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FOURIER TRANSFORM INFRARED SPECTROPHOTOMETRIC ANALYSIS OF FUNCTIONAL GROUPS FOUND IN *RICINUS COMMUNIS* L. AND *CUCURBITA MAXIMA* LAM. ROOTS, STEMS AND LEAVES AS HEAVY METAL ADSORBENTS

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Abstract: As industrialization continues to be the major economic activity in the country, levels of heavy metals in the environment continue to increase. Most of the strategies that have been used to remove heavy metals from the environment are either costly or ineffective. *Cucurbita maxima* Lam. and *ricinus communis* L. have been identified as cost effective adsorbents and their use in adsorption of copper, cadmium and lead ions was investigated. Study was done to identify the active functional groups in the adsorption process. The response of the functional groups is characterized by observing the absorption of infrared radiation (IR) within the mid –IR region (650-4000cm^{-1}). The presence and nature of the functional groups among other factors provide information on the ability of metals to bind on the plant biomass. Roots, stems and leaves of the plants were used. Characterization of the functional groups was done through interpretation of Fourier Transform Infrared (Fourier transform IR) spectra for metal loaded and unloaded samples of plant biomass. The work reported in this paper was designed to evaluate and establish the efficiency of organic functional groups in *ricinus communis* L. and *Cucurbita maxima* Lam. as adsorbents of copper, lead and cadmium ions. The results showed that on loading the biomass with metal ions (Cu, Pb and Cd), specific bands in the spectra shifted to either higher or lower frequencies. This shows that the metal ions bound to the active sites of the biosorbents either through electrostatic attraction or complexation mechanisms. The functional groups found present include O-H, -C=C- C≡N- C-O C-H and C=O among others. According to Karunakaran and Thamilarasu (2010), activated carbon prepared from *ricinus communis* Lam. seed shell for the removal of Fe(III) adsorption showed that it fitted best in Freundlich isotherm at 313 K (temp) with an r^2 value of 0.9945 as compared with Langmuir isotherm, r^2=0.9846. It also showed that the % removal of Fe (III) at 10 ppm and 30^0C was 93.48% as compared with 50ppm at 30^0C which was 79.19%. Mean concentrations (µg g^{-1} dry weight) in washed and unwashed *cucurbita maxima* Lam. were compared, Yusuf and Oluwole (2009). The mean concentrations for Cu, Zn and Pb were found to be 17.38±1.30, 33.28±2.76 and 2.76±0.07 for unwashed samples and11.04±0.83, 22.23±1.42 and 2.56±0.2 for washed samples in the urban area. For remote area, the unwashed samples mean concentrations for Cu, Zn and Pb were 3.76±1.23, 22.10±3.60 and 1.57±0.62 and 3.71±0.45, 21.80±3.60 and 1.57±0.60 for the washed samples respectively. These results show that these plants are good heavy metal adsorbents.

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Keywords: Fourier transform infrared spectroscopy; *cucurbita maxima* Lam; *ricinus communis* L.

