

Morphological Characteristics Of Cassava Peel And Its Effect On The Adsorption Of Heavy Metal Ions From Aqueous Media

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Abstract—Elevated levels of heavy metals like copper and nickel in aqueous system have deleterious effect. In this work, the efficacy of cassava peel (CP) as alternative low cost biosorbent for removal of Ni²⁺ and Cu²⁺ from aqueous solutions has been investigated. Batch adsorption studies were carried out to evaluate the effects of solution pH and initial metal concentration on extraction efficiency.

The adsorption experiments were conducted keeping the concentration of biosorbent (CP) constant (100 mg) at different concentrations of metal ions. The CPs recorded high extraction efficiencies (EEs) of > 90 % in extracting the Cu and Ni ions. Specifically, the maximum removal was found to be 99.8 % for Ni²⁺ and 98.9 % for Cu²⁺. Cassava peel was found to be efficient for all the considered metal ions at acidic pH of 6.0.

The morphologies, thermal stabilities and biosorption mechanisms of the CPs were studied using Scanning Electron Microscope (SEM), Thermogravimetry Analyzer (TGA) and Fourier transform-infra red (FTIR) Spectrometer. The CP sorbents were therefore found to be efficient sorbents that are well suited for handling trace metals in aqueous media.

Keywords—Adsorption, Characterization, Metal Ions, and Cassava peel

INTRODUCTION

There are many heavy metals in our environment both naturally and from pollution. Several heavy metal ions such as Pb(II), Cu(II) and Ni(II) etc. have been included in the U.S. Environmental Protection Agency's list of priority pollutants [1]. Heavy metal contamination has become a fundamental issue for the past decades

until now. The main sources of generation of these toxic pollutants are smelting and refining processes, electroplating industry, municipal and industrial wastes [2].

Aggregation of heavy metal ions in the human body can lead to many enervating effects and numerous other health problems [3-4]. Thus, the complete removal of these metal ions form an important effort in the protection of environment and water resources. A wide range of conventional methods are available for the removal of metal ions from aqueous solutions. These include oxidation, reduction, precipitation, seashells, pyrolysis, membrane filtration, ion exchange and adsorption [5]. Among all methods mentioned above, adsorption process has been the most promising and frequently applied method [6].

Various materials have been employed as the adsorbents in the previous researches, such as sawdust [7], fly ash [8], zeolite [9], modified clay [10], and so on. In recent times, biosorption process using agricultural waste products are becoming the new alternative for removal of toxic and deleterious metals from aqueous solution due to its selectivity, low operational cost, high efficiency and sludge free [11,12].

Cassava is grown in tropical regions, especially Nigeria [13]. It is one of the major sources of staple carbohydrate food [14]. It has two layers, the outer and inner layer. The inner layer is used in food processing, while the outer layer is the major by – product called the cassava peel (CP)[15].

Cassava peel is one of the major biomass wastes in Nigeria obtained from production of cassava tuber for human consumption, starch production and industrial applications [16].

Hence, this paper aims to investigate the possibility of using cassava peel waste as an alternative adsorbent for copper and nickel removal from wastewater, and also to study the chemical compositions and morphological properties of cassava peel sorbent.

MATERIALS AND METHODS

Chemicals

All the chemicals were of analytical grade and were used without any further purification. Metallic solutions were obtained from a stock standard (1000 mg/L) of Cu(II) and Ni (II) supplied by Buck Scientific Incorporation (Norwalk, United State of America). All glassware was soaked overnight in 4 M HNO₃ solution prior to use.

Preparation of biosorbent

Cassava peels used in this study as shown in figure 1, were collected as refuse from a local processing factory in Odo-aye community area of Ijebu-Ode in Ogun state, Nigeria. The method as described by Kosasih *et al* [12] was used. Firstly, cassava peel was washed with tap water repeatedly to get rid of surface dirt. The peel was afterwards dried in open air for at least 24 h before dried further in oven at 100 °C for another 24 h to substantially reduce its moisture content. The dried peel was then crushed to fine powder by an IKA-Laborotechnick grinder and passed through the 75µm sieve.



