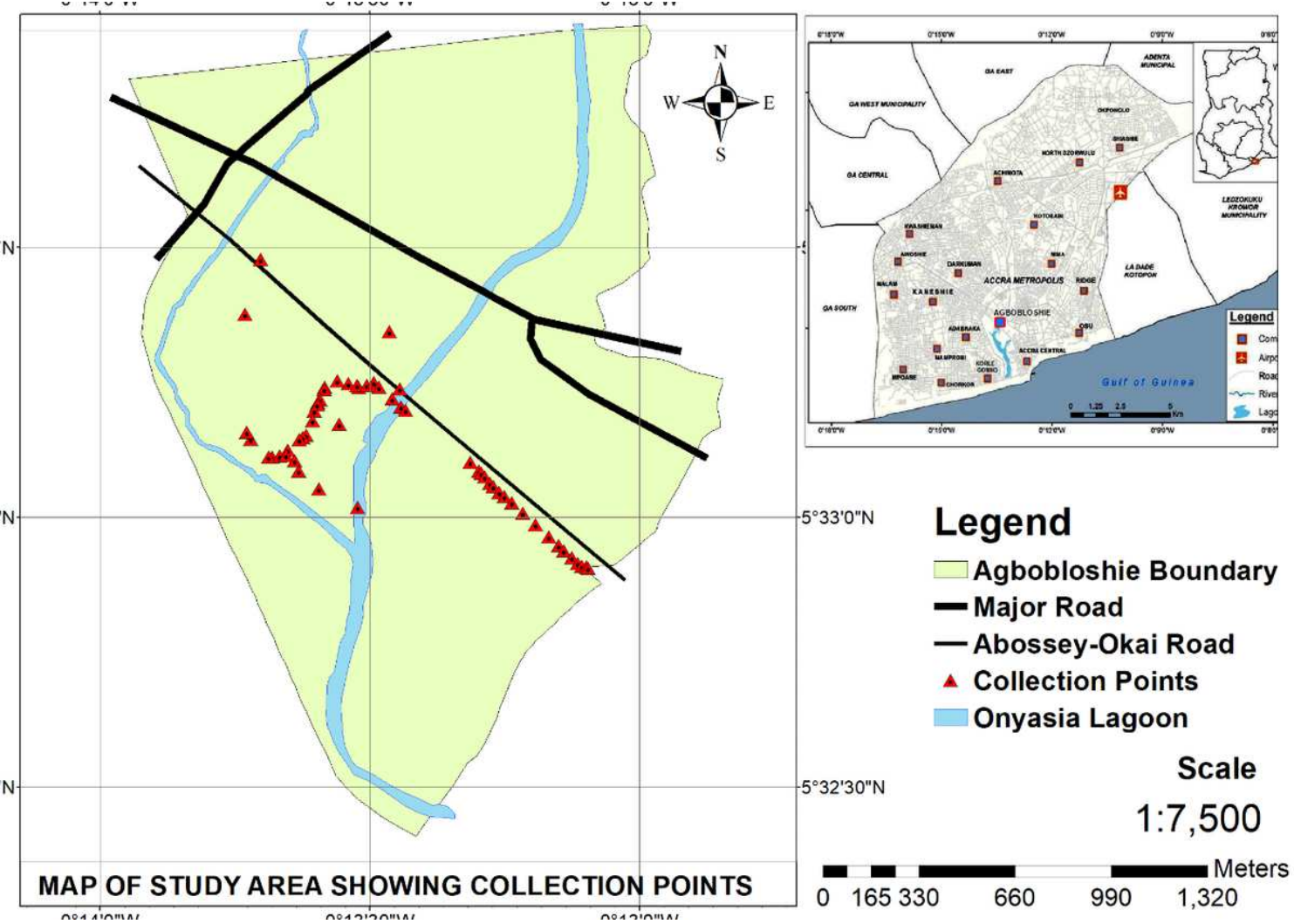


Figure 1

Map of the study area showing sampling sites

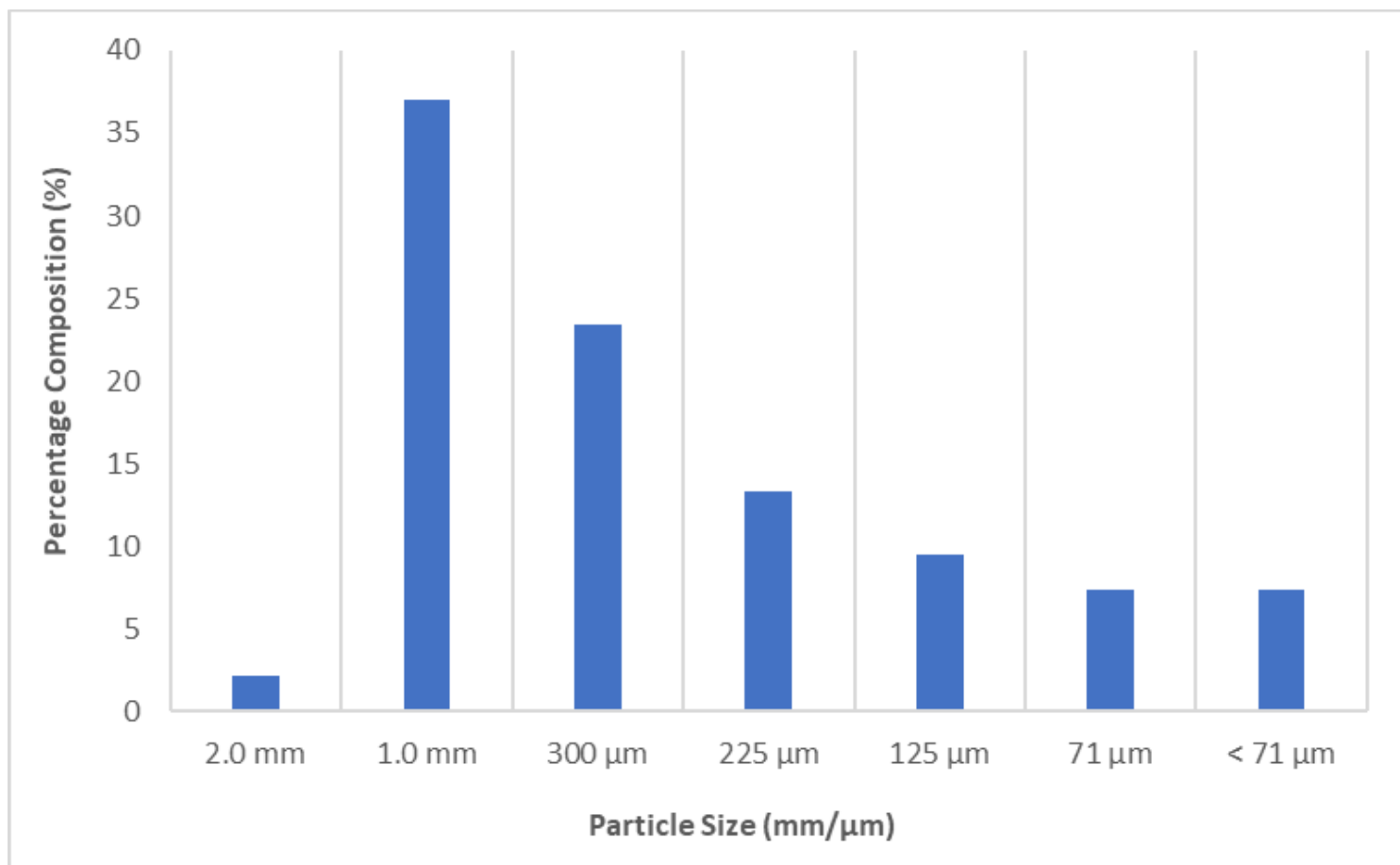


Figure 2

