

SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY 2021 VIRTUAL CONFERENCE

ADSORPTION STUDIES OF ZINC, COPPER, AND LEAD IONS FROM PHARMACEUTICAL WASTEWATER ONTO SILVER MODIFIED CLAY ADSORBENT

AJALA, Mary Adejoke^{1,2,4*}; ABDULKAREEM, Ambali Saka^{2,4}; KOVO, Abdulsalami Sanni^{2,4};
TIJANI, Jimoh Oladejo^{3,4}; ADEYEMI, Ayomide Samuel¹

¹ Department of Chemical Engineering, University of Ilorin, Ilorin, Kwara State, Nigeria.

² Department of Chemical Engineering, Federal University of Technology, Minna

³ Department of Chemistry, Federal University of Technology, Minna, Niger State, Nigeria.

⁴ Nanotechnology Research Group, Centre for Genetic Engineering and Biotechnology (CGEB), Federal University of Technology, P.M.B 65, Bosso, Minna, Niger State, Nigeria.

*Corresponding author

email: ajala.ma@unilorin.edu.ng

Received 15 October 2021; received in revised form 06 January 2022; accepted 24 January 2022

ABSTRACT

Clay-supported silver nanoparticles were green synthesized using the aqueous leaf extract of *Parkia biglobosa*. The phytochemical analysis and FTIR results of the *Parkia biglobosa* showed that the leaf contains phenol, tanning, and flavonoids, which act as reducing, capping, and stabilizing agents required for the synthesis of the silver nanoparticles. The prepared adsorbent has good morphology, is rich in silica, and contains functional groups suitable for heavy metal binding. The adsorptions of Zn, Cu, and Pb from pharmaceutical wastewater onto the silver-modified clay were studied as an adsorbent dosage and contact time. From the percentage removal results obtained, the adsorbent had up to 99.96%, 99.5%, and 99.44% removal efficiency for Zn, Pb, and Cu, respectively. The present work shows that the synthesized silver nanoparticles supported on local clay can be used as a potentially low-cost adsorbent to remove heavy metal ions from industrial wastewater.

Keywords: Green synthesis, *Parkia biglobosa*, Silver oxide, Nanoadsorbent, heavy metals.

1. INTRODUCTION

The pharmaceutical industry is a major producer of wastewater effluents containing pollutants such as heavy metals (zinc (Zn), copper (Cu) and lead (Pb)), microbes (bacteria), and dyes (yellow). The pollutants reduce the photosynthetic activity of aquatic life and could poison certain forms of aquatic life (Gardare *et al.*, 2014). Therefore, Zn, Cu, and Pb in pharmaceutical wastewater are hazardous and harmful to human health. Although Zn is an essential element in human beings because it could serve food supplements, its excess is extremely dangerous as it may cause paralysis and neurological problems. Excess Zn may also lead to a state of depression and other unwanted effects such as dizziness, breathing problems, and chest pain (Kaur and Sharma, 2017). The WHO guidelines gave the maximum admissible

concentration of Zn in an aqueous solution as 5.0 mg/l (WHO, 2008). Also, Cu has been reported to have adverse effects on human health. These include mental disorders, anemia, arthritis/rheumatoid arthritis, hypertension, and liver enlargement (Lakherwal, 2014).

Furthermore, the WHO gave the maximum admissible concentration of Cu in an aqueous solution as 0.05 mg/l (Bankole *et al.*, 2019). On the other hand, lead is responsible for lung dysfunction, liver damage, reduced pulmonary function, and cardiovascular dysfunction (Balali-mood *et al.*, 2021). Hence, Zn, Cu, and Pb removal from pharmaceutical wastewater are essential for human and aquatic survival.

Several conventional techniques such as photocatalytic oxidation, chemical coagulants, bioremediation, ion-exchange resins, reverse osmosis, membrane filtration, solvent extraction, and electrolysis have been reported for the removal of various heavy metals from wastewater

(Dave and Chopda, 2014). However, they are inadequate with some challenges and drawbacks, such as cost-effectiveness, disposal after use, efficiency, and lack of eco-friendliness of the technological processes (Dutta *et al.*, 2021). Therefore the need for more research on some other methods such as adsorption.

