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Preliminary Adsorption Studies of Pb (II) With Gmelina Sawdust; Zn-Oxalic Acid (Zn-Oxa) and Cu-OXA MOFs

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Abstract

This work is about sorption of Pb (II) with using Gmelina sawdust, Zn-OXA and Cu-OXA MOFs. Gmelina sawdust biosorbent was prepared by carbonization and subsequently activated, whereas, the MOFs sorbents were prepared using slow evaporation method. These materials were characterised using FTIR. The analyses revealed principally the presence of carboxyl, carbonyl, hydroxyl, and amine functional groups in the biomaterials, then hydroxyl and carbonyl for the MOFs. There was decrement in the FTIR absorption values of hydroxyl and carbonyl of the oxalic acid as observed in the spectra of the MOFs, implying that oxalic acid bonded to the Zn and Cu ions via O-H and C=O groups in the MOFs. The trend of sorption Pb (II) by these products is: Cu-OXA MOF (57%), Zn-OXA MOF (95%), uncarbonised sawdust (97%), and carbonized sawdust (99%). The presence of different functional groups (i.e. as listed above) of the sawdust sorbents and the MOFs is the reason they performed well in terms of the Pb (II) adsorption. However, the sawdust products and Zn-OXA MOF are more effective for the lead (II) removal than the Cu-OXA MOF.

Article History

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Keywords

Metal Organic Framework (MOF); Sawdust; Sorbent; Oxalic Acid.

Introduction

Adsorption method as a means of wastewater treatment has been widely reported using different adsorbents. It has been be found to be promising because adsorptionis simple, selective, efficient, cheaper, and handy to operate (Asemave & Goja, 2021). Relatedly, lignocellulosic biomass are available in large quantity and known to contain multifunctional groups which have ability to remove several pollutants (Asemave, Thaddeus, & Tarhemba, 2021). Furthermore, biosorbents are highly sustainable and environmentally friendly products (Asemave *et al.,* 2021). Thus, rice husk ash, straw, bagasse, wood, grass, sawdust etc have been used as biosorbents for removal of Pb and other metals. Hence there have been

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several studies of sorption of pollutants with them. Besides sorption applications, sawdust has been used as fuel and making of products like board, packing materials etc. Recently, it has been highly considered as aninexpensive adsorbent of metal pollutants. This is so because it has substantive levels of cellulose and lignin, 45–50% and 23–30%, respectively. The presence hydroxyl, carboxylic and phenolic groups in cellulose and lignin in turn give them the capacity to bind metal ions (Albadarin *et al.,* 2011).

On the other hand, frameworksof metal–organic (MOF) have been widely studied (Mahmoud, Fouad, & Mohamed, 2020). They consist of central metal ions bonded to organic moieties known as linkers to give one or more dimensional frameworks. MOFs have high porosity, high surface area, amenable pore sizes etc that has generated wide stake about them (Zhang *et al.,* 2022). Good number of inorganic and organic components could be used, and this elasticity has allowed the rational design and assembly of materials with peculiar characteristics (Getachew *et al.,*2014). There are different methods of synthesizing MOFs, such as slow evaporation, solvothermal, hydrothermal, ultrasonic, mechano-chemical, and electrochemical methods (Mahmoud *et al.,* 2020). More so, many biomaterials and MOFs have been demonstrated as adsorbents (Sulaiman, Ajayi, & Olakunle, 2022). However, there are little information about the comparison of MOFs and biosorbents in terms of pollutants sorption capacities. Therefore, this research compares the sorption of Pb (II) with Gmelina sawdust, Cu-OXA and Zn-OXA MOFs.

