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Comparative Studies On Infrared Analysis of Some Waste Biomass in Heavy Metals Adsorption

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Abstract: *IR analysis of waste biomass used in the adsorption of toxic heavy metals from aqueous solution is critical for the evaluation of functional groups supporting adsorption. In this work, IR analysis of unmodified and modified Telfairia occidentalis (fluted pumpkin seed coat), Pentaclethra macrophylla (oil bean seed shell) and Cola nitida (kola nut pod husk) wastes biomass was carried out concerning the the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} from aqueous solution. Experimental parameters like the initial metal ion concentration, particle size, biosorbent dose, pH, temperature and contact time were considered in the adsorption study. From the results, O-H group (due to alcohol), C-H from an alkane, C-O from alcohol, C=C from alkenes and C-H from aromatic compounds were the functional groups observed in the spectra of unmodified Telfairia occidentalis, Pentaclethra macrophylla and Cola nitida showing that they were useful for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} from aqueous solutions while O-H, C-H, C=O, C=C, C-C and C-O functional groups due to the presence of alcohol, alkane, acid, ester and aromatic compounds were respectfully observed in the modified samples and assigned for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} from their aqueous solutions by modified Telfairia occidentalis, Pentaclethra macrophylla and Cola nitida. These functional groups appearing in both unmodified and modified Telfairia occidentalis, Pentaclethra macrophylla and Cola nitida were useful in rendering almost 100% removal efficiency for Cd^{2+}, Ni^{2+} and Pb^{2+}. Based on the IR analysis, the functional groups in the modified Telfairia occidentalis, Pentaclethra macrophylla and Cola nitida are more than those found in the unmodified samples. However, better adsorptions were observed concerning the unmodified Telfairia occidentalis, Pentaclethra macrophylla and Cola nitida. Therefore, adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified Telfairia occidentalis, Pentaclethra macrophylla and Cola nitida wastes can be actively analysed by FTIR.*

Keywords: *Adsorption, IR analysis, fluted pumpkin seed coat, oil bean seed shell and kola nut pod husk.*

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1.0 Introduction

Adsorption of toxic heavy metals from industrial effluents is very crucial since anthropogenic activities have resulted in elevated concentrations of these metals in the environment according to Ankley *et al.*, (1994). These toxic metals are not biodegradable hence, they can easily accumulate in the environment to constitute environmental threats (Garg *et aI.*, 2022).. Lead ions in wastewater have been shown to accumulate in agricultural areas, leading to increased concentrations in agricultural produce and farm animals (ATSDR, 1993). Evidence suggests that lead may cause fatigue, irritability, information-processing difficulties, memory problems, reduction in