Adsorption technique is advancing to remove heavy metals, colors, and microbes from wastewater. Since the process is highly efficient, adsorbate-specific, cost-effective, easy to handle, and eco-friendliness (Dutta *et al.*, 2021). Adebayo *et al.* (2020), however, justified the use of nanomaterials as good adsorbents for the removal of heavy metals. Furthermore, it was reported that nanomaterials have appropriate adsorption surfaces that possess unique characteristics vis-à-vis a very high surface-area-to-volume ratio. All of these advantages give a tremendous driving force for diffusion, especially at high temperatures [9].

Several nanomaterials have been used for the removal of heavy metals from wastewater. For example, Mustapha *et al.* (2019) utilized modified kaolinite clay to remove Zn and Cr from tannery wastewater [10]. Bankole *et al.* (2019) also eliminate Zn and Cu from electroplating wastewater using nanoadsorbent (Bankole *et al.*, 2019). Kariim *et al.* (2020) used nanoadsorbent to treat pharmaceutical wastewater [11].

Therefore, this study investigated the development of Ag Nps/clay adsorbent to remove Zn, Cu, and Pb from pharmaceutical wastewater.

2. MATERIALS AND METHODS

2.1. Preparation procedures

2.1.1 Beneficiation of clay

The ball clay collected from Akerebiata, Ilorin, Kwara state was soaked in water for 48 h to allow the clustered clay to dissolve. It was then sieved to ease the removal of the sand particles and later allowed to sediment to get the fine particles of the clay. The fine particles obtained were sun-dried, oven-dried at 100°C, pulverized, and then sieved with a sieve mesh of < 0.2µm.

2.1.2 Preparation of leaf extract

Fresh leaves of *Parkia biglobosa* were washed with clean water and air-dried for two weeks at room temperature to prevent the destruction of the thermolabile constituents present in the plant by direct sun rays. The room dried leaves were then pulverized, and the phytochemical analysis for the plants was carried out. Next, 100 mL of deionized water was added to 5g of the pulverized leaf. The solution was then boiled at 60°C for 30min to extract the reducing and

stabilizing agents. Finally, the aqueous extract was filtered using a muslin cloth and filter paper (Whatman no.1). The filtrate was kept in a refrigerator for the biosynthesis of silver nanoparticles.

2.1.3 Green synthesis of silver nanoparticles

The adopted plant was pulverized. 5g of the pulverized plant was added to 100 mL of deionized water, boiled at 60°C, and stirred continuously for 30 min using a magnetic stirrer to extract the reducing and stabilizing agents. The solution was filtered using a muslin cloth and filter paper (Whatman no.1). The varied volume of leaf extract was added to a varied volume of 1mM AgNO₃ solution following the data gotten from the factorial design of the Design Expert. The solution was allowed to stand for 20 minutes. The pH of the resultant solution was adjusted between pH 4 and pH 10 with either 2 M NaOH or HCl. The color change from green to brown indicates the formation of nanoparticles. The solutions were characterized using a UV-Visible spectrophotometer.

2.1.4 Silver/Clay loading procedure

Forty grams (40 g) of the beneficiated clay was weighed on an analytical balance and added to a flask containing 400 mL of 1 mM AgNO₃. The flask was sealed and shaken at room temperature for 24 hours in a thermostatic water batch shaker (SHA-C); the suspension was filtered using a filter paper (Whatman no.1) and gradually dried at 50°C for 24 h. Based on the result obtained, the silver ions present in the silver-synthesized clay were reduced by adding 20 mL of the leaf extract of *Parkia biglobosa* under continuous stirring for a few minutes. After reduction, the solution was filtered using a filter paper (Whatman no.1) and washed several times with deionized water to remove residual Ag⁺ ions.

2.2 Adsorption Studies

The investigations were carried out in batches of adsorbent dosage and contact time to check the proclivity of the adsorption process. After undergoing the required experimental procedures, 100 – 1000 mg/L concentration was adopted. In each 100 mL measuring flasks, 25 mL of the wastewater of known concentrations was poured having a known amount of adsorbent. The mixture was shaken for 60 min, the supernatant was filtered through Whatman Filter Paper No. 1, and the wastewater was analyzed.