Size composition of the activated carbon

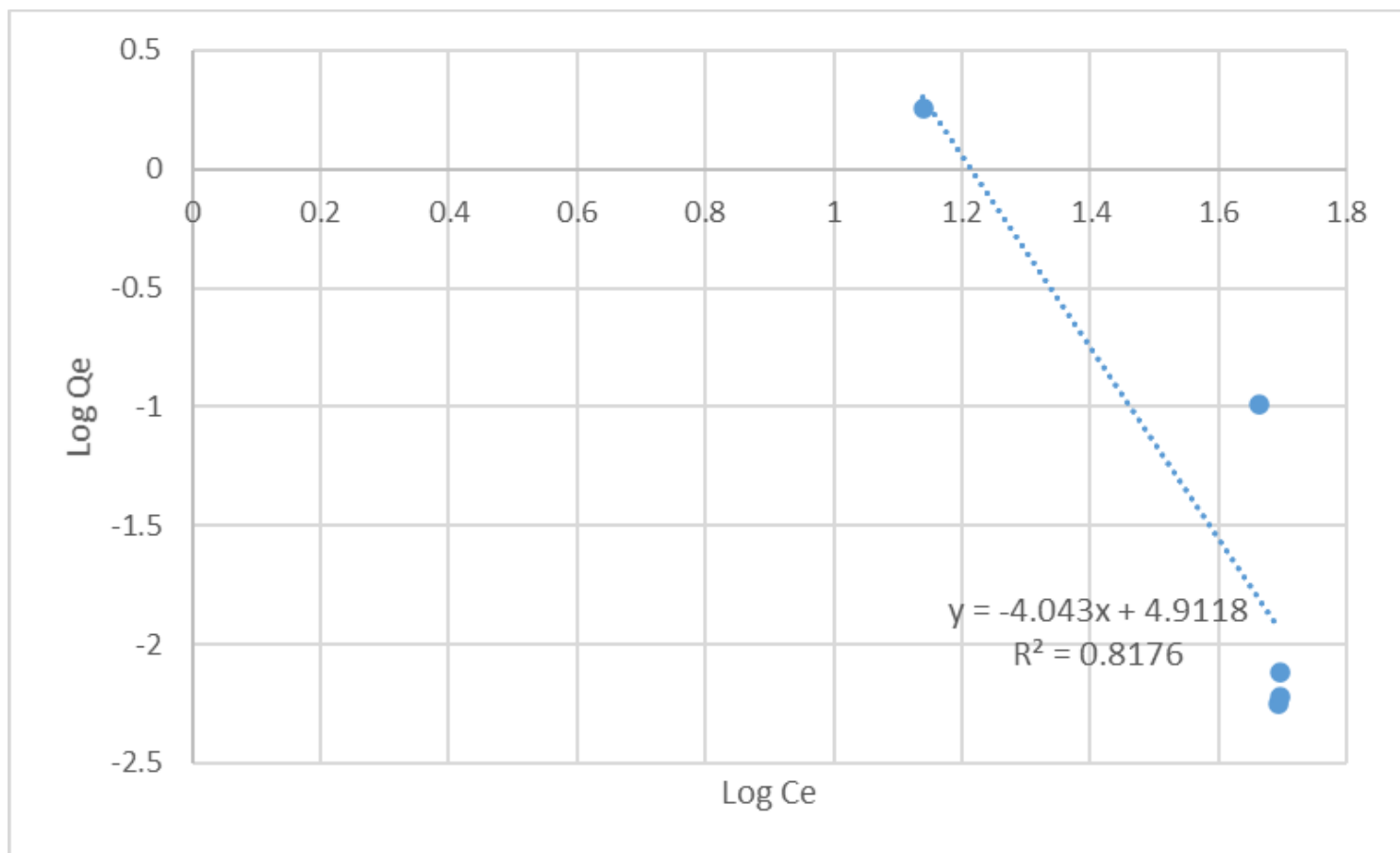


Figure 3

Adsorption isotherm for copper