Materials and Methods

Apparatus/ Reagents/ Equipment

Wood shaving of *Gmelina arborea,* Muffle furnace (Ney-252 model), desiccator, mortar and pestle, Sieve (2 mm mesh size), beakers, pH meter, oven, spatula, analytical weighing balance, stop watch, Whatman Filter paper, measuring cylinder, conical flask, plastic funnel, speed adjusting multi-purpose vibrator, volumetric flask, distilled water, hydrochloric acid (JHD - AR, 36%), lead (II) nitrate (JHD - AR, 99%), stirrer, sample bottle, separating funnel, crucible, petri-dish, copper (II) nitrate (JHD - AR, 99%), zinc (II) nitrate (JHD - AR, ≥99%), absolute ethanol (JHD - AR, 99.7%), and oxalic acid (JHD - AR, ≥99.5%) were used.

Sample Collection

Saw dust sample of *Gmelina arborea* were obtained from timber workshop at George Akume Way, International Market Makurdi, Benue State -Nigeria.

Carbonization of the Sawdust

The obtained sawdust was properly washed with distilled water for removal of impurities and sundried for 7 days. A portion of the dried sawdust was modified through carbonisation at 400 ºC for 1 h using muffle furnace. The charred sample was removed from the furnace, cooled in the desiccator for 30 min, and pulverized. This was then sieved using 2 mm mesh size sieve to obtain uniformly fine particles. The uncarbonised sample was pulverized and sieved as well. The wt % yield after carbonisation was 16.90.

Activation of the Carbonized Sawdust

About 5 g carbonized materials was placed inside beaker. 5 mL concentrated hydrochloric acid (36%) was added and kept for 48 h with intermittent stirring. The beaker was then heated in fume cupboard for 5 h at 180 ºC. Thereafter, the content was repeatedly washed and decanted until a pH of 7 was obtained. The Gmelina adsorbent was filtered and dried at 105 ºC. After 3 h, it was then removed and cooled in the desiccator (Asemave *et al.,* 2021).

Preparation of the Zn- and Cu- MOFs

The MOFs were prepared using the slow evaporation method at room temperature as similarly and previously established in (Mansab & Rafique, 2015). Oxalic acid (0.25 g) was weighed into a beaker and then dissolved with absolute ethanol (10 mL). In another beaker, 1.0 g copper nitrate or zinc nitrate (1.20 g) was dissolved in distilled water (10 mL). Contents of the two beakers were then coalesce together with continuous whirling for 30 min. Resultant solution was left standing for 5 days. In the end, the resultant product was filtered. The product was then left to dry. After drying, the weight of the dried product was taken and yield calculated. Therefore, the wt % yields are 16.80 ± 2.5 (Zn-OXA MOF) and 22.35 ± 2.9 (Cu-OXA MOF). The MOFs obtained are presented in Figure 1.

Fig. 1: The photos of the prepared MOFs (blue = Cu-OXA MOF and white = Zn-OXA MOF)

Preparation of the Pb(II) Solution

35 mg of Pb (II) nitratewas dissolved in 250 mL beaker with small amount of distilled water. This was transferred into volumetric flask (1 dm^3). Subsequently, the beaker was washed and emptied into the volumetric flask. The solution was then thoroughly shaken and made up to the mark with distilled water to from stock solution of 35 mg/L.

Adsorption Studies

Batch adsorption experiment was adopted from (Ahile *et al.,* 2019). About 20 mL of the Pb (II) nitrate solution (35 mg/L) was applied to 0.2 g of adsorbents (uncarbonized sawdust, carbonized sawdust, and the MOFs) in separate conical flasks. The mixtures were placed on the vibrator for 1 h of agitation. Then they were unmounted and left to equilibrate for 30 min before filtration. The filtrates were then transferred into sample vials for determination of residual Pb (II)ions level using AAS. Then the % removal of Pb(II) was deduced accordingly.