INTRODUCTION

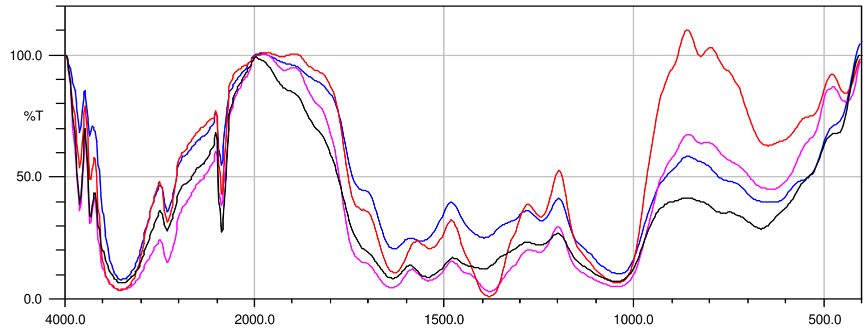
Heavy metals are among the toxic substances which are found in water. They are non-biodegradable and therefore persist in the environment thus become threat to human life and the environment at large (Harder *et al*., 2014, Horsfall *et al*., 2006). The traditional methods of removing heavy metals from the environment are generally expensive and inefficient especially when the concentration of the ions in the solution is very low (Rani *et al*., 2010, Igwe and Abia, 2006). It has been established that use of plant biomass is an emerging and renewable way of removing heavy metals from waste waters (Davis *et al*., 2003, Gupta and Rastogi, 2009). Heavy metals may be removed from the waste waters by binding on the functional groups that are found in the biomass (Jalali *et al*., 2002, Barakat and Kumar, 2014). This method is cheap and forms biodegradable products. Electrostatic attraction between cationic metals and negatively charged surface sites such as phosphate, carboxyl, amino and hydroxyl groups could be the reason for heavy metal adsorption (Mata *et al*., 2008, Das *et al*., 2008). *Cucurbita maxima* Lam. and *ricinus communis* L. were used in removing copper, lead and cadmium ions from their aqueous solution and the data on how they interacted with the functional groups was shown on Fourier transform infrared spectroscopy(FTIR) spectra. FTIR is an advanced rapid and non-destructive technique frequently used to characterize the functional groups responsible for heavy metals adsorption (Csematoni *et al*., 2013, Sahira and Bhadra, 2012).It offers an excellent potential in providing quantitative and qualitative data. It has been used to investigate biochemical changes in plants as well as obtain quantitative information about the functional groups of chemical compounds (Saymanska-Chargot *et al*., 2013). Fourier transform infrared allows the whole IR spectra range to be obtained simultaneously providing rapid and accurate measurements of the samples used (Csematoni *et al*., 2013, Subramanian *et al*., 2015). The present paper reports copper, lead and cadmium metal ions interaction with the functional groups found in *ricinus communis* L. and *Cucurbita maxima* Lam. roots, stems and leaves using FTIR. The spectra for biomass that is unloaded and that which is loaded with heavy metal were compared in order to establish the functional groups that are involved when the metal ions in the waste waters are binded to the plant biomass. The specific bonds in the functional groups that were found to shift include O-H, C-H, C=C, C=O and C-O.

MATERIALS AND METHODS

Fresh roots, stems and leaves of *ricinus communis* L. and *cucurbita maxima* Lam. were sampled from Kadudu sewage plant in Murang'a County, Kenya. They were transported to the laboratory where they were washed with tap water several times and rinsed with distilled water. They were then sun dried in the open for twenty four hours and in the oven for eight hours at 80^0C. The dry samples were ground and sieved to< 1 mm particle size and stored in plastic sealable bags. Six beakers each containing 50mls of 0.25M lead nitrate solution were prepared and 0.2gm of the dry ground samples of roots, stems and leaves of *cucurbita maxima* Lam. and *ricinus communis* L. were added separately to each beaker. The mixtures were left for two hours to allow maximum adsorption. They were filtered and the residue was dried. The KBr pellets were prepared by mixing 1mg of finely ground and dried samples with 250 mg KBr (FT-IR grade) pressed and mounted for acquisition of IR spectrum. Characterization was carried out using FTIR (8400 shimadzu model), scanning range was 4000 to 400cm^{-1} resolution of 4cm^{-1} and 20 spectra were obtained and apodization done using the shimadzu equipment manufacturer software. This was done for both loaded and unloaded biomass for comparison to identify the functional groups that were involved in the adsorption of metal ions. This procedure was repeated with copper nitrate and cadmium nitrate solutions. The shifts in the respective IR spectra bands were observed and reported. These shifts indicated that the metal ions interacted with respective functional groups present in the biomass.

RESULTS

The functional groups responsible for adsorption of cadmium, copper and lead metal ions on *Cucurbita maxima* Lam. and *Ricinus Communis* L. roots, leaves and stems were investigated by FTIR analysis. Since adsorption is done using non-living biomass, it takes place extracellularly. There are several chemical groups that would sequester the metals in biomass. These include structural polysaccharides of fungi, hydroxyl, carboxyl and sulphates in polysaccharides, amino and phosphate groups in nucleic acids, CH_3 group, ketones and alkaniods (Ahalya *et al.,* 2003). The FTIR spectra for free and loaded biomass samples are shown in figures 1-6 below. The metals that were used in the adsorption process are represented with the following colours. Cadmium (red), copper (pink), lead (blue) and green for unloaded for all the spectra.