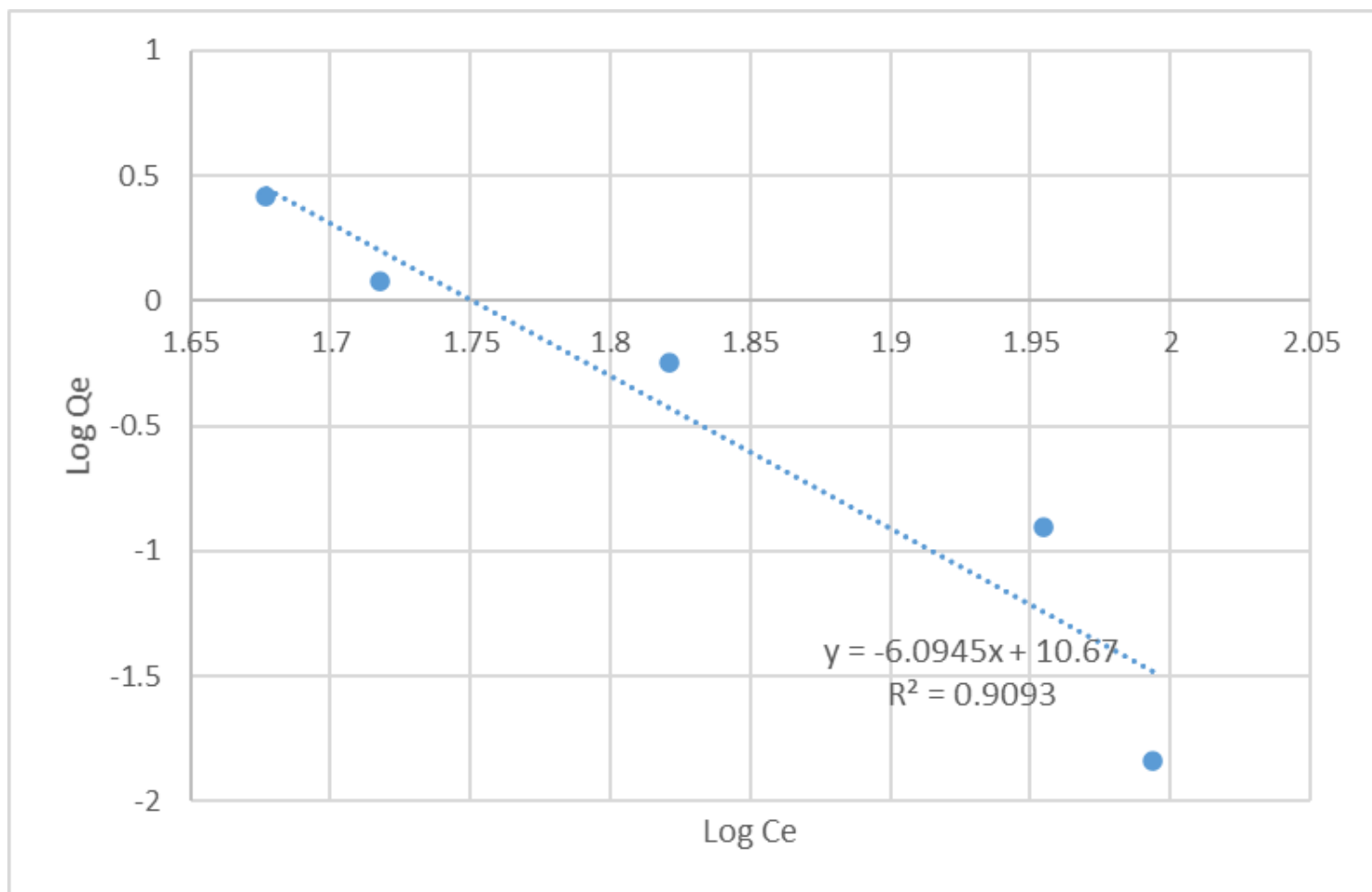


Figure 4

Adsorption isotherm for iron

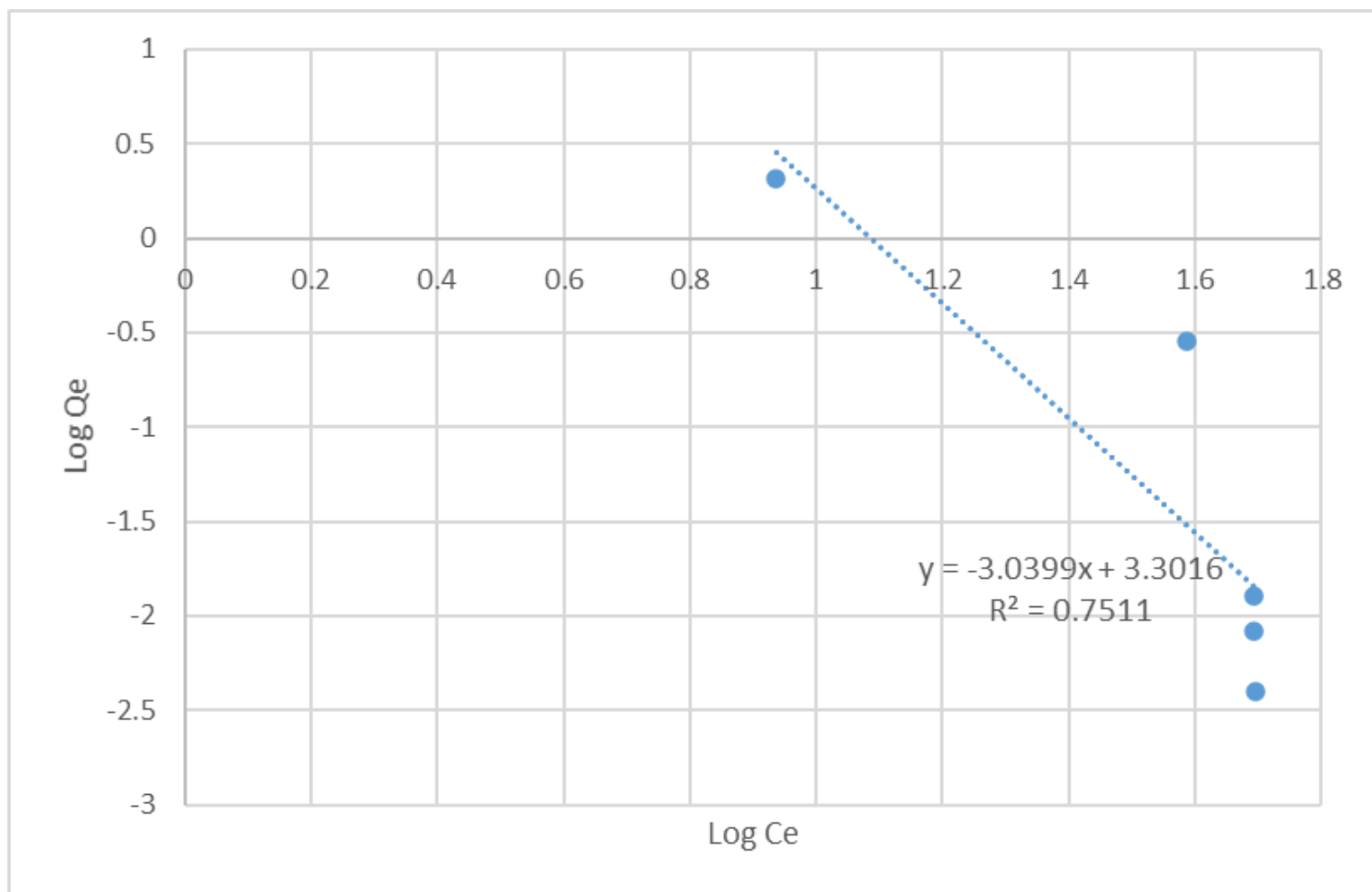


Figure 5

Adsorption isotherm for cadmium

