



Facile Comparison of Adsorption of Pb²⁺ from aqueous solution using Gmelina sawdust and Zinc-Oxalic acid (Zn-OXA) Framework

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Abstract: This work is aimed at the comparison of sorption of Pb²⁺ from aqueous solution using Gmelina sawdust and Zn-Oxalic acid (Zn-OXA) framework. Gmelina sawdust biosorbent was prepared by carbonization and subsequently activated; whereas, the Zn-OXA framework sorbent was prepared using slow evaporation method. These materials were characterised using FTIR. The analysis revealed principally the presence of COOH, C=O, CHO, C(O)-O-C and most likely amine functional groups in the biomaterials. The decrement in the FTIR absorption value of O-H and C = O of oxalic acid as observed in the Zn-OXA framework clearly implied that oxalic acid bonded to the Zn²⁺ ion via O - H and C=O functional groups. It was observed that the removal of Pb²⁺ by these adsorbents is: Zn-OXA framework (95%) < un carbonised sawdust (96.67%) < carbonized sawdust (99%). The multifunctionalities and may be higher porosity for the sawdust biosorbent is likely the reason it has performed better than Zn-OXA framework in terms of the Pb²⁺ adsorption. However, both the sawdust product and Zn-OXA framework are effective in the sorption of the Pb²⁺ from aqueous solution.

Keywords: Metal Organic Framework (MOF); Sawdust; Sorbent; Adsorption

1. Introduction

Adsorption method as a means of wastewater treatment has been carried out severally by different researchers using different adsorbents. It is also reported to be more promising due to its simplicity, selectivity, high efficiency, low cost, and operational convenience.^[1] Lignocellulosic biomass is available in large quantity and also known to include variety of functional groups which have potential sorption capacities for several pollutants.^[2] In addition, biosorbent is highly sustainable and environmentally friendly products.^[2] Hence there have been several studies of sorption of pollutants with biosorbent. On the other hand, metal-organic framework (MOF), also known as porous coordination polymer (PCP), has been widely studied.^[3] MOFs consist of metal ions or metal clusters coordinated to organic molecules to form one, two, or three-dimensional structures that in turn composed of the tuneable metal clusters and organic linkers. MOFs have gained significant interest due to their numerous attractive characteristics including high porosity, high surface area, and adjustable pore sizes.^[3] A wide variety of inorganic and organic components could be used, and this elasticity has allowed the rational design and assembly of materials with peculiar characteristics.^[4] MOFs can be synthesized through different methods such as slow evaporation, solvothermal, hydrothermal, ultrasonic, Mechano-chemical, and electrochemical

methods.^[3] In the recent times many biomaterials and MOFs have been demonstrated as adsorbents. However, there is little information about comparison of biosorbents with MOFs in terms of pollutants sorption. Therefore, this research is aimed at the comparison of sorption of Pb²⁺ from aqueous solution using Gmelina sawdust and Zn-OXA framework.

2. Materials and Methods

2.1. Apparatus/ Reagents/ Equipment

Wood shaving of *Gmelina arborea*, sample container, masking tape, 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, lead (II) nitrate, stirrers, sample bottles, separating funnels, crucibles, petri-dishes, oxalic acid were used.

2.2. Sample Collection

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

Table 1. FTIR (cm^{-1}) Absorption Analysis for Uncarbonised and Carbonized Gmelina Sawdust

Uncarbonised	Carbonized	Functional Groups
3809.3 – 3336.0	3716.2 – 3343.4	O-H group of carboxylic acid, or amine stretch ^[13]
2914.8	-	Aliphatic C-H group ^[13,14,15]
1736.9	1684.8	C=O stretch ^[13,16,17]
1591.6	1580.4	C=C stretch, amine bending ^[13]
1423.8 – 1461.1	1423.8	C-H bending ^[14]
1367.6	-	O-H bending ^[14]
1028.7	1200.2	C-O, S=O stretch ^[14,13]
898.3	-	C=C bending
-	670.9	C-S stretch ^[13]

2.3. Carbonization of the Sawdust Collection

The obtained sawdust was washed thoroughly with running tap water and rinsed three times with distilled water to remove impurities and sundried for seven days. A portion of the dried sawdust was modified through carbonisation at 400°C for 1 h using muffle furnace. The charred sample was removed from the furnace and cooled in the desiccator for 30 min. Thereafter, pulverization was carried out using mortar and pestle. This was then sieved using a 2 mm mesh size sieve to obtain uniformly fine particles. The uncarbonised sample was pulverized and sieved too. The wt % yield after carbonisation was 16.90.