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sensory and motor reaction times, decision-making impairment and lapses in concentration (Ehle and McKee, 1990). At blood concentrations above 70 mcg/dl, lead has been shown to cause anaemia, characterized by a reduction in haemoglobin levels, and erythropoiesis i.e. a shortened life span of red blood cells (Goyer 1988; U.S. EPA 1986a). Cadmium has carcinogenic and teratogenic effects, its effect has also been observed in epidemiological studies on animals (ATSDR, 1997; Calabrese and Kenyon, 1991; U.S.EPA 1999). Sorhan and Esmen, (2004); VerougstRatete *et al*., (2003) reported lung cancer due to chronic inhalation of cadmium. Inhalation exposure to some nickel compounds can cause a toxic effect on the respiratory tract and immune system (Smialowicz *et al*., 1984, 1985, 1987; ATSDR, 1988; Goyer, 1991). Acute inhalation of nickel may produce headache, nausea, respiratory disorders and death (Rendall *et al*., 1994). Therefore it is important to detoxify these metals-bearing effluents before discharge. The conventional methods for the treatment of effluents contaminated with heavy metals involve physicochemical processes such as electrodialysis, ultrafiltration, ion exchange, reverse osmosis, flocculation, crystallization, chemical oxidation or reduction etc. However, the aforementioned techniques are very expensive, may produce a large volume of waste, and sludge and are not economically feasible for small and medium industries (Volesky, 1990; Aksu 2005). Adsorption processes using natural adsorbents or agricultural waste products are becoming the new alternative for wastewater treatment because they are cheap, simple, sludge free, do not require additional nutrients, and regeneration of adsorbent and metals recovery possible (Kratochivil *et al*., 1998a). Heavy metals adsorption technology by biomass has some major advantages over conventional methods especially its effectiveness in reducing the concentration of heavy metal ions to very low levels and the adsorbent materials themselves are inexpensive (Volesky, 1994). Several researchers have reported on the use of agricultural wastes as a good substrate for the removal of metal ions from aqueous solutions such as tea waste (Mahri *et al.*, 2005), coconut fibre (Igwe *et al.*, 2006), maize cobs (Akporhonor *et al.*, 2007), cassava waste (Agiri and Akaranta, 2009) and so many others. These studies demonstrated that considerable amounts of metal ions can be removed from aqueous solutions by agricultural by-products rich in π-electron functional groups such as fluted pumpkin seed (*Telfairia occidentals*) coat, oil bean seed (*Pentaclethra macrophylla*) shell and kola nut pod (*Cola nitida*) husk. The fluted pumpkin seed coat is the waste generated during the processing of the fluted pumpkin seed. It has been reported that this waste serves as livestock meal but its digestibility is considered poor due to its anti-nutritional factors (Zuzana *et al.*, 2008). Due to the proximate composition of the fluted pumpkin seed (*Telfairia occidentalis*) coat (Agatemor, 2009), it has been classified as a lignocellulosic material, hence the interest in finding out its feasibility of adsorbing heavy metals from solutions. The shell from oil bean is also a waste or by-product for processing the seeds of *Pentaclethra macrophylla* and its nutritive quality has been reported (Odoemelam, 2005). When discharged into an environment such as an aquatic ecosystem, pollutes the aquatic bodies with a foul smell and obnoxious taste due to its decomposition in such a location. The presence of bromine as an anti-nutritional factor restricts its consumption and its high proximate composition (Allinor and Oze, 2011) had also classified it as a good cellulosic material and hence, can be used as an adsorbent. The husk of the kola nut pod is also wasted from processing the seed. Considerable quantities of this waste are suitable for use as feed components are lost or underutilized. Oluokun and Olalokun (1999) reported that Nigeria produced 2 million metric tons of kola nut annually which represented 70% of world kola nut production and its waste generated. Moreover, the presence of anti-nutritional factors such as theobromine, caffeine and tannin could reduce nutrient digestibility at high levels (Bate-Smith, 1973) hence, its use is limited and larger waste is generated. However, its proximate composition (Oladayo, 2010) classified it as a cellulosic material and its tannin composition also classified it as a good adsorbent for a wide range of solutes particularly bivalent metal cations (Laszlo *et al.*, 1994). The utilization of these wastes will minimize environmental pollution and equally manage waste. As waste management, they can be effectively utilized in the detoxification of heavy metal ions from an aqueous solution system. Therefore, this research undertakes the IR analysis of both modified and unmodified fluted pumpkin seed coat, oil bean seed shell and kola nut pod husk for the removal of Cd^{2+} Ni^{2+} and Pb^{2+} from their aqueous solutions.

2.0 Materials and Methods

2.1 Sample collection and preparation

All reagents used were of analytical grade, purchased and used without further purification. These wastes biomass were gotten by removing the shell of the oil bean seed, the coat of the fluted pumpkin seed and the husk of the kola nut pod which were obtained from Umuahia main Market, Abia State. These wastes were crushed, milled and washed with deionized water and oven dried at 50 ^{0}C for 12 hrs. They were sieved to obtain 250 µm size and activated with 2% (v/v) nitric acid overnight, washed with deionized water and finally oven-dried at 105^{0}C for 6hrs. The activated samples represented the unmodified sample. About 5 g portion of the activated 250 µm particle size of the samples was taken from the bulk of the activated samples and modified by soaking the samples into 1000 cm^3 of 0.3M mercaptoacetic acid at 25^{0}C for 24hrs. The mixtures were filtered, washed with deionized water and then with methanol. They were finally washed with de-ionized water and dried at 50^{0}C, the samples represented the modified samples for the experiment. 2g of both unmodified and modified samples each were soaked in methanol for 24 hrs. They were filtered and their filtrates were subjected to IR analysis.