1/cm

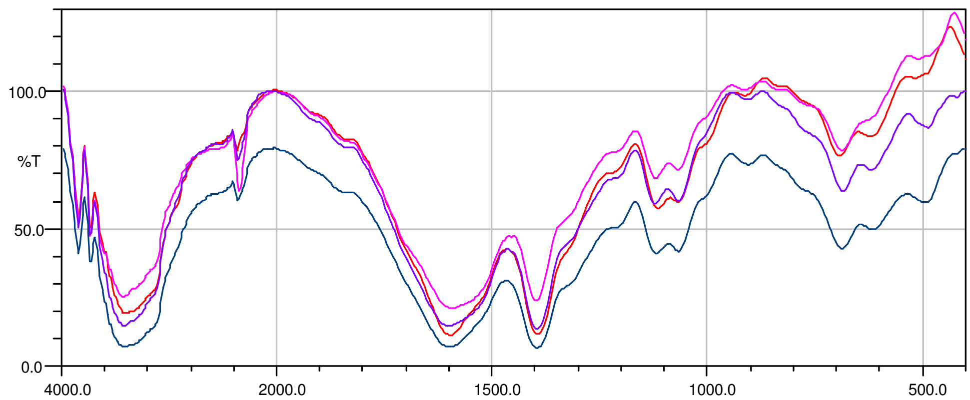
Fig 1: FTIR spectra for *Cucurbita maxima* Lam. Stem (CS).

Superimposed spectra of *cucurbita maxima* Lam. stem (CS) before and after loading with copper, lead and cadmium ions.

Table 1: FT-IR analysis of functional groups for *Cucurbita maxima* Lam. Stem

Peak position for *Cucurbita maxima* Lam. stem before loading cm^{-1}	Peak position after loading cm^{-1}			Possible functional groups
	Cu	Pb	Cd	
3421.5	3421.5	3444.6	3425.3	O-H $_{str}$,
2927.7	2923.9	2927.7	2923.9	C-H $_{str}$
1639.4	1639.4	1639.4	1635.9	C=C $_{str}$, ,C=O $_{str}$
1542.9	1542.9	1542.9	1542.9	N-O $_{str}$
1396.4	1380	1380.9	1384.8	C-C$_{str}$,
1253.6	1253.6	absent	1249.8	C-N $_{str}$
1049.2	1045.3	1041.5	1045.3	C-O$_{str}$

After adsorption of copper, lead and cadmium ions, slight changes were observed in some peaks frequencies while others did not change at all. For instance, the peak at 3421.5 cm^{-1} attributed to hydroxyl group shifts slightly to 3446.6 cm^{-1} with lead and to 3425.3 $cm^{-1}$with cadmium.



1/cm

Fig 2: FTIR spectra for *cucurbita maxima* Lam. leaves (CL).

Superimposed curves of *Cucurbita maxima* Lam. leaves (CL) before and after loading with copper, lead and cadmium ions.

Table 2: FT-IR analysis of functional groups for *Cucurbita maxima* Lam. leaves

Peak position for *Cucurbita maxima* Lam. leaves before loading cm^{-1}	Peak position after loading cm^{-1}			Possible functional groups
	Cu	Pb	Cd	
3436.9	3433.1	absent	3336.6	$O\text{-}H_{str}$
1593.1	1604.7	1596.9	1600.8	$C{=}C_{str}$
1400.2	1398.4	1396.4	1396.4	$C\text{-}C_{str}$
1122.5	1122.5	1118.6	1122.5	$C\text{-}N_{str}$, C-C
1068.5	1068.5	1068.5	1068.5	$C\text{-}O_{str}$,

The curves show presence of several functional groups. These include O-H at 3436.9cm^{-1}, C=C at 1593.1

cm^{-1}, C-N at 1122.5cm^{-1}, C-C1068.5cm^{-1} and C-O at 1068.5cm^{-1}.