3. RESULTS AND DISCUSSION

3.1 Characterization result

3.1.1 FTIR of *Parkia Biglobosa*, Clay and Ag-clay

The structural exposition and macromolecules of *Parkia biglobosa* were evaluated using FTIR technique (Figure 1). The FTIR spectra showed characteristic peaks of hydrogen-bonded O-H stretch at 3533.71, 3417.98, 3363.97, and 3271.38 cm^{-1} . The peak at 3055.35 cm^{-1} indicates C=C-H asymmetric stretch. The peaks at 3417.98, 3363.97, 3271.38, and 3055.35 cm^{-1} indicate N-H stretch. Peaks of H-C-H asymmetric and symmetric stretch were shown at 2924.18 and 2862.46 cm^{-1} , while 2746.73 cm^{-1} indicates C-H stretch off C=O; the peak at 2345.52 cm^{-1} is as a result of C \equiv N stretch. The peaks at 1728.28 and 1627.97 cm^{-1} indicate C=O stretch; 1535.39 and 1442.80 cm^{-1} are due to H-C-H bend and C-C=C asymmetric stretch. The peaks at 1373.36, 1327.07, and 1026.16 cm^{-1} indicate the C-O stretch. The presence of the O-H stretch, which is related to phenol, serves as a reducing and stabilizing agent in the formation of the silver nanoparticles.

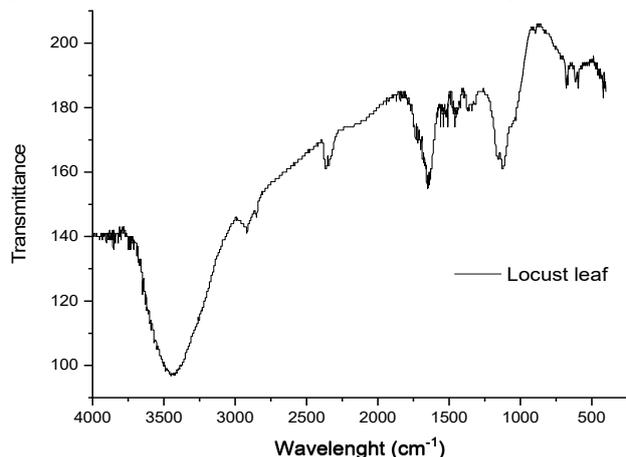


Figure 1: FTIR spectrum of *Parkia biglobosa*

The Fourier transform infrared (FTIR) spectroscopy of the clay was evaluated in Figure 2a. The characteristic peaks at 3701.70 and 3615.89 cm^{-1} represent the O-H stretch of alcohols, and phenolic group, the peak at 1111.01 cm^{-1} represents the C-O stretch of esters, while the C-O stretching peak at 1004.77 cm^{-1} is of ethers. The peaks at 914.87, 792.28, and 706.47 cm^{-1} are attributed to the Si-O-Si and Al-O-Si bonds of silicate clay. The FTIR spectra of the silver-clay in Figure 2b shows several peaks indicating the functional groups embedded in the adsorbent. The characteristic peak of the hydrogen-bonded O-H stretch, at 3305.86 cm^{-1} , is the phenolic and alcohol group. Bonded O-H of carboxylic acids is observed at 2928 cm^{-1} . The peaks at 1621 and 1600 are attributed to the C=O stretch of carbonyl and ketones. Other peaks at 1298 cm^{-1} , 1251 cm^{-1} , and 1186 cm^{-1} depict C-O stretch attributed to esters and ethers,

indicating a shift from the previously observed in unmodified clay likely due to the chemical modification (Dhand *et al.*, 2016). Si-O-Si and Al-O-Si bonds of silicate clay are at 910 cm^{-1} , 800.24 cm^{-1} , and 700 cm^{-1} . New peaks, which deviated entirely from those on the clay spectral, are observed at 534.78 cm^{-1} , 462.34 cm^{-1} , and 432.66 cm^{-1} attributed to Ag loading, which is similar to the findings of Krishnan and Mahalingam (2017).