Fig. 1. Cassava processing factory at Odo-aye community

Biosorption studies

The adsorption experiment was performed on a mechanical shaker at room temperature by adding an optimal quantity of the CP (100 mg) to 20 mL of metal solutions with initial concentrations of Cu and Ni in aqueous solution ranging from 10 to 40 mg/L. Initial pH of the solutions was adjusted to desired pH by adding 0.1M HCl and/or NaOH solutions to the medium to maintain a constant pH. After shaking for 6 h, the CPs were separated by centrifugation at 12,000 rpm for 5 min, and the concentration of each metal ion in the mixed solution was determined by Atomic adsorption spectrophotometer. Three replicate extractions and

measurements were performed for each solution. The extraction percentage of each metal was calculated from Eq. 1;

$$\text{Extraction (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i = is the initial metal concentration (mg/L)

C_f = is the metal concentration at adsorption equilibrium (mg/L)

Scanning electron microscopy (SEM)

The method as described by Awokoya *et al* [17] was used to determine the surface morphologies of the CPs. The sorbents were dusted onto a carbon sticker, and then coated with gold using a sputter coater FL-9496 (Balzers Union, Balzers, Liechtenstein) for 30 min. Images were recorded using Vega Tescan SEM fitted with an Oxford instrument INCA PentaFETx3 EDS.

FT-IR spectroscopy

The Fourier transform infrared (FT-IR) spectra of the CPs were obtained using a PerkinElmer (Waltham, MA, USA) Spectrum 100 FT-IR spectrometer with an AutoIMAGE system as described by Awokoya *et al* [17]

Thermogravimetric analysis (TGA)

The method as described by Awokoya *et al* [17] was used to determine the thermal stability of the CPs. Approximately 2 mg of the CPs were placed in an open aluminum pan. The sample was heated at a rate of 10 °C min⁻¹ from 45 °C to 650 °C under a nitrogen atmosphere (flow rate = 20 mL min⁻¹) using a PerkinElmer TGA 7 with System 2000 FTIR spectrometer.

RESULTS AND DISCUSSION

Characterization of CPs

The surface morphology of cassava peel at four different magnifications is presented in Fig. 2. An observation of the cassava peel surface revealed that pore space development within the biomass was very noticeable. As can be seen, Fig. 2 confirmed the heterogeneity characteristics and complex nature of cassava peel surface. Similar observations were reported by the previous researchers for sequestering of Cu (II) from aqueous solution using cassava peel [12].

Fig. 3 shows the Fourier Transform Infrared (FTIR) results of the original and metal loaded cassava peel. The molecular structure of a sorbent material is fundamental in understanding its adsorption process. The FTIR spectra of cassava peel before and after adsorption of metal ions were carried out to advance better understanding into the functional groups available on the surface of the studied sorbent.

From the FTIR spectrum, it was observed that for the metal loaded cassava peel, some peaks were altered in terms of wavenumber which is an evidence that these functional groups were involved in metal

binding. After adsorption of the metal ions, the spectrum revealed bands at 2858 and 3223 cm^{-1} which were assigned to C–H, O–H stretching vibration, respectively. In addition, existence of the peak at 1600 cm^{-1} was also observed, representing C–O stretch of the metal carboxylate group.

TGA curves of the cassava peel and cassava peel loaded with metal are given in Fig. 4. TG analysis is useful in obtaining sufficient knowledge on the sorbent relative thermal stability, and it also helps with the

choice of materials for analytical purposes focused on metal binding studies [18]. The TG curves showed that the materials until 100°C present a loss of 5 wt% corresponding to the humidity. In the range between 300 and 390°C occurred a loss of 80 wt% in cassava peel and of 75 wt% in cassava peel loaded with metal which might be due to the decomposition of organic groups, namely, hydroxyl, carboxyl and carboxylate. The weight loss around 570°C for cassava peel loaded with metal offered confirmation that metal binding unto the sorbent was successful.