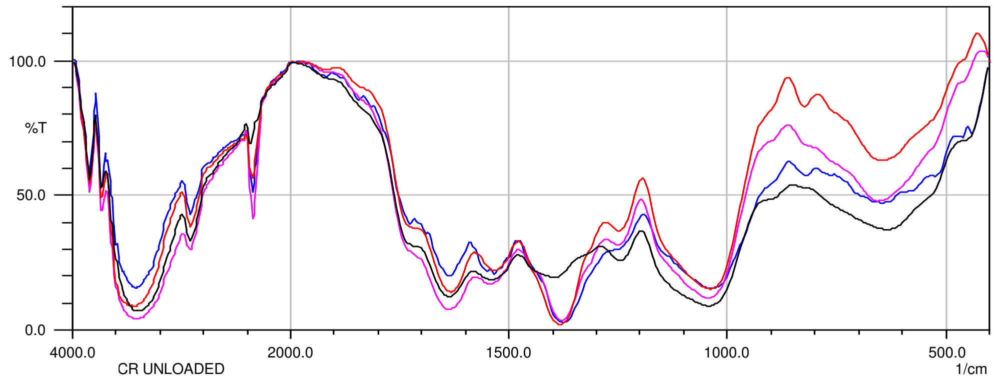


Fig 3: FTIR spectra for *Cucurbita maxima* Lam. roots (CR).

Superimposed spectra for *Cucurbita maxima* Lam. roots before and after loaded with copper, lead and cadmium ions.

Table 3: FTIR analysis of *Cucurbita maxima* Lam roots.

Peak position for *Cucurbita maxima* Lam. roots before loading cm^{-1}	Peak position after loading cm^{-1}			Possible functional groups
	Cu	Pb	Cd	
3421.5	3436.9	3436.4	3444.6	O-H $_{str}$
2927.7	2927.7	2923.9	2927.7	C-H $_{str}$ CH_3
1639.4	1639.4	1639.4	1635.5	$C{=}C_{str}$, $C{=}O_{str}$
1542.9	absent	1535.2	1535.2	$N\text{-}O_{str}$
1396.4	1384.8	1377.1	1384.8	$C\text{-}C_{bend}$
1249.8	1249.8	1249.8	1249.8	$C\text{-}N_{str}$
1045.3	1045.3	1041.5	1041.5	$C\text{-}O_{str}$

From the result, there were some shifts that were noted. There was shift from 3421.5cm^{-1} to 3436.4,34446 and 3436.4 cm^{-1}on loading copper, cadmium and lead ions respectively.

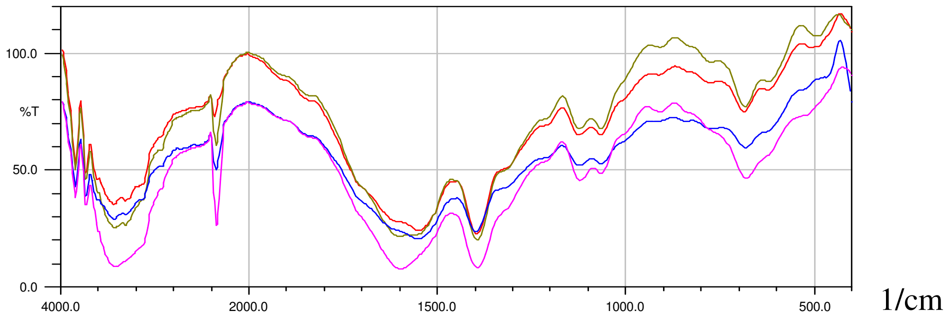


Fig 4: FTIR spectra for *ricinus communis* L. leaves (RL).

Superimposed spectra for *ricinus communis* L. leaves before loading and after loaded with copper, lead and cadmium ions.

Table 4: FTIR analysis of *ricinus communis* L. leaves

Peak position for *ricinus communis* L. leaves before loading cm^{-1}	Peak position after loading cm^{-1}			Possible functional groups
	Cu	Pb	Cd	
3444.6	3444.8	3433.1	3436.9	O-H$_{str}$
2657.7	2684.7	2553.0	2592.2	C≡Cstr, C≡N$_{str}$
1558.4	1542.9	1600.8	1558.4	N-Ostr
1400.2	1396.4	1398.4	1396.4	C-Cstr
1068.5	1068.5	1068.5	1068.5	C-O$_{str}$

The groups that are present in the biomass include O-H, C=C, N-H, C-H and C-O all of which are in stretch mode. On loading, some of the peak frequencies were noted to shift while others did not show any significant changes.