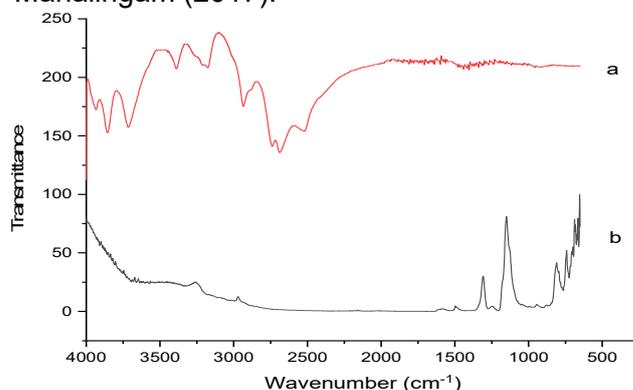


Figure 2: FTIR spectrum of (a) Clay and (b) Ag supported on clay Adsorbent

3.2 Morphology and Structure

The Scanning Electron Microscope was used to examine the surface morphology of the prepared adsorbent. Figure 3 reveals an evenly distributed arrangement of spherical nanocomposites. The flat-lying stacks are pseudo-hexagonal in a structure having curved edges, which are the characteristics of kaolinite clays. The even arrangement implies polydispersity and intercalation of the silver nanoparticles into the clay structure. The EDS result presented in Figure 4 shows that the clay is truly rich in silica of 13.97%, bonded oxygen is up to 42.27% of the entire weight, titanium and iron have low weight percent of 0.29 and 1.77%, respectively.

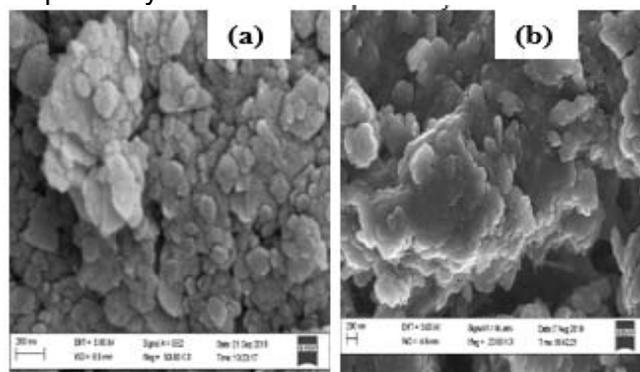


Figure 3: SEM Image of (a) Clay (b) Silver-Clay Adsorbent

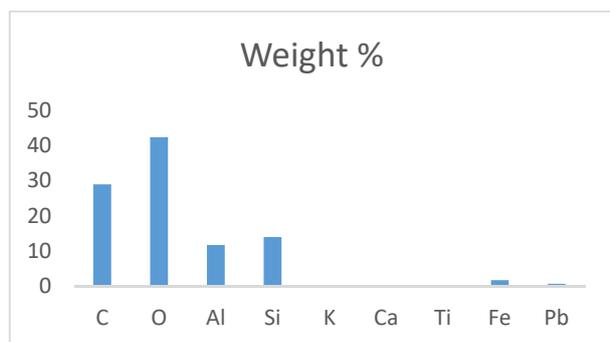


Figure 4: EDS of the Silver-Clay Adsorbent

3.2 Adsorption studies

3.2.1 Effect of adsorbent dose on the removal of the heavy metals

As adsorbent dosage increases from 0.1 g to 0.3 g, the percentage removal of Zn^{2+} , Pb^{2+} and Cu^{2+} increases and then begins to decline as adsorbent dosage increases beyond 0.3 g, as shown in Figure 5. This is because at lower adsorbent concentration number of active sites is higher. In addition, with the increase in adsorbent dosage, aggregation of particles occurs due to the low volume of solution. As a result, removal efficiency and adsorption of Zn^{2+} , Pb^{2+} , and Cu^{2+} decreases.

3.2.2 Effect of contact time on the removal of the heavy metals

Figure 6 shows the effect of time on adsorption. As the adsorption time was changed from 30 to 240 minutes, efficiency for Zn^{2+} , Pb^{2+} , and Cu^{2+} increased from 92.3%, 81.2%, and 80.1% at 30 minutes to 97.82%, 85.83%, and 85.39% at 90 minutes respectively, and remained constant afterward. As time progresses, the surface coverage of the adsorbent is high, and further, no adsorption takes place.