3.0 Results and Discussion.

Fig 1-6 depicts the spectra for both unmodified and modified oil bean seed shell, fluted pumpkin seed coat and kola nut pod husk before adsorption while Table 1 shows the frequencies and functional groups of IR absorption by unmodified and modified oil bean seed shell, fluted pumpkin seed coat and kola nut pod husk.

Table 1: Frequencies and functional groups of IR absorption by unmodified and modified oil bean seed shell, fluted pumpkin seed coat and kola nut pod husk

Unmodified			
FPSC	**OBSS**	**KNPH**	**Assigned functional group**
3356.52	3362.62	3336.52	O–H stretch due to alcohol
2914.57	2920.71	2914.57	C – H stretch due to alkanes
1064.59	1061.52	1061.52	C – O stretch due to alcohol
892.84	886.71	-	C=C bend due to alkene
-	-	883.64	C – H bend due to aromatic compound
773.23	773.23	773.23	C – H bend due to aromatic compound
665.89	665.89	665.95	C=C bend due to alkene
Modified			
FPSC	**OBSS**	**KNPH**	**Assigned functional group**
3424.04	3448.59	3436.31	O – H stretch due to alcohol
2920.71	2914.57	2920.71	C – H stretch due to alkanes

2847.05	2840.92	2847.05	O – H stretch due to acids
1742.37	1739.31	1742.37	C = O stretch due to esters
1647.59	1644.23	1647.30	C = C stretch due to aromatic compounds
1460.22	1463.28	1463.28	C – C bend due to alkane
1273.14	1260.57	1263.94	C – O stretch due to alcohol
1159.66	1113.66	1159.66	C – O stretch due to ester
1021.65	1018.58	1024.94	C – O stretch due to ester
742.56	748.69	742.56	C – H bend due to aromatic compound

OBSS = oil bean seed shell, FPSC = fluted pumpkin seed coat, KNPH = kola nut pod husk.