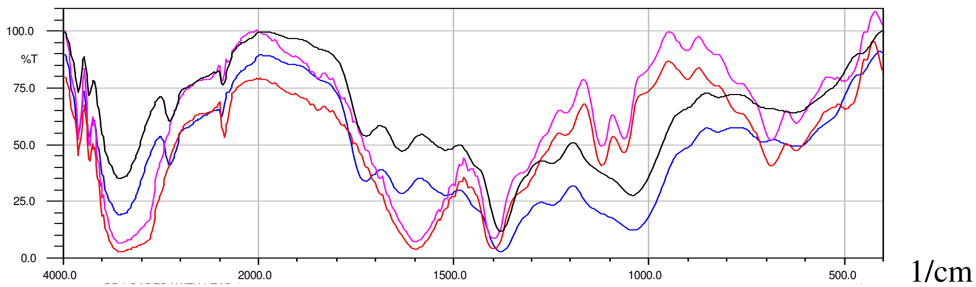


Fig 5: FTIR spectra for *ricinus communis* L. roots (RR)

Superimposed spectra for *ricinus communis* L. roots before and after loaded with copper, lead and cadmium ions

Table 5: FTIR analysis of *ricinus communis* L. roots.

Peak position for *ricinus communis* L. roots before loading cm^{-1}	Peak position after loading cm^{-1}			Possible functional groups
	Cu	Pb	Cd	
3417.6	3436.9	3433.1	3421.5	$O\text{-}H_{str}$
3325.0	3328.9	3325.0	3325.0	$N\text{-}H_{str}$
2538.1	2511.1	2522.7	2584.3	$C{\equiv}N_{str}$ $C{\equiv}C_{str}$
1593.1	1600.8	1593.1	1600.8	$N\text{-}H_{bend}$
1400.1	1400.2	1396.4	1392.5	$C\text{-}C_{str}$
1122.5	1122.5	1126.4	1122.5	$C\text{-}N_{str}$
1068.5	1064.6	1068.5	1064.6	$C\text{-}O_{str}$,

From the results above, the functional groups that are present include O-H, C=C, C-O CH_3 among others. The O-H group was seen to be predominantly present.

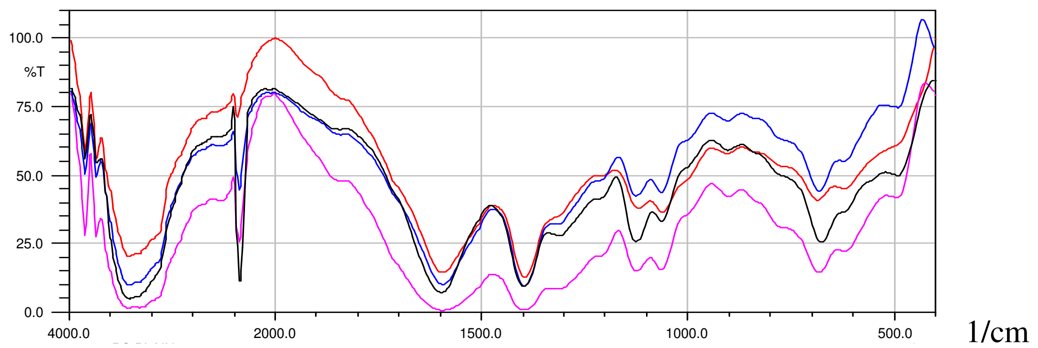


Fig 6: FTIR spectra for *ricinus communis* L. stem (RS)

Superimposed spectra for *ricinus communis* L. stems before and after loaded with copper, lead and cadmium ions.

Table 6: FTIR analysis of *ricinus communis* L. stem

Peak position for *ricinus communis* L. stem before loading cm^{-1}	Peak position after loading cm^{-1}			Possible functional groups
	Cu	Pb	Cd	
3392.8	3321.2	3326.0	3332.8	$O\text{-}H_{str}$
2538.1	2522.7	2518.9	2580.6	$C{\equiv}N_{str}$
1600.8	1598.5	1598.9	1596.9	$N\text{-}H_{str}$,
1400.2	1398.4	1396.4	1396.4	$\text{-}C\text{-}C_{str}$
1126.4	1126.4	1128.4	1122.5	$C\text{-}N_{str}$
1064.6	1068.5	1068.5	1064.6	$C\text{-}O_{str}$

The functional groups found in *ricinus communis* L. stem as shown in table 5 include O-H, C=C, -C-H, C-O. The peak frequencies also shifted, for example the O-H shifted from 3392.8 cm^{-1}to3326.0cm^{-1} on loading with copper and 3332.8cm^{-1} for both cadmium and lead.