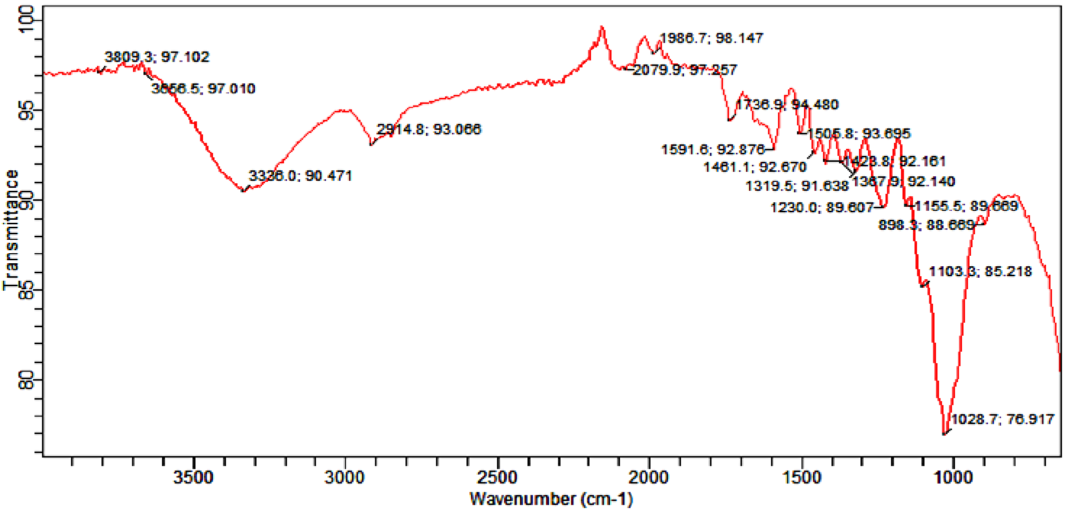

Fig. 2: FTIR spectrum for the uncarbonised Gmelina sawdust

Results and Discussion

FTIR Results

The prepared sorbents were carefully elucidated with the help of their FTIR spectra as previously reported (Koppula, Surya, Katari, Dhami, & Nair, 2022). Therefore, the spectra of the uncarbonised and carbonized sawdusts were obtained and compared (see Figures 2 and 3, respectively). On the other hand, the FTIR spectra of oxalic acid, Zn-OXA and Cu-OXA MOFs were also analysed as given in Figures 4, 5, and 6, respectively. The FTIR absorption values (with reference to Figures 2 and 3) found at 1736.9 cm-1 and 1684.8 cm^{-1} implied C=Opresence(Deepa & Suresha, 2014)(Bartczak *et al.,* 2015)(Ogunleye, Adio, & Salawudeen, 2014)(Hashem, 2007). The analyses revealed principally the presence of COOH/ O-H (3809 – 3336 cm^{-1}), C=O (1736 -1684 cm^{-1}), and C=C/ N-H (1591 – 1580 cm^{-1}) functional groups present in the uncarbonised and carbonized biomaterials (Deepa & Suresha, 2014)(Bartczak *et al.,* 2015).