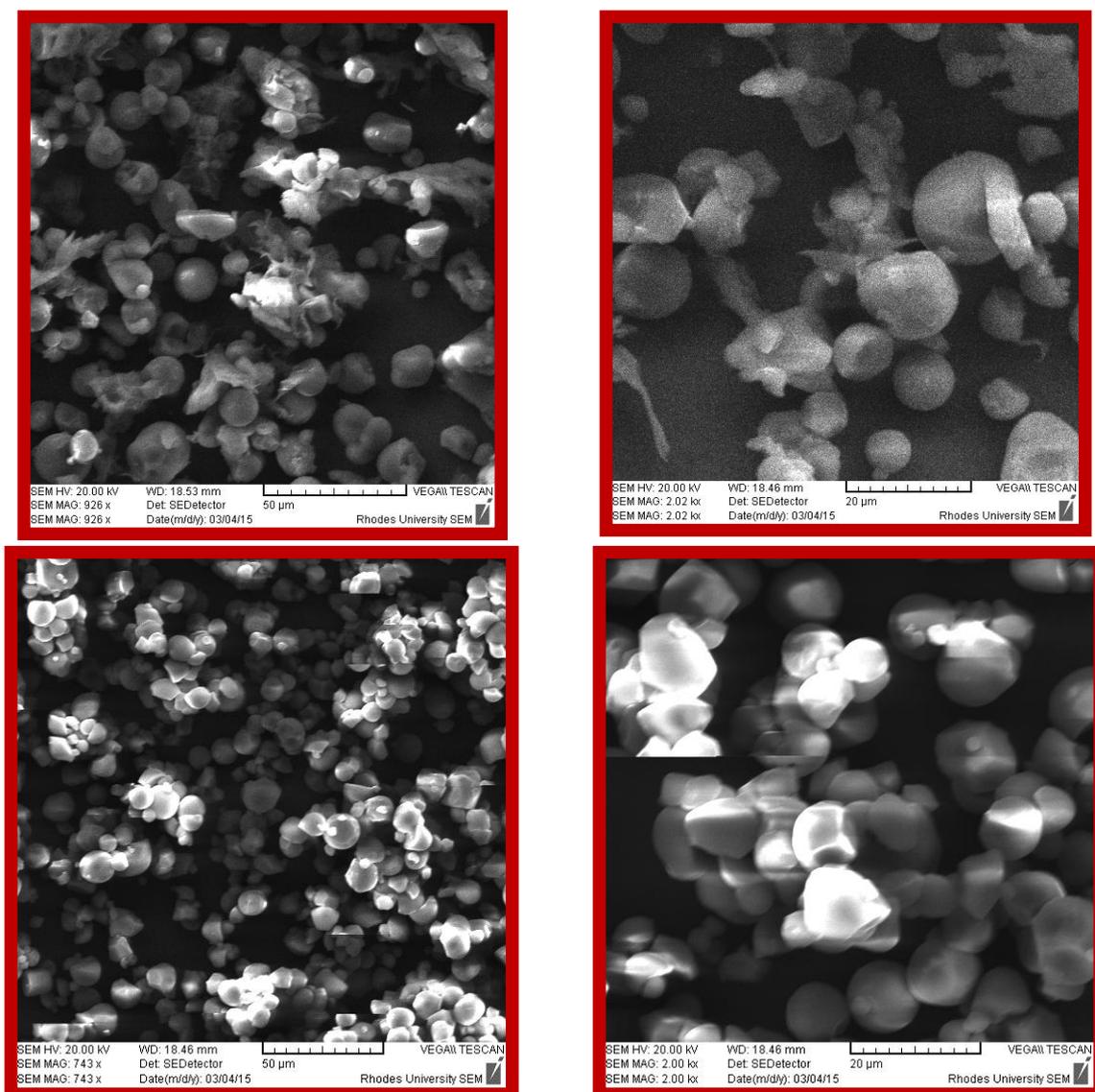


Fig. 2. SEM micrographs of cassava peel at four magnifications 926 x, 2.02 kx, 743 x, and 2.00 kx.