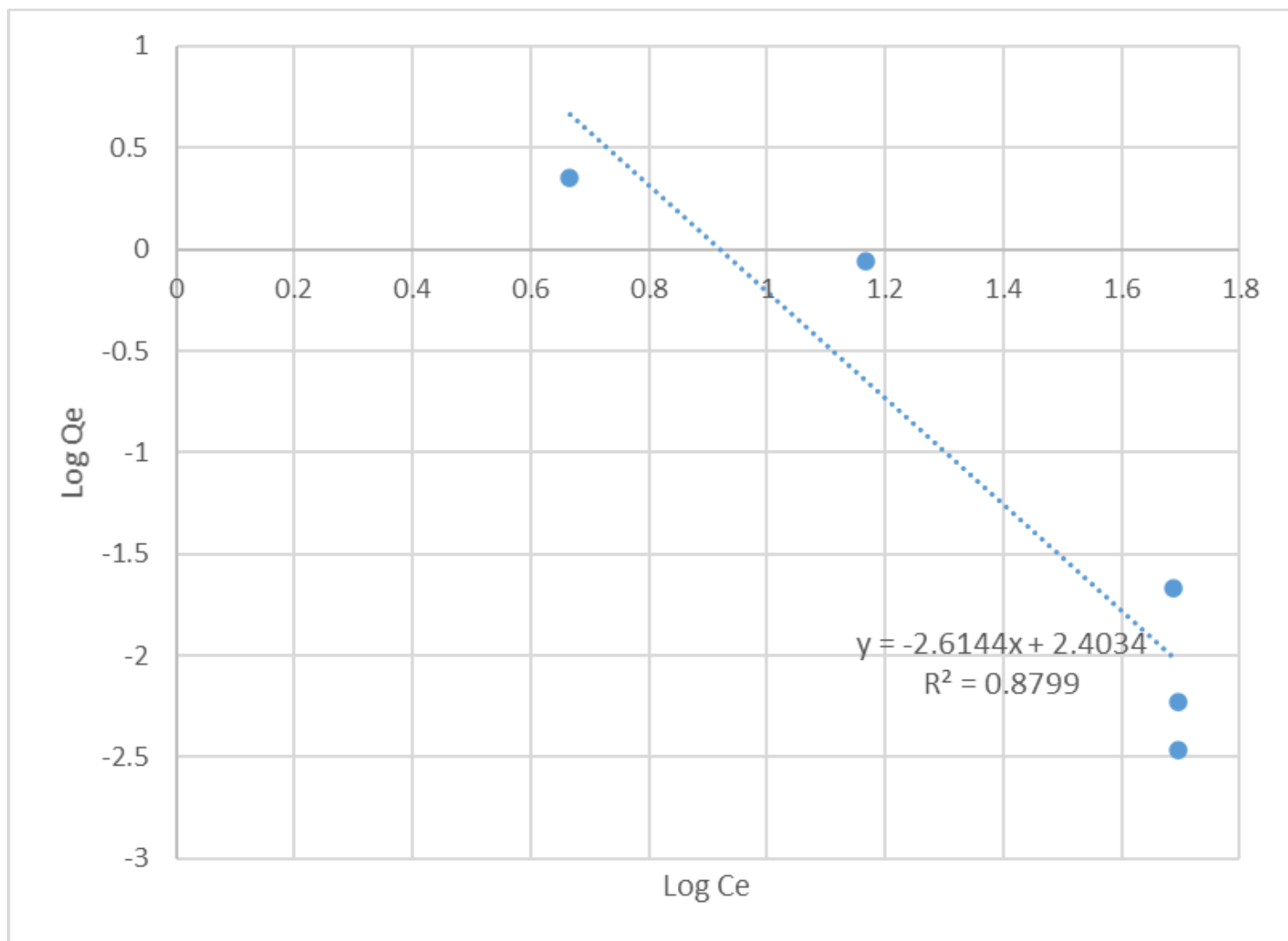


Figure 6

Adsorption isotherm for chromium

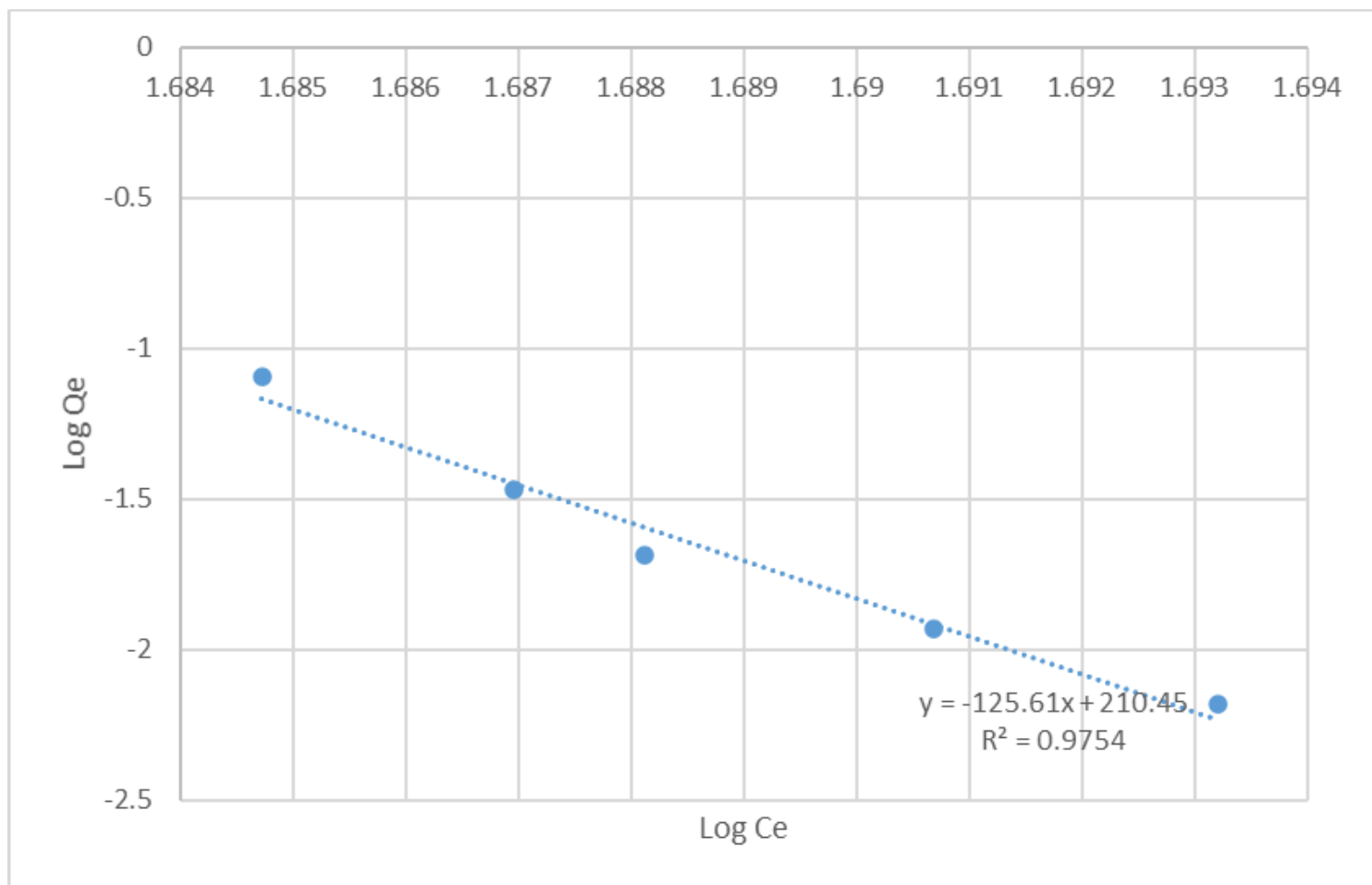


Figure 7