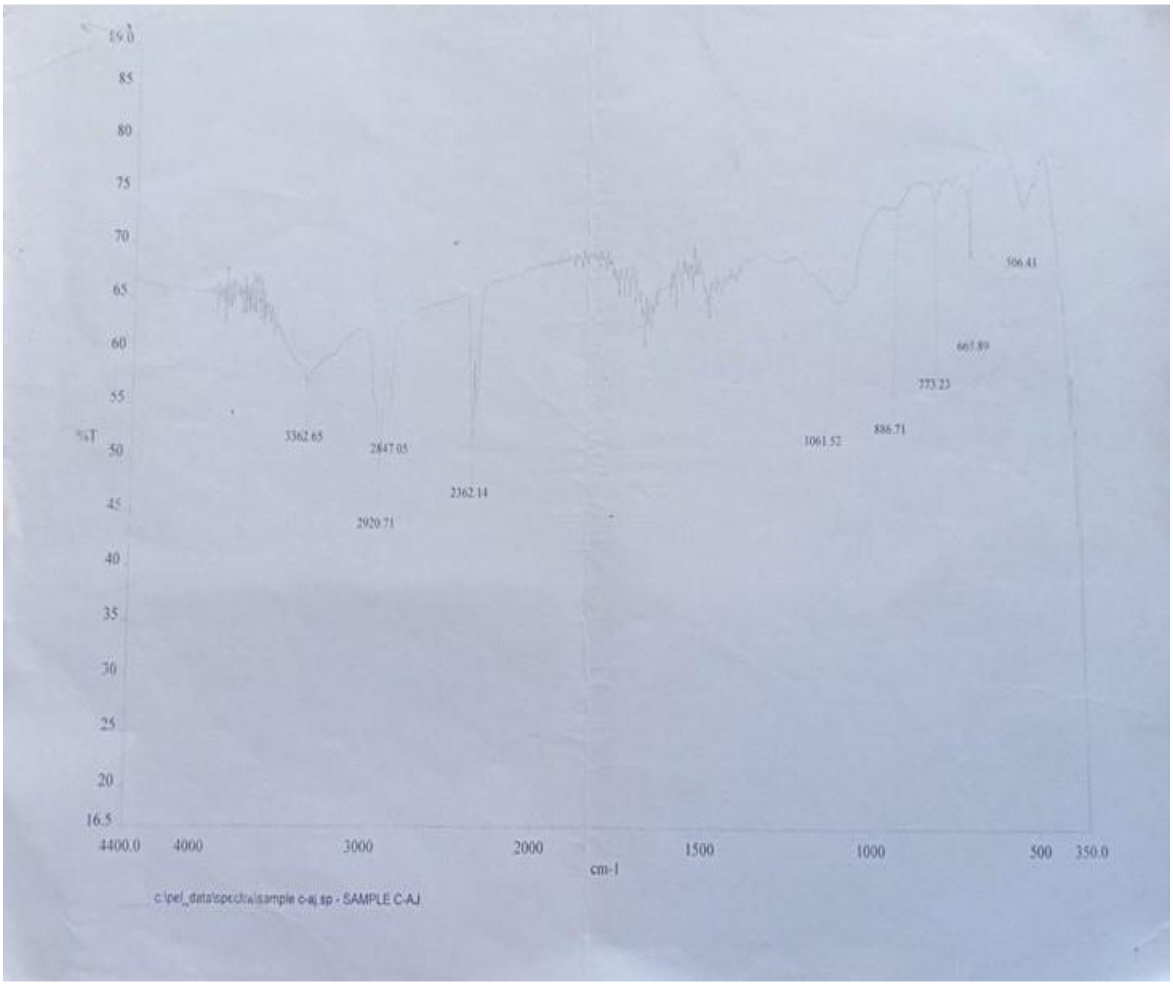

Fig 1: Spectrum of unmodified OBSS

The spectra of unmodified OBSS, FPSC and KNPH (Fig. 1-3) were compared with that of modified OBSS, FPSC and KNPH (Figs.4-6) The assigned functional groups of these spectra were shown in Table 1. From the results, the IR spectra of unmodified OBSS, FPSC and KNPH which showed the presence of a broad peak at 3356.52, 3362.65 and 3356.52 cm^{-1} indicated the presence of O-H functional group due to alcohol. Observed peaks at 2914.57, 2920.71 and 2914.57 cm^{-1} are due to the presence of C-H functional group attributed to alkane in their spectra respectively. C-H functional group was also observed at 2853.19 cm^{-1} in the FPSC sample. Peaks near 1064.59, 1061.52 and 1061.52 cm^{-1} are typical for C-O functional group due to alcohol. C=C bend due to alkene was also observed at peaks located at 892.84 and 886.71 cm^{-1} in FPSC and OBSS which was equally seen at peaks positioned in

665.89, 665.89 and 668.95 cm^{-1} for OBSS, FPSC and KNPH while C-H bend due to aromatic compound was observed at peak located at 883.64 cm^{-1} in KNPH.