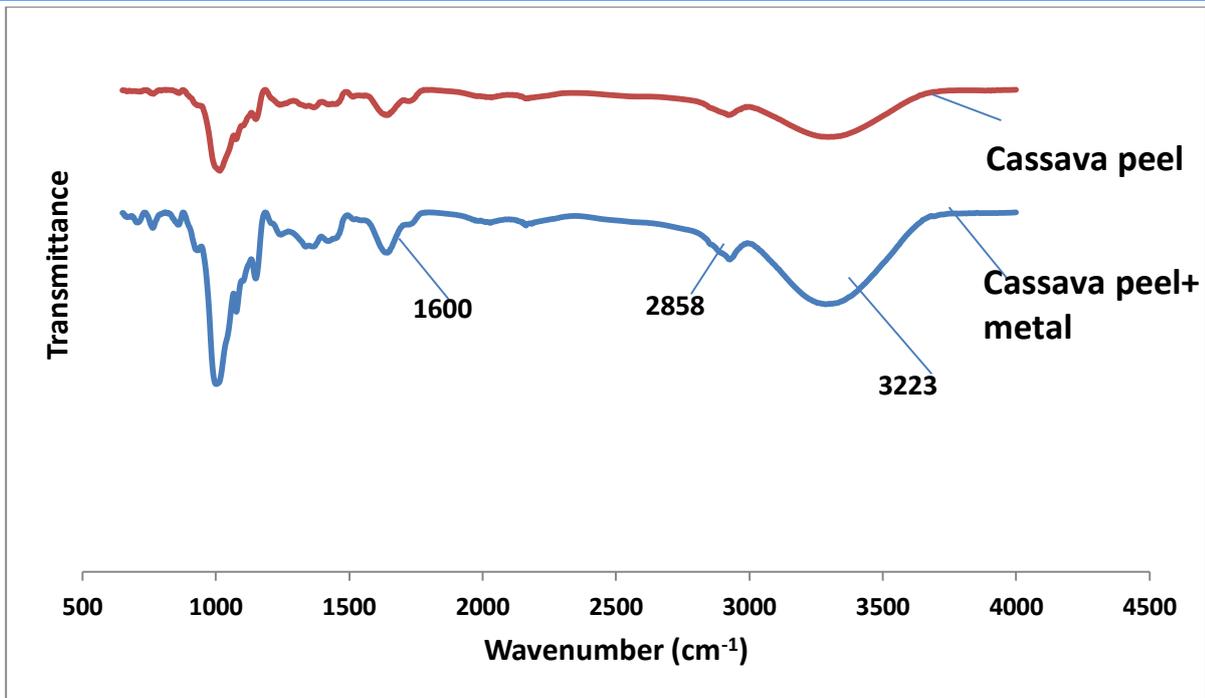


Fig. 3. FTIR spectra for cassava peel before and after loaded with metal

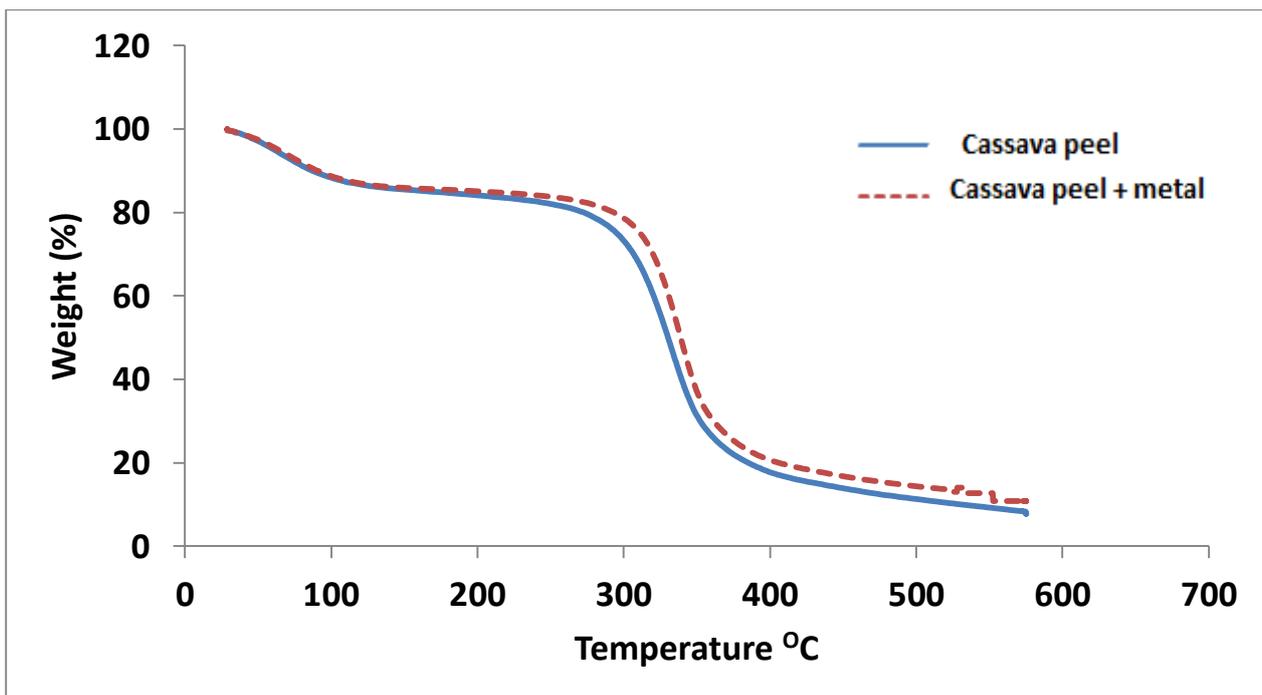


Fig. 4. Thermogravimetry analysis (TGA) curves of cassava peel before and after loaded with metal

Adsorption of Cu^{2+} and Ni^{2+}

Adsorption has been defined by many authors but conventionally it is accepted as the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface [19]. The percentage adsorption of heavy metal ions at different metal concentrations are shown in Figs. 5 and 6.

Equilibrium batch adsorption experiments were conducted keeping the concentration of biosorbent (CP) constant (100 mg) at different concentrations of

metal ions. The CPs recorded high extraction efficiencies (EEs) of > 90 % in extracting the Cu and Ni ions.

Specifically, the maximum removal was found to be 99.8 % for Ni^{2+} and 98.9 % for Cu^{2+} . The results indicated that energetically all the biosorbent sites were involved in the metal binding interactions. The heavy metal uptake could be attributed to different mechanisms of ion-exchange processes as well as to the adsorption process. This observation lends

credence to similar results that have been reported [20].