Adsorption isotherm for lead

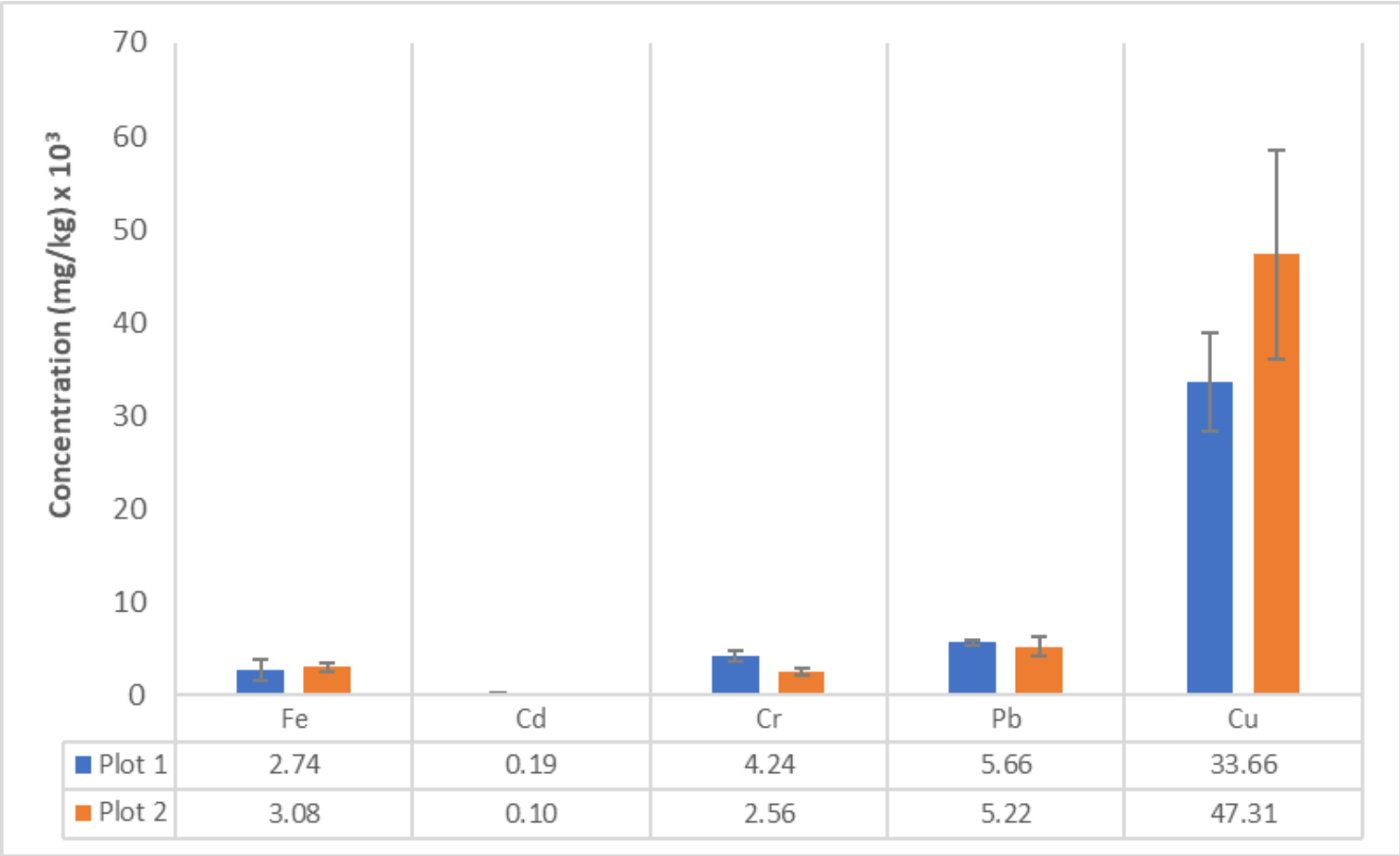


Figure 8

Mean concentrations of metals before treatment