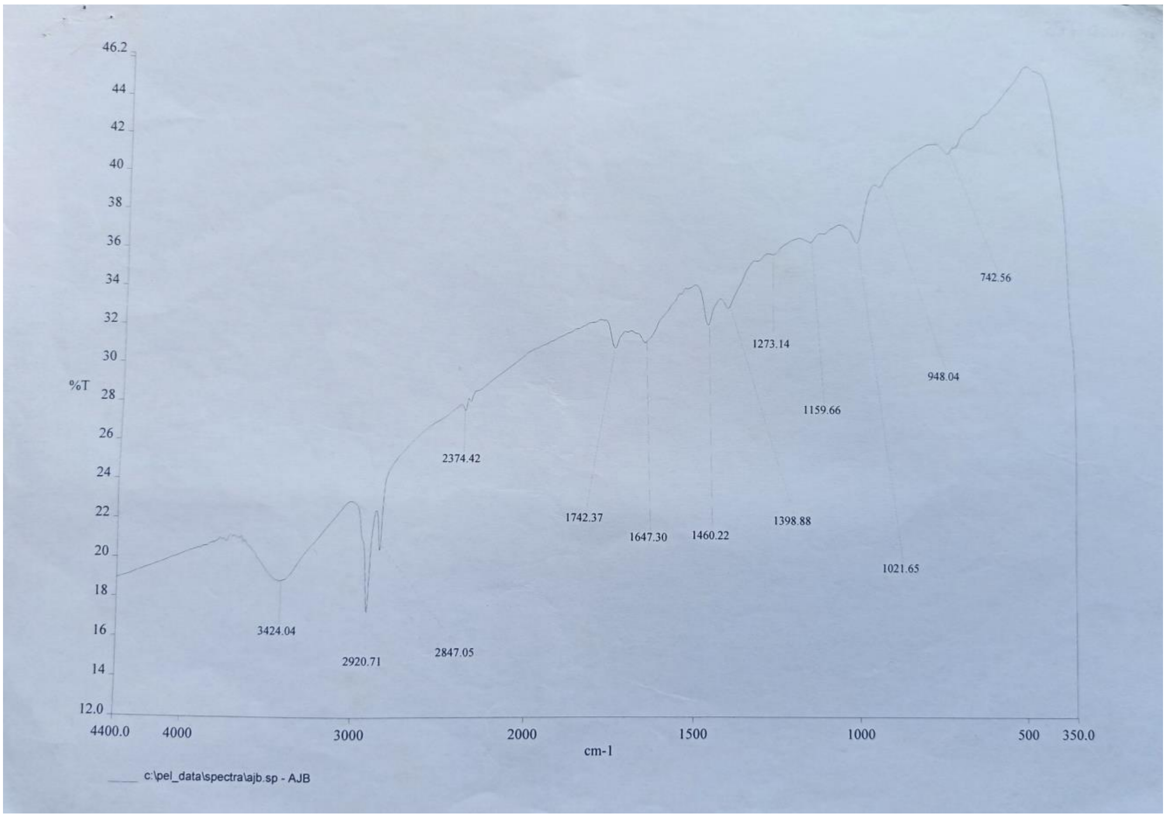

Fig 2: Spectrum of unmodified FPSC

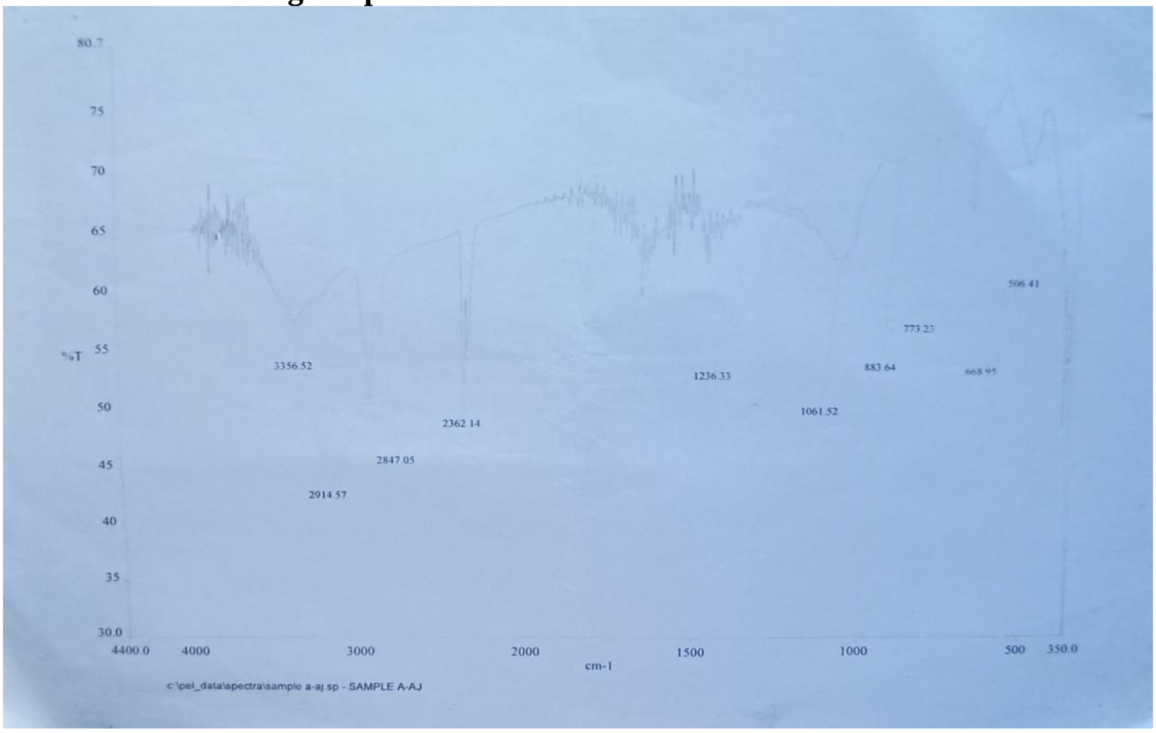

Fig 3: Spectrum of unmodified KNPH

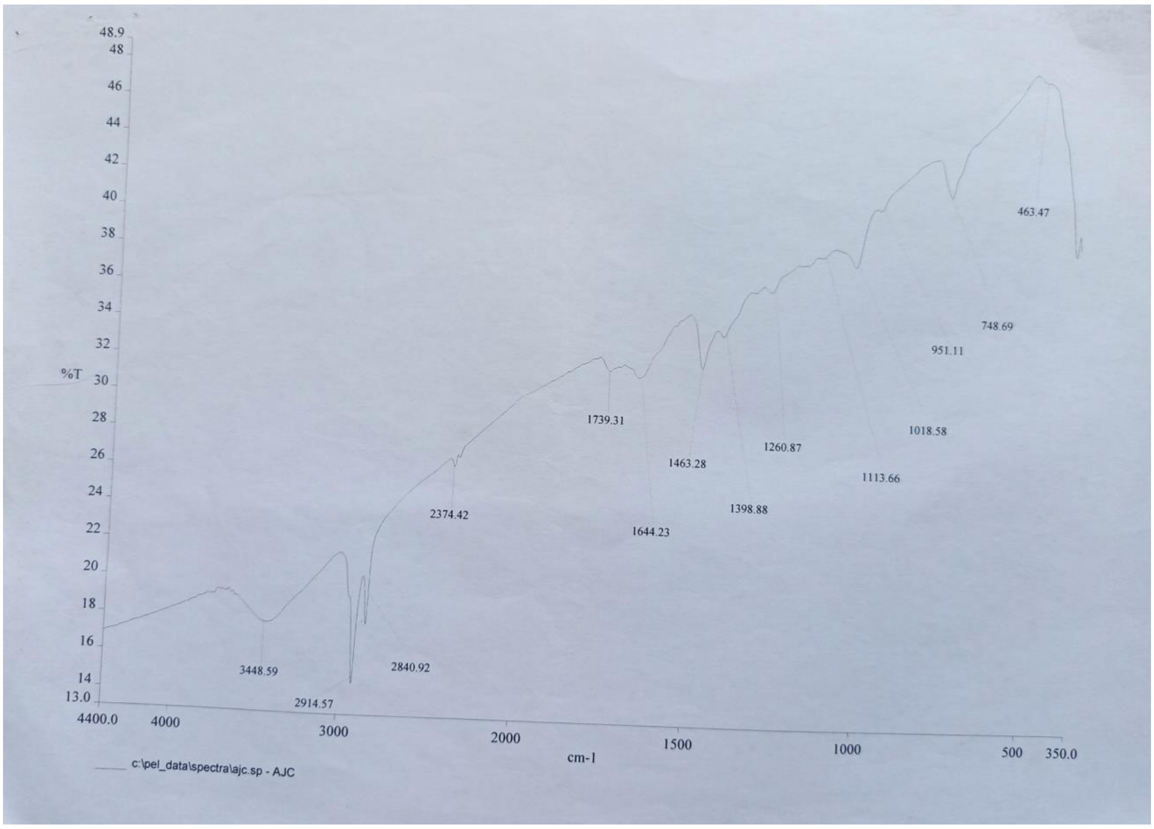

Fig 4: Spectrum of modified OBSS

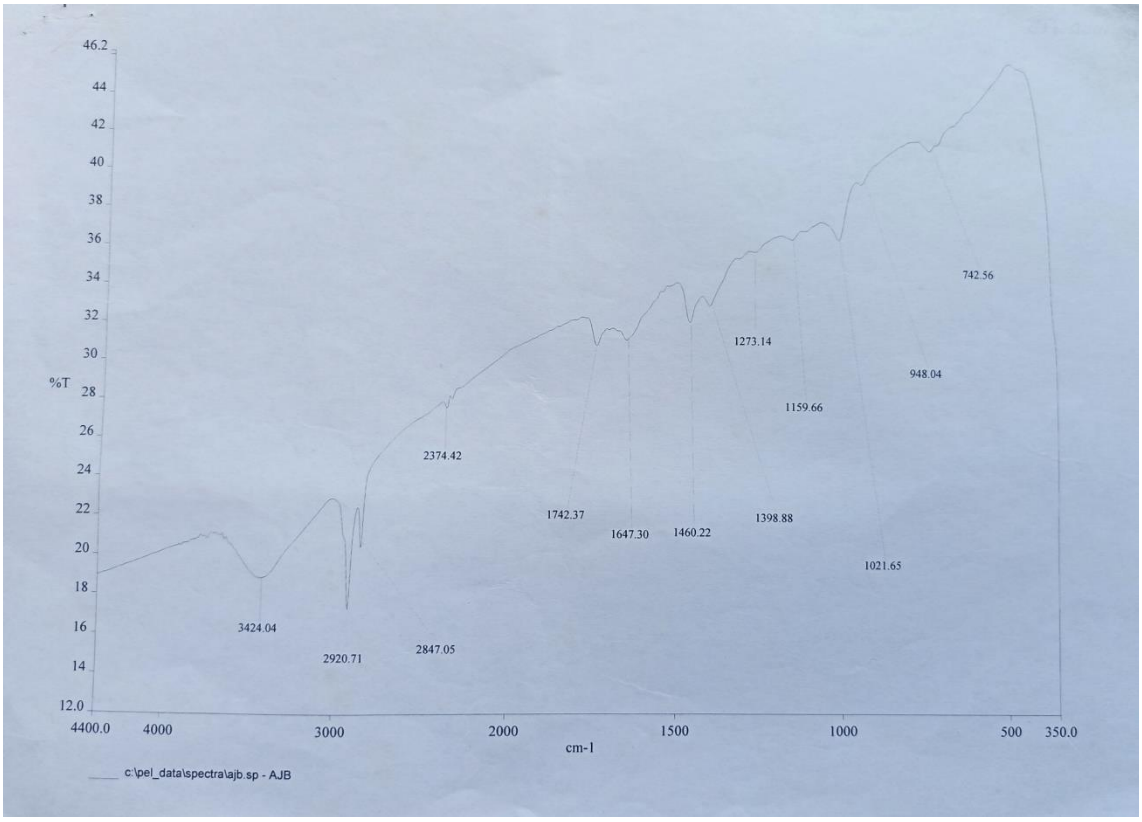

Fig 5: Spectrum of modified FPSC

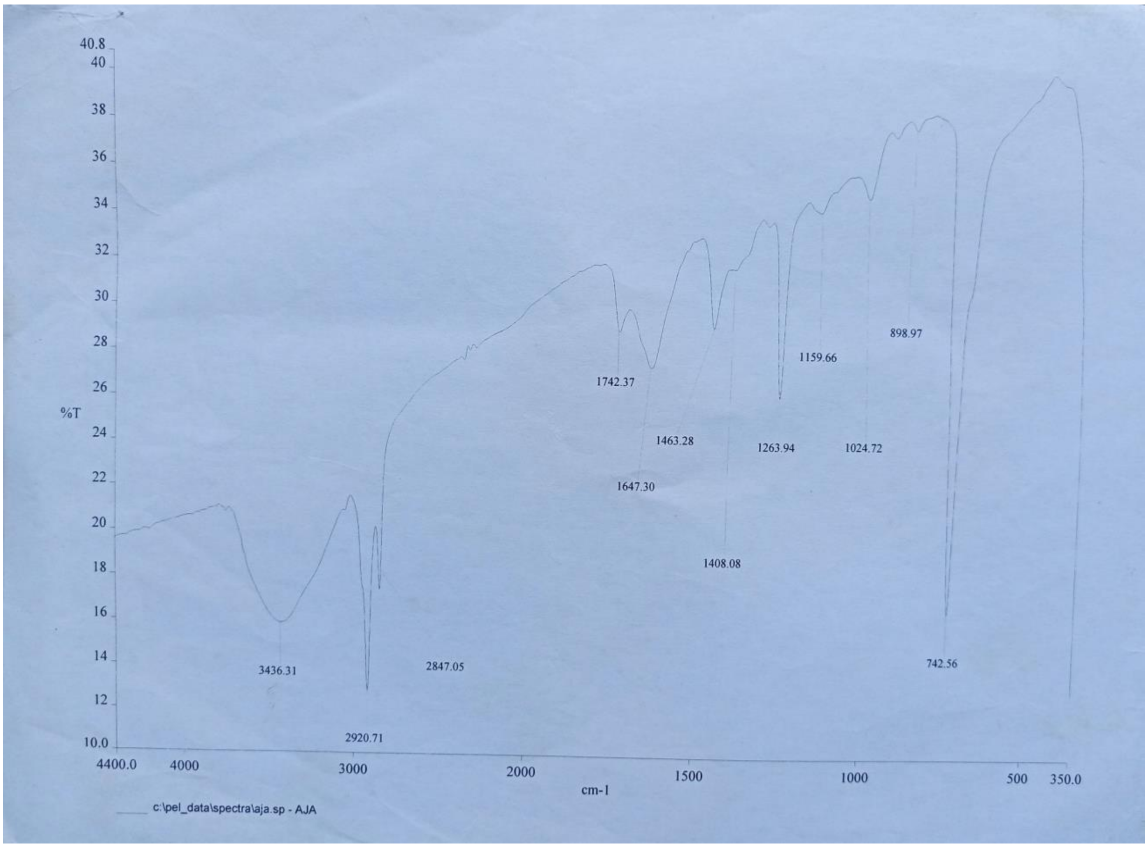

Fig 6: Spectrum of modified KNPH

The same C-H functional group was equally observed at peaks located at 773.23 cm^{-1} in the three wastes. For the modified samples of OBSS, FPSC and KNP, peaks at 3424.04, 3448.59 and 3436.31 cm^{-1}show the same O-H functional group due to alcohol and C-H functional group due to alkane also appearing at peaks located at 2920.71, 2914.57 and 2920.71 cm^{-1}.