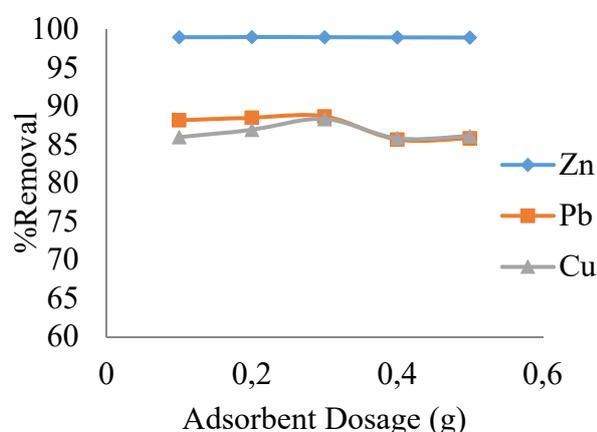


Figure 5: Effect of adsorbent dosage on % removal

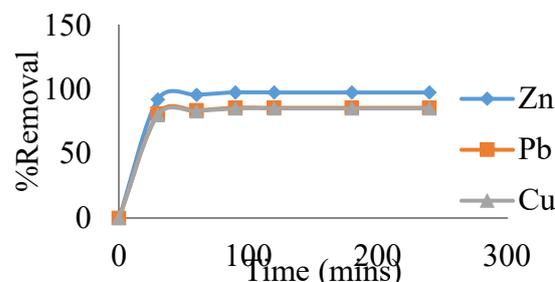


Figure 6: Effect of contact time on % removal

4. CONCLUSIONS

A new adsorbent was synthesized using local clay from Akerebiata, Ilorin modified with silver nanoparticles. The synthesis of Ag nanoparticles in a green process confirms the suitability of *Parkia biglobosa* leaf extract as a reducing, capping, and stabilizing agent. The local clay was also confirmed kaolinite in nature, rich in silica, and contains functional groups capable of binding metal ions to themselves. The adsorption of three heavy metal ions such as Zn^{2+} , Pb^{2+} , and Cu^{2+} onto the silver-modified clay was feasible, spontaneous, and exothermic in nature in the order $Zn^{2+} > Pb^{2+} > Cu^{2+}$. Therefore, the silver-clay adsorbent is suitable and efficient for removing heavy metal ions from an aqueous solution.

5. REFERENCES

1. Adebayo, G. B., Adegoke, H. I., and Fauzeeyat, S. *Applied Water Science*, **2020**, 10(9), 1.
2. Balali-mood, M., Naseri, K., Tahergorabi, Z., and Khazdair, M. R. *Frontiers in Pharmacology*, **2021**, 12(April), 1.
3. Bankole, M. T., Abdulkareem, A. S., Mohammed, I. A., Shaibu, S., Tijani, J. O., and Abubakre, O. K. *Scientific Report*, **2019**. May 2018, 1.
4. Dave, P. N., and Chopda, L. V. *Journal of Nanotechnology*, **2014**, 14.
5. Dutta, D., Borah, J. P., and Puzari, A. *Adsorption Science and Technology*, **2021**, 1.
6. Gardare, V. N., Yadav, S., Avhad, D. N., and Rathod, V. K. *Desalination and Water Treatment*, **2014**, December, 37.
7. Kariim, I., Abdulkareem, A. S., and Abubakre, O. K. *Scientific African*, **2020**, 7.
8. Kaur, A., and Sharma, S. *Indian Journal of Science and Technology*, **2017** 10(34), 1.
9. Lakherwal, D. *International Journal of Environmental Research and Development*, **2014**. 4(1), 41.
10. Mustapha, S., Ndamitso, M. M., Abdulkareem, A. S., Tijani, J. O., and Mohammed, A. K. *Heliyon*, **2019** 5(October), 1.
11. World Health Organization (WHO). (2008). *Guidelines for Drinking-water Quality. Third Edit*, Third Edition Incorporating First and Second Adden.