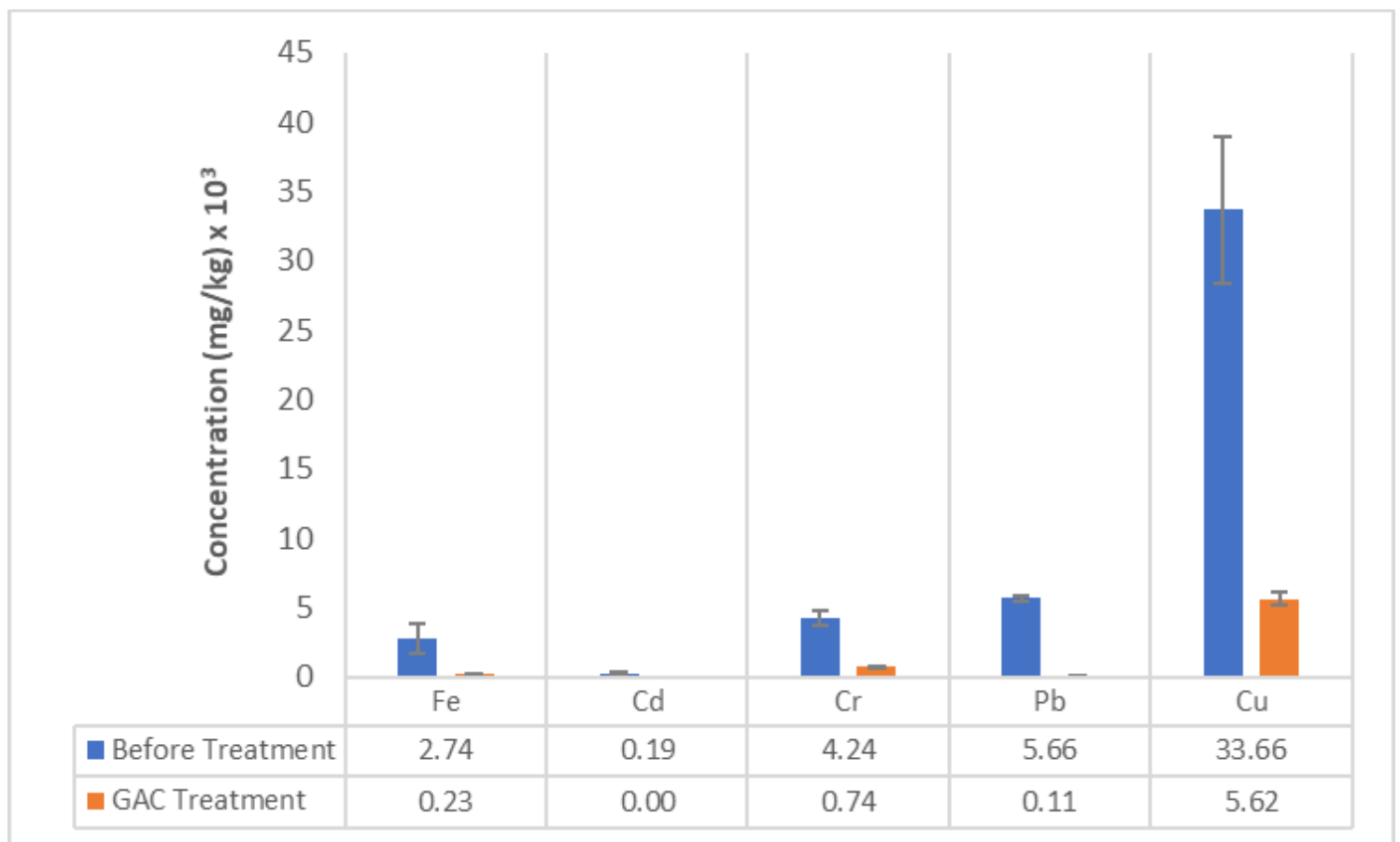


Figure 9

Mean metal concentrations of plot 1 samples treated with GAC

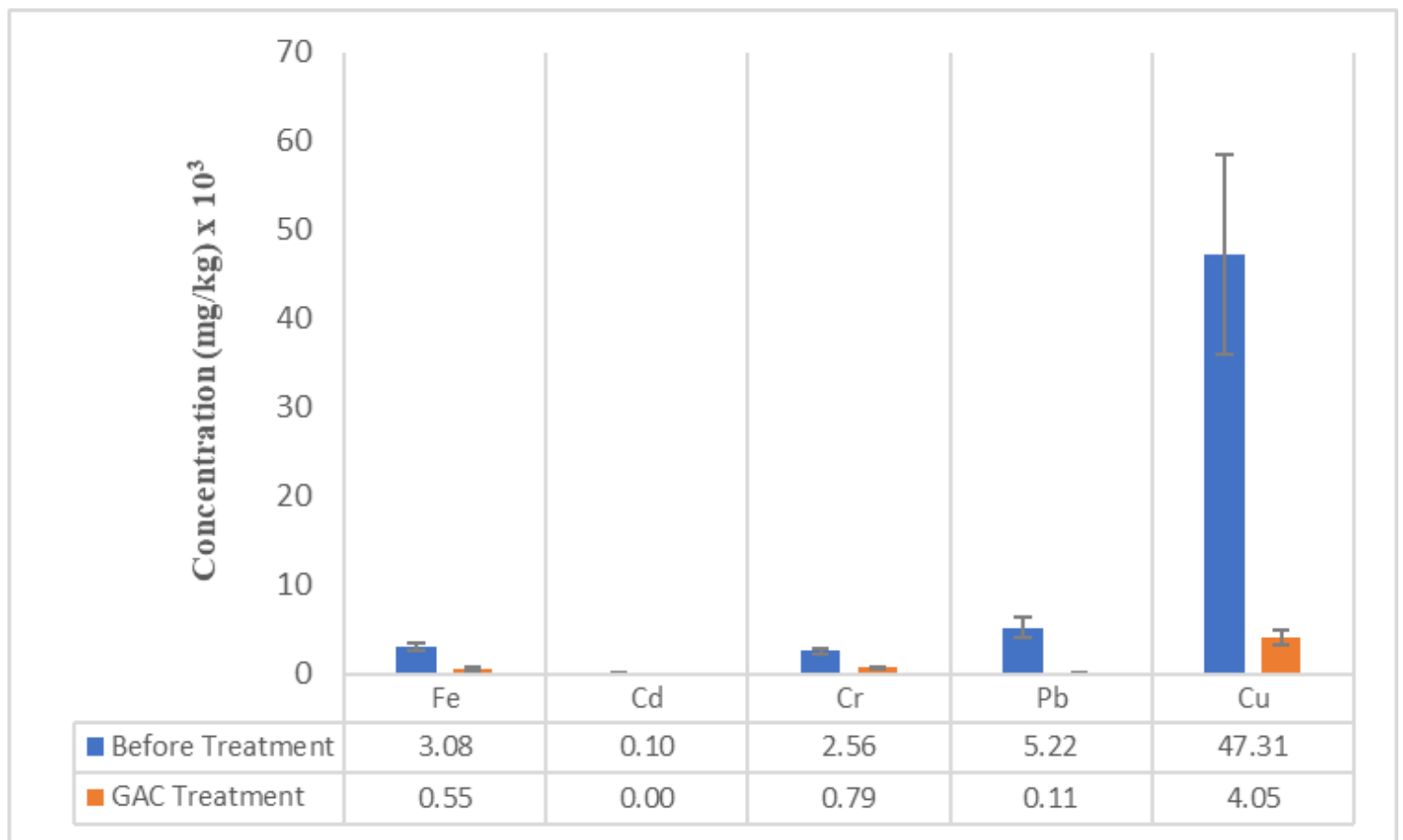


Figure 10