Peaks located at 2847.05, 2840.92 and 2847.05 cm^{-1} indicated the presence of O-H functional group due to acids. C=O and C-O functional groups due to ester were observed at frequencies of 1742.37, 1739.31, 1273.14, 1260.87, 1263.94, 1159.66, 1113.66, 1159.66^{1}, 1021.65, 1018.58 and 1024.72 cm^{-1}. C=C functional group located at 1647.37, 1644.23 and 1647.30 cm^{-1} suggests the presence of the aromatic compound. Also, C-H bend at 742.56, 748.69 and 742.56 cm^{-1} may be attributed to aromatic deformities. Peaks at 1273.14, 1260.87 and 1263.94 cm^{-1} indicated the presence of C-O functional group due to alcohol while C-C bend due to alkane was found at 1460.22 and 1463.28 cm^{-1}.

It is evident from the above IR analysis that functional groups in the modified samples are more than those found in the unmodified samples. From the adsorption point of view, the greater the number of π-electron-rich functional groups, the better the expected extent of adsorption. However, the present results revealed that in almost all the samples, better adsorption potentials were attributed to the unmodified samples rather than the modified samples (Okwunodulu and Odoemelam, 2012, 2014; Okwunodulu and Eddy 2014; Okwunodulu *et al*., 2015, 2016, 2018, 2019). Therefore, the adsorption of Cd^{2+}, Ni^{2+} and $Pb^{2+}$by FPSC, OBSS and KNPH wastes is not solely dependent on the number of functional groups present in the adsorbent.

Missings shifted and new peaks observed after adsorption are the ones that were involved in adsorption (Eddy *et al*., 2023).

4. 0 Conclusion

IR analysis of waste biomass for toxic metal adsorption from aqueous solutions should be considered an important factor since it can ascertain the functional groups responsible for such adsorption. In this work, IR analysis of both unmodified and modified *Telfairia occidentalis, Pentaclethra macrophylla and Cola nitida* wastes biomass were determined which pointed out more functional groups in the modified samples than in unmodified samples indicating that adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by these samples is not solely dependent on the number of functional groups present in the adsorbent since better adsorption potentials were attributed to the unmodified samples.

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