2.4. Activation of the Carbonised Gmelina Sawdust

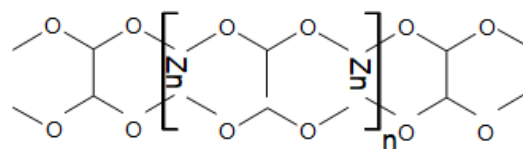
About 5g of the carbonized sample was transferred into beaker. 5 mL of concentrated hydrochloric acid was added and kept for 48 h with intermittent stirring. The beaker was then heated in fume cupboard for 5 h at 180°C . Thereafter, the content was repeatedly washed and decanted until a pH of 7 was obtained. The Gmelina adsorbent was filtered using filter paper and dried in the oven at 105°C for 3 h; it was then cooled in the desiccator.^[2]

2.5. Preparation of Zn-OXA Framework

Zinc-OXA framework was prepared using the slow evaporation method at room temperature as previously described in Mansab et al.,^[5] Oxalic acid (0.25 g) was weighed into a beaker and then dissolved with absolute ethanol (10 mL). The mixture was stirred until complete dissolution of the acid. In another beaker, zinc nitrate (1.20 g) was dissolved in distilled water (10 mL). This was also stirred until complete dissolution of the salt. Contents of the two beakers were then mixed together with continuous stirring for 30 min. The solution was then kept for five days with close monitoring. After five days, the solution was filtered using a Whatman filter paper in a separation funnel. The filtrate was then left to dry. After drying, the weight of the dried product was taken and yield calculated. Therefore, the wt % yield is 16.80 ± 25 .

2.6. Preparation of Pb^{2+} Solution

A stock solution of Pb^{2+} nitrate (35 mg/L) was prepared as described below. About 35 mg of Pb^{2+} nitrate was weighed and dissolved with 100 mL of distilled water in a 250 mL beaker. The solution was transferred into a 1000 mL volumetric flask containing 500 mL of

**Fig. 1.** Proposed structure of Zn-OXA framework

distilled water. The beaker was also rinsed and emptied into the volumetric flask. The solution was then thoroughly shaken and made up to the mark with distilled water.

2.7. Adsorption Studies

Batch adsorption experiment was used. About 20 mL of the Pb^{2+} nitrate solution (35 mg/L) was applied to 0.2 g of adsorbents (uncarbonized sawdust, carbonized sawdust, and Zn-OXA framework) in separate conical flasks. The mixtures were placed on the vibrator for 1 h of agitation. Then they were removed and left to equilibrate for 30 min before filtration. The filtrates were then transferred into sample vials for determination of residual Pb^{2+} ions level using AAS.^[6,7,8] From there the % adsorption was determined accordingly.

3. Results and Discussions

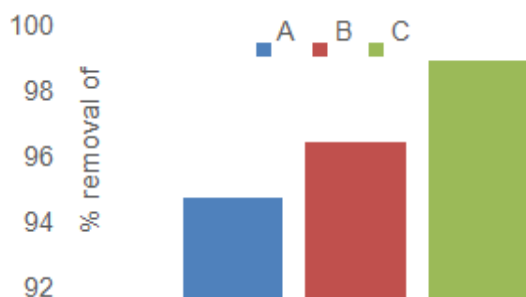
3.1. FTIR Results

The prepared sorbents were carefully elucidated with the help of their FTIR spectra. Therefore, the spectra of the uncarbonised and carbonised sawdust were obtained and compared on one hand (Table 1). On the other hand, the FTIR spectra of oxalic acid and Zn-OXA framework were also analysed and given in Table 2. The FTIR peaks found at 1736.9 cm^{-1} and 1684.8 cm^{-1} are the characteristics of carbonyl group stretching from aldehydes, ketones, and esters.^[9,10,11,12] The analysis revealed principally the presence of COOH, C(O), CHO, C(O)-O-C and most likely amine functional groups in the biomaterials.^[9,10] Thus, the biomaterial is multifunctional in its un carbonised and carbonized form. The detail interpretation can be seen in the Table 1.

More so, The FTIR spectrum of oxalic acid has a broad peak at 3418 cm^{-1} which attests for the presence of O-H functional group; and 1654 cm^{-1} peak indicates the presence of C=O.^[18,19] The FTIR spectrum of the Zn-OXA framework has intense absorption band at 3362.1 cm^{-1} is attributed to stretching vibration of O-H. And the peak at 1625.1 cm^{-1} indicated the presence of C=O functional group.^[18,19] Furthermore, the absorption value of O - H and C=O for free oxalic acid are 3418 cm^{-1} and 1654 cm^{-1} . These values decreased to 3362.1 cm^{-1} and 1625.1 cm^{-1} respectively in the Zn- OXA framework. The decrement in the FTIR absorption value of O-H and C = O as seen in the Zn-OXA framework clearly implied that oxalic acid bonded to the Zn^{2+} ion via O - H and C= O functional groups.^[18,19] For detail interpretation of the spectra of the oxalic acid and the Zn-OXA framework look at the Table 2. Therefore, the structure of Zn-OXA framework is proposed in Fig. 1.