DISCUSION

Results from FTIR analysis for *Cucurbita maxima* Lam. stems, leaves and roots as given in Tables 1, 2and 3 respectively show the presence of O-H, C-H, N-H and C-O ,C=O and C=C. All the bonds are in stretch mode. The spectra for the unloaded and the loaded samples were compared and they showed that there were shifts in most of the functional groups. In *Cucurbita maxima* Lam. stem, several shifts were noted. The band at 3421.5 cm^{-1} which is attributed to O-H shifted to 3444.6and 3425.3 cm^{-1} on loading with lead and cadmium ions respectively. Another band that was observed to shift was at 1396.4cm^{-1} which shifted to 1380.9cm^{-1} on loading with copper and lead ions. In the leaves, there was a shift from 3436.9cm^{-1} which is associated with O-H to 3433.1 and 3336.6cm-1 on loading copper and cadmium ions respectively. In the roots, similar results were observed. The changes in adsorption magnitude and shifts of the peaks were attributed to adsorption of the metals to the functional groups. This was probably due to the presence of the unfilled orbitals found in the metals where the lone pairs of electrons were used for bonding. This is likely to take place in the functional groups containing elements that have lone pairs of electrons. These include C=O, C-O and N-H. Substitution of hydrogen atom by the metal atoms is also a possible reaction. The functional groups that have a hydrogen atom, for example O-H and N-H can possibly have the atom replaced by the metal atom. It was found that the functional groups present in the roots, stem and leaves of *Cucurbita maxima* Lam. were the same as would be expected. However they were found at slightly different frequencies. This is due to presence of different compounds like phenols, alkaniods ,aldehydes ,ketones and others. The FTIR analysis of *ricinus communis* L. leaves, roots and stem are represented in Tables 4, 5 and 6 respectively. The functional groups found in the biomass were O-H, N-H, C-C, C-N, C=C among others. The presence of these functional groups allow the heavy metals to be adsorbed on to the biomass. These results were also observed in work recorded in literature (Younis *et al.*, 2009, Atiku *et al.*, 2014). The adsorption as observed in the case of *Cucurbita maxima* Lam. where presence of unfilled orbitals in the metals allow bonding with the lone pairs of electrons found in the functional groups present. It can also be seen that some of the functional groups, for example O-H and N-H contain hydrogen atom which can possibly be substituted by the heavy metals thus causing a shift in the frequency as stated above.

Generally, metal biosorption involves complex mechanisms of ion-exchange, chelating, adsorption by physical forces, entrapment of the ions by inter and intra fibrillar capillaries and spaces of the cell structural network of a biosorbent. The status of biomass (living or non-living), types of biomaterials, property of metal in solution and environmental conditions such as pH all greatly influence the mechanism of metal biosorption (Das *et al.,* 2008). The FTIR allowed easy discrimination by comparison between the metal ion loaded and unloaded biomass samples. The data presented in the study showed that FTIR spectroscopy is an adequate technique to evaluate the functional groups responsible for heavy metal ions adsorption by plant biomass (Tajuddin *et al*., 2014).Chelating and complexation are possible reactions in the adsorption process. The metal ions could also be adsorbed by substitution reactions or by electrostatic forces of attraction to the electron cloud. The results also showed that functional groups present in *Cucurbita maxima* Lam. and *ricinus communis* L. plants are similar being dominated by O-H,C=C C-O methyl group ,phenolic among others. However, the peaks for the groups appeared at different frequencies showing that the bonds formed have different bond energies.

CONCLUSION

Cucurbita maxima Lam. and *ricinus communis* L. were found to be suitable adsorbents for heavy metals since they contain functional groups where the metal ions attach. However, when the two plants are compared it was observed that there were more shifts in *cucurbita maxima* Lam. than in *ricinus communis* L. implying that it is a better adsorbent of the heavy metals being studied.. The adsorption of the different metals used gave different results. This could be attributed to size of the ion, availability of metal ions at the site or electronegativity of the metal and also the type of adsorbent being used. Lead metal is more electronegative than cadmium and copper metal, however, there was no major difference in adsorption between lead metal and the other metals used (from the functional groups shifts).

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