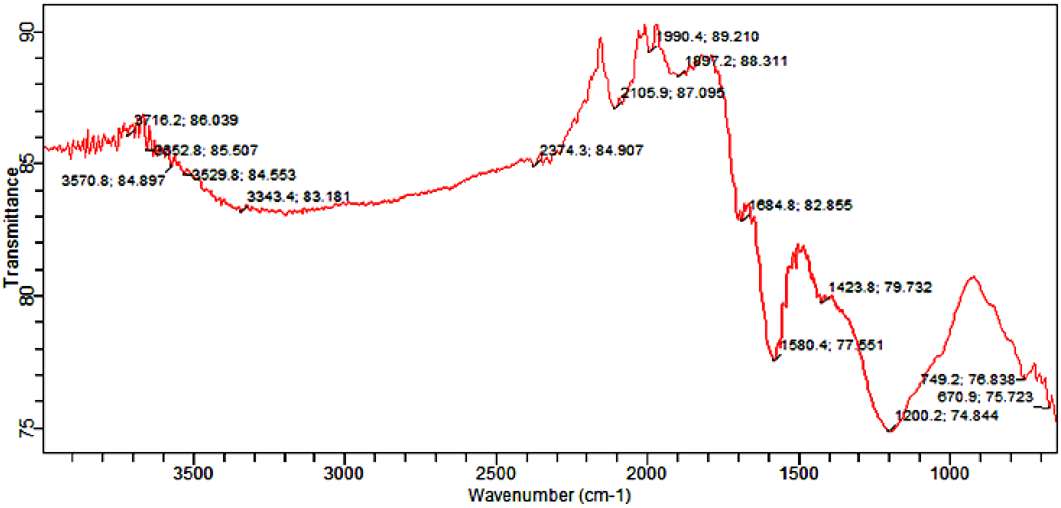

Fig. 3: FTIR spectrum for the carbonized Gmelina sawdust

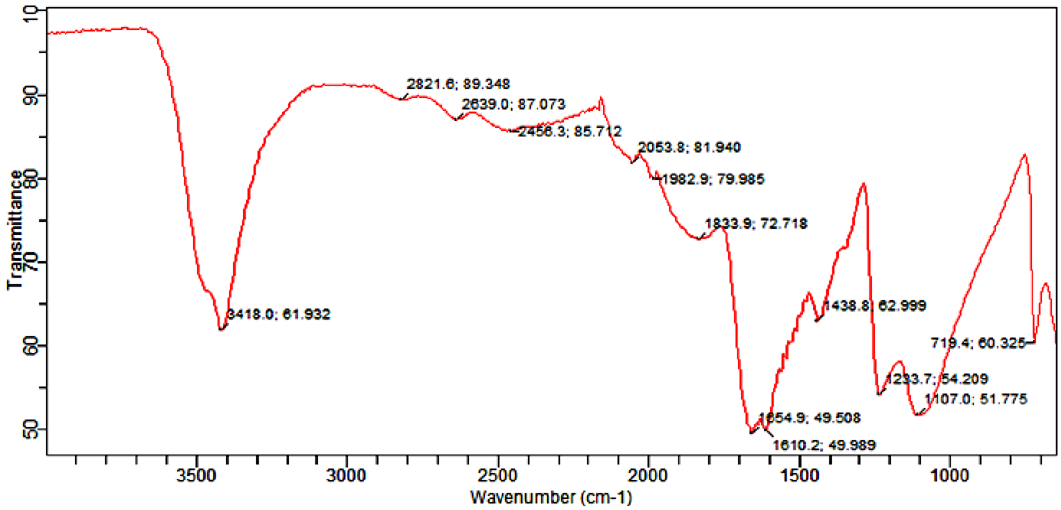

Fig. 4: FTIR spectrum of the oxalic acid

More so, The FTIR spectrum (see Figure 4) of the free oxalic acid has a substantial absorption at 3418 cm^{-1} which attests for O-H presence (from COOH) functional group. It also has absorption at 1654 cm^{-1}, coming from C=O. The intense FTIR absorption band at 3362 -3377 cm^{-1} in the MOFs spectra are attributed to stretching vibration of O-H. In addition, the peaks at 1606 - 1625 cm^{-1} indicate the presence of C=O functional group. Furthermore, the FTIR absorption values of O - H (3418 cm-1) and C= O (1654 cm^{-1}) for free oxalic acid were decreased to 3362 -3377 cm^{-1} and 1606 - 1625 cm^{-1}, respectively in the MOFs (Figures 5 and 6).