Mean metal concentrations of plot 2 samples treated with GAC

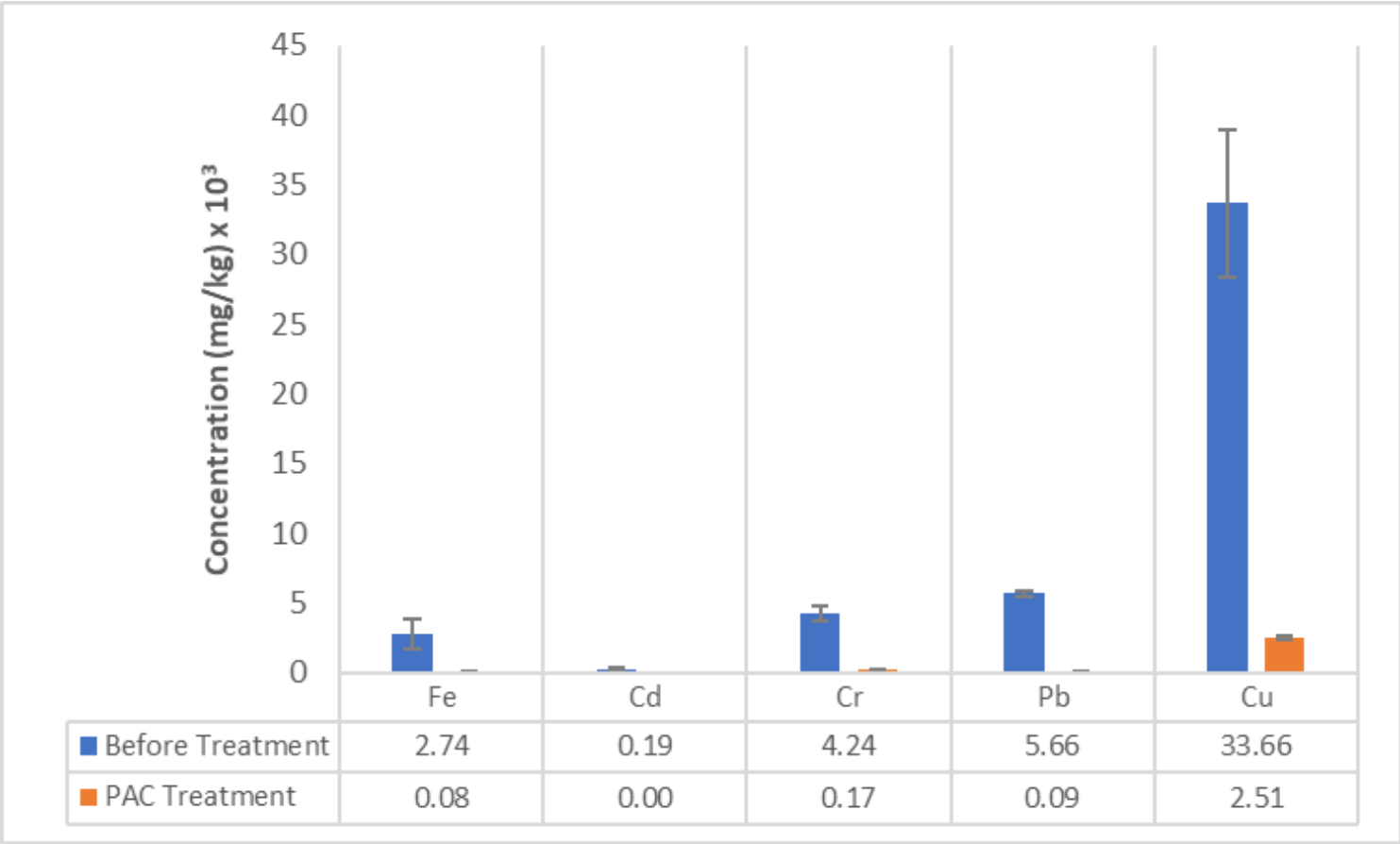


Figure 11

Mean metal concentrations of