Table 2. FTIR (cm^{-1}) Absorption Analysis for Oxalic and Zn-OXA Framework

Zn-OXA Framework	Oxalic acid	Functional Group
3362.1	3418	O-H ^[16,20,21]
-	2821	C-H ^[16,20,21]
1625.1	1654	C=O ^[16,20,21]
1364.2	1438.8	C-H bending ^[14]
1315.8	1233.7 – 1107.0	C-O stretch ^[14,13]

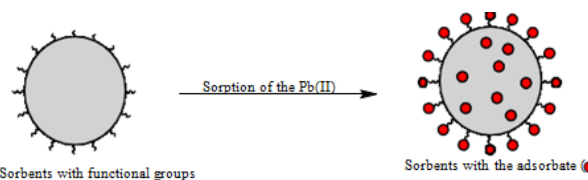
**Fig. 2.** % Removal of Pb^{2+} using A (Zn-OXA Framework), B (Uncarbonized Sawdust), and C (Carbonized Sawdust)

3.2. Adsorption Results

The carbonised and activated sawdust as well as the Zn-OXA framework were tested in terms of their abilities to remove Pb^{2+} from the aqueous solution. The results of the Pb^{2+} adsorption are depicted in the Fig. 2.

From the results in Fig. 2 above it can be seen that the order of the removal of Pb^{2+} by these adsorbents is: Zn-OXA framework (95%) < uncarbonised Gmelina sawdust (96.67%) < carbonized Gmelina sawdust (99%). Therefore, the presence of different functional groups on the surfaces of these materials are responsible for making the removal of the Pb^{2+} effective via chemical and physical attractions^[10] as represented in Fig. 3. In addition, multifunctionalities of the biosorbents and likely higher porosity (especially the carbonized sawdust) are the reason the biosorbents gave higher % values of Pb^{2+} adsorption than the Zn-OXA framework. It is worthy to note that the performance of the Zn-OXA framework and the biosorbents are not significantly different from each other in terms of the removal of the Pb^{2+} from aqueous solution.

Our results on the % removal of Pb^{2+} from aqueous solution were in complete conformity with previous related findings. Hence, bio sorption of Pb^{2+} ions from aqueous solutions onto rice husk and its ash was found to be 87.75% and 94.75%, respectively at contact time 60 min and initial concentration of 30 mg/L.^[22,23] Meanwhile, maize leaf has potential for nearly 100% removal of lead ions from industrial wastewater within contact time of about 1 h.^[24] In another development, the adsorption of Pb^{2+} by activated carbon of birbira (*Militia ferruginea*) indicated maximum removal of 97.3% at 3 h, dose of 4.0 g, and at pH of 4.0.^[25] Ogunleye et al.^[13] observed that the maximum percentage removal of Pb^{2+} from aqueous solution using banana stalk-based activated carbon was 97.90% at equilibrium time of 120 min.^[13] Our research work here again agrees with the report of Hashem^[14] who observed that the adsorption of Pb^{2+} from aqueous solution by okra wastes reached 99% removal. More so, 99.5% of Pb^{2+} was removed using leaves of *Araucaria cookii* from an

**Fig. 3.** Chemical and Physical Attractions of the Pb^{2+} ions onto the Sorbents Surface

initial Pb^{2+} concentration of 50 mg/L and the quantity of biosorbent was kept constant at 2 g/L, pH 6 maintained with contact time 60 min.^[9]

In addition to the adsorption studies, we can see that the biomaterials, sawdust (hitherto considered as waste) is highly available with scarce applications. Therefore, leverage can be taken 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.^[20] Also, the synthesis of the Zn-OXA framework 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'.^[26,12,27] These are other benefits of the research besides the ultimate removal of Pb^{2+} from aqueous phase.

4. Conclusions

Gmelina sawdust and Zn-Oxalic framework sorbents have been prepared using known and reported procedures. Thereafter, their facile comparison for the sorption of Pb^{2+} from aqueous solution was demonstrated. It was observed that the removal of Pb^{2+} by these adsorbents is: Zn-OXA framework (95%) < uncarbonised sawdust (96.67%) < carbonized sawdust (99%). The multi functionalities and may be higher porosity for the sawdust biosorbent is likely the reason it has performed better than Zn-OXA framework in terms of the Pb^{2+} adsorption. However, the performance of the Zn-OXA framework and the biosorbent is not significantly different from each other in terms of the removal of the Pb^{2+} . Therefore, both the sawdust product and Zn-OXA framework are effective in the sorption of the Pb^{2+} from aqueous solution. Indeed, the biomaterials and MOFs have similar capacity as adsorbents.

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Conflicts of Interest

The author declares no conflict of interest.

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