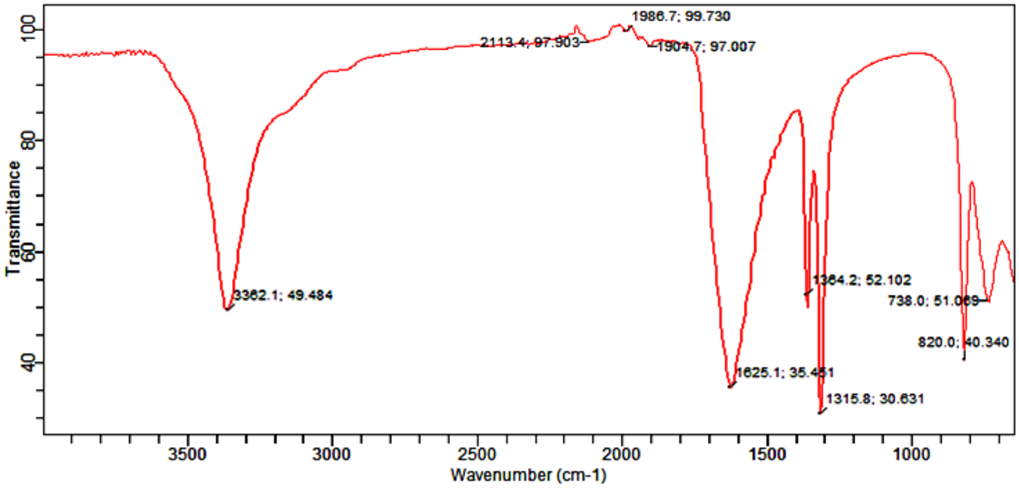

Fig. 5: FTIR spectrum of the Zn-OXA MOF

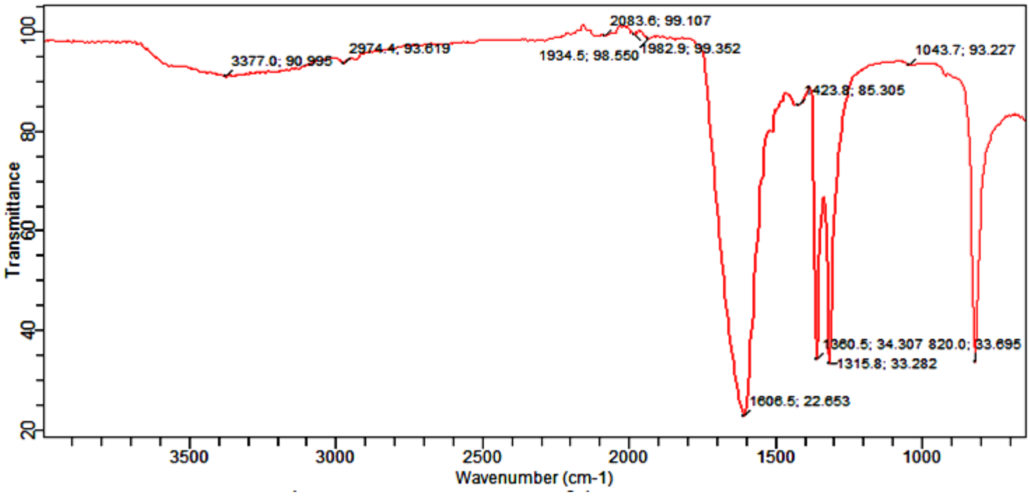

Fig. 6: FTIR spectrum of the Cu-OXA MOF

Adsorption Results

Prior to the adsorption studies, the MOFs were tested for their solubility in aqueous phase. Both the Zn-OXA and Cu-OXA MOFs were observed to be completely insoluble in water, hence their suitability for use as sorbents of pollutants from aqueous systems. It's also on records that oftentimes, MOFs are insoluble in water. Therefore, the sawdust products as well as the MOFs were tested in terms of their abilities to adsorb Pb (II) as similarly demonstrated for other metals (Koppula, Jagasia, Panchangam, & Surya, 2022). The results of the Pb (II) adsorption is depicted in the Figure 7 as follows.