Plot 1 samples treated with PAC

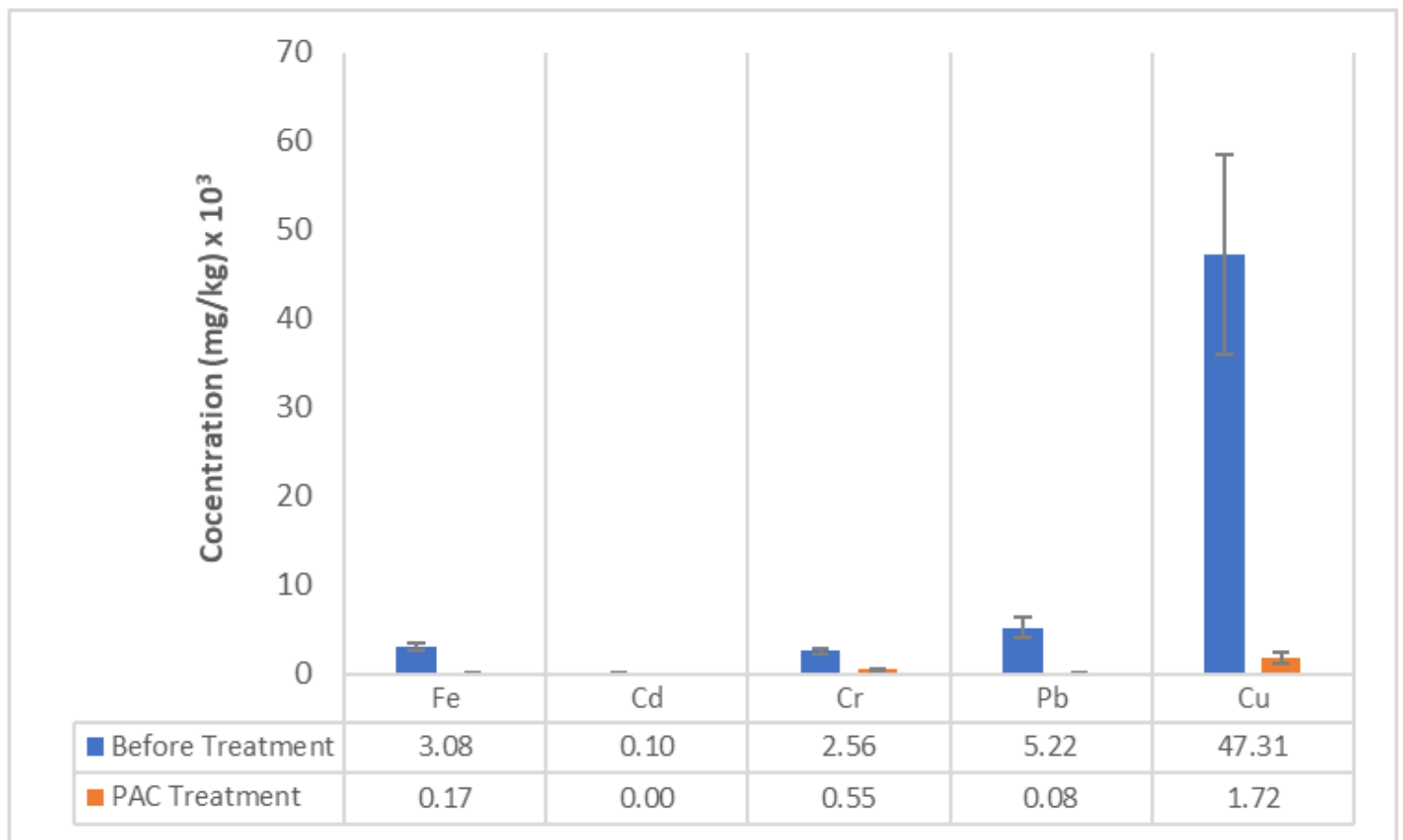


Figure 12

Metal concentrations of Plot 2 samples treated with powdered AC