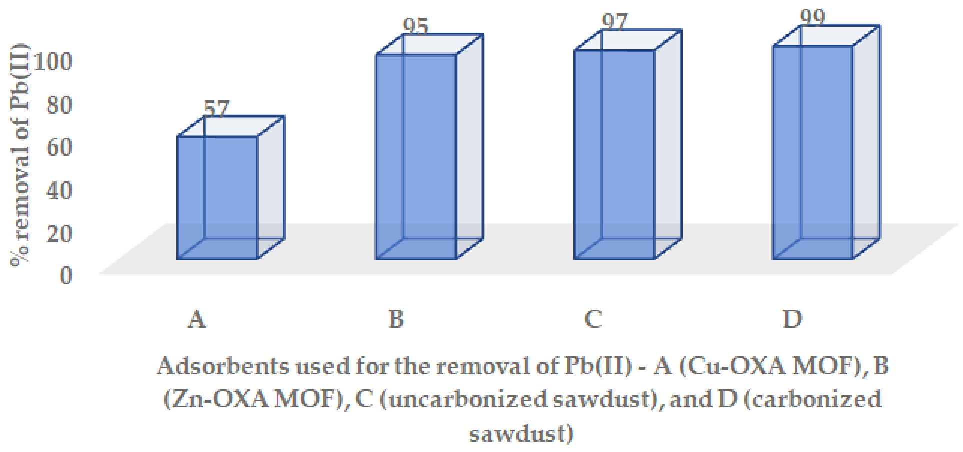

Fig. 7: % removal of Pb (II) using the different adsorbents

From the results in Figure 7 above it can be seen that the order of the removal of Pb (II) by these adsorbents is: Cu-OXA-MOF (57) < Zn-OXA framework (95%) < uncarbonised Gmelina sawdust (97%) < carbonized Gmelina sawdust (99%). These results are comparable to similar previous findings as described in Table 1.

Table 1: % removal of Pb (II) using the different adsorbents

Sorbents	Contact time	Initial Pb (II) concentra-tion (mg/L)	pH	Dose of adsorbent (g/L)	% removal of Pb (II)
Cu-OXA-MOF	1 h	35	-	10	57this study
Zn-OXA framework	1 h	35	-	10	95this study
Uncarbonised Gmelina sawdust	1 h	35	-	10	97this study
Carbonized Gmelina sawdust	1 h	35	-	10	99this study
Rice husk and its ash	60 min	30	-	-	88 and 95 (El-Said, 2010)
Maize leaf	1 h	-	-	-	100(Babarinde, Babalola, & Sanni, 2006)
AC of birbira (Militia ferruginea)	3 h	-	4	-	97(Mengistie *et al.*, 2008)
AC of Banana stalk-based	120 min	-	-	-	98 (Ogunleye *et al.*, 2014)
Leaves of Araucaria cookii	60 min	50	6	2	100 (Deepa & Suresha, 2014)
MOF 1	60 min	-	7	-	53.9 (Zheng *etal.*, 2021)
Tb-MOFs	50 min	90	5.5	0.15	55 (Zhu *et al.*, 2019)
MOF-5	30 min	200	5	-	55 (Rivera *et al.*, 2016)

Discussion

The decrement in the FTIR absorption value of O-H and C = O as seen in the Cu- and Zn- MOFs clearly implied that oxalic acid bonded to the Zn and Cu ions via O - H and C= O functional groups. Therefore, the schematic structure of the MOFs is given in Figure 8, where each of the anion (oxalate) is acting as tetradentate ligand, and the metal (M) may have additionally coordinated water molecules. Such scheme for a polymeric structure of metal oxalates has been similarly described by (D'Antonio *et al.,* 2009).

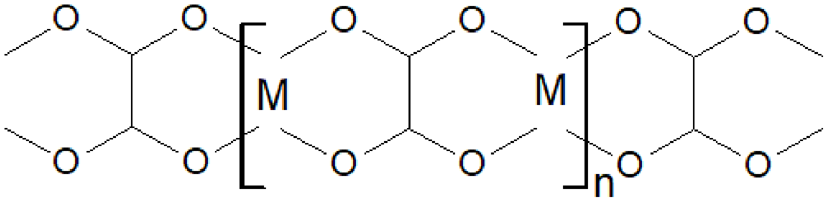

Fig. 8: Schematic structure of the MOFs (M= Zn or Cu)

In general, the presence of functional groups on adsorbents can facilitate metals removal (Bartczak *et al.,* 2015). Thus, the presence of carboxyl, carbonyl, hydroxyl, and amine for the sawdust, and carboxyl, carbonyl, and hydroxyl for the MOFs is partly the reason they performed well in terms of the Pb (II) sorption. Except for A, the removal of the Pb (II) by B, C, and D is well comparable. This may be due to lower surface area of A as compared to B, C, and D. Therefore, Figure 9 represents sorption mechanism of the Pb (II) by the biomaterials and these MOFs.

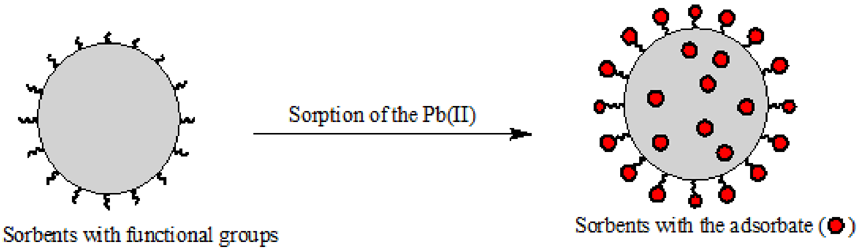

Fig. 9: Sorption mechanism of the Pb (II) ions onto the sorbents surface

Our results on the levels (%)of Pb (II) removed were in complete conformity with previous similar findings. The sorption of Pb (II) ions by rice husk and husk ash was found to be 88% and 95%, respectively at condition of 60 min and 30 mg/L Pb (II) (El-Said, 2010) (Naiya*et al.,* 2009). Meanwhile, maize leaf removed nearly 100% of Pb (II) ions from industrial wastewater within contact time of 1 h (Babarinde *et al.,* 2006). In another development, the removal of Pb (II) by birbira (*Militia ferruginea*) activated carbon indicated maximum removal of 97% at 3 h, dose of 4 g, and at pH of 4 (Mengistie *et al.,* 2008). Ogunleye *et al.* observed that the maximum percentage removal of Pb (II) using banana stalk-based activated carbon was 98% at equilibrium time of 120 min (Ogunleye *et al.,* 2014). Our research work here again agrees with the report of Hashem (Hashem, 2007) who observed that the adsorption of Pb(II) by okra wastes reached 99%. More so, about 100% of Pb (II) was removed using leaves of *Araucaria cookii* at 50 mg/L Pb(II), 2 g/L biosorbent, pH 6, and 60 min (Deepa & Suresha, 2014).

In addition to the sorption studies, we can see that the biomaterials, sawdust (hither to considered as waste) is highly available with scarce applications. Therefore, we can leverage on its cheap source to develop appropriate technologies that can harness this product, especially in the area of environmental remediation and reclamation. And this has greatly been the concerns in Green Chemistry for ensuring environmental benignness and waste control &

minimization. Also, the synthesis of the Zn and Cu MOF was carried out in highly energy efficient manner at room temperature. Thus, the procedure is highly sustainable and in tandem to the 6th principle of Green Chemistry which advocates for 'design for energy efficiency'(Kaana Asemave, 2016). These are other benefits of the research besides the ultimate removal of Pb (II).

Conclusions

Gmelina sawdust; Cu- and Zn- MOFs sorbents have been prepared using known and reported procedures. Thereafter, their sorption of Pb (II) was demonstrated. The sorptionof Pb(II) by these adsorbents were. Cu-OXA MOF (57%), Zn-OXA MOF (95%), uncarbonised sawdust (97%), carbonized sawdust (99%). The presence of the functional groups in the sawdust sorbents (carboxyl, carbonyl, hydroxyl, amine) and the MOFs (carboxyl, carbonyl, and hydroxyl) is the reason they performed well in terms of the Pb (II)adsorption.However, the sawdust products and Zn-OXA MOF are more effective in the sorption of the Pb (II) than the Cu-OXA MOF.

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Conflicts of Interest

The authors declare no conflict of interest.

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