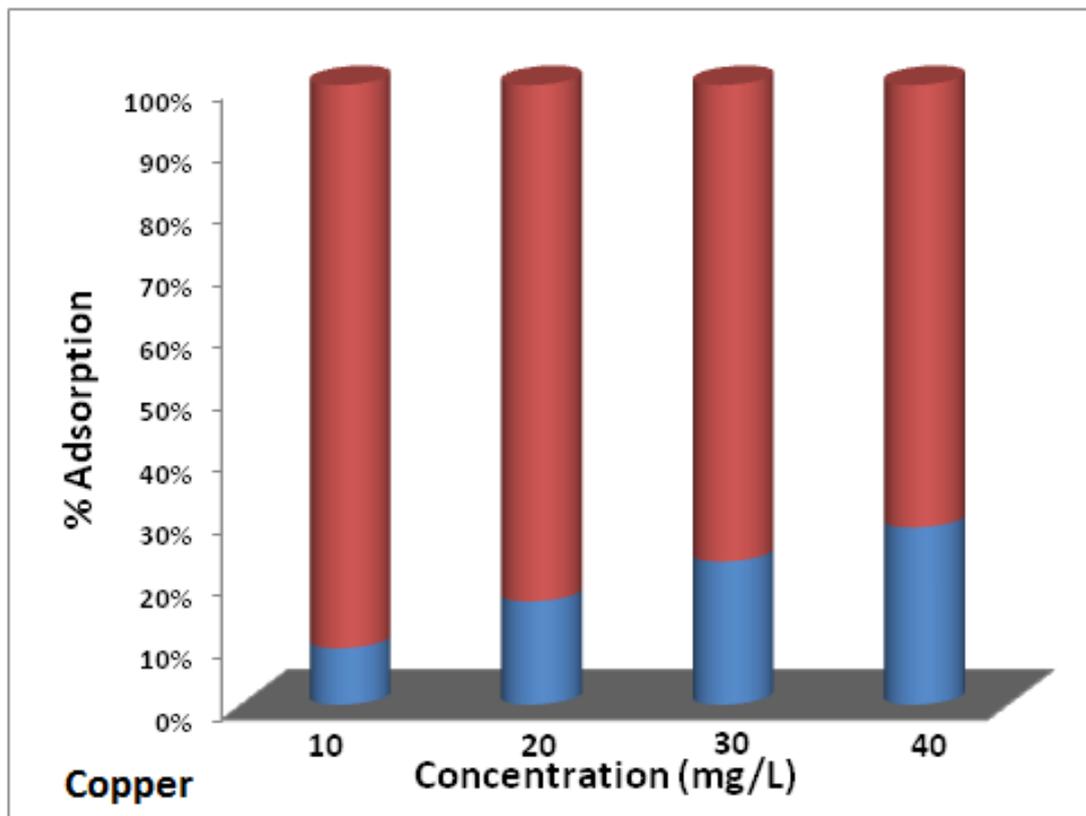


Fig.5. Analysis of the rebinding of CP with Cu(II) ion at room temperature for 6 h

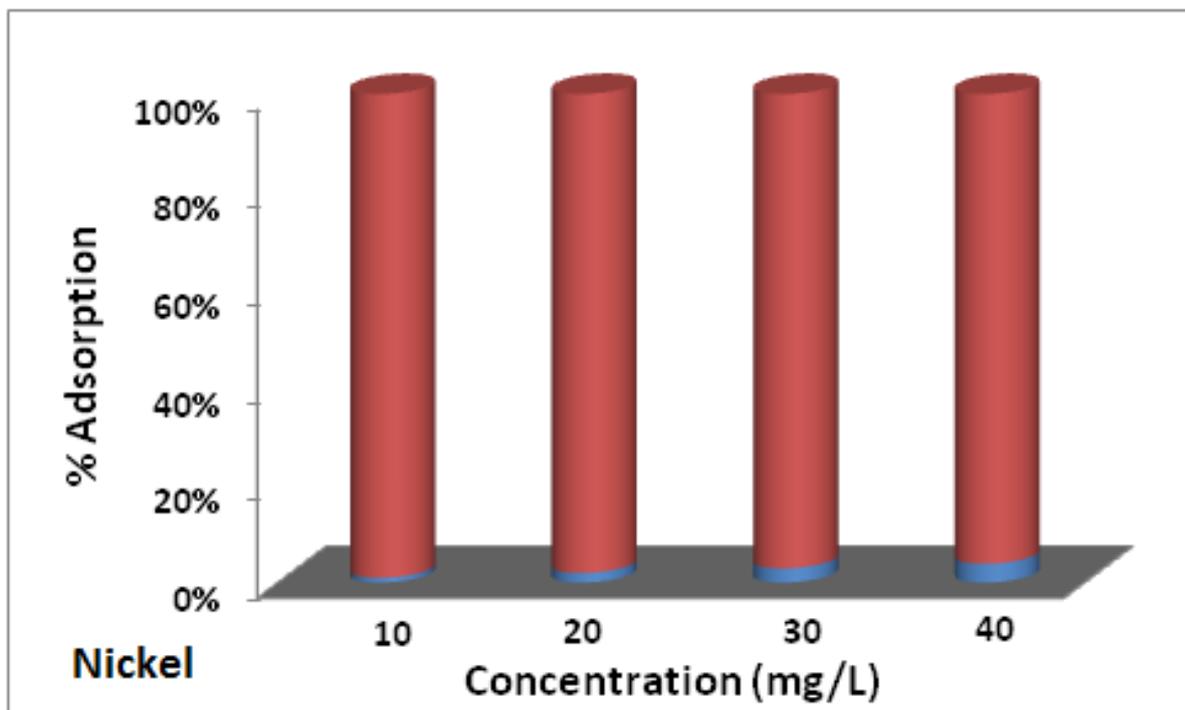


Fig.6. Analysis of the rebinding of CP with Ni(II) ion at room temperature for 6 h

Effect of pH on adsorption

One of the most important factors affecting adsorption capacity of metal ions is the acidity of solutions because H^+ ions compete with the metal cations for the binding sites on the CPs [21,22]. The concentration of H^+ ion in an acidic solution is relatively high and they tend to fill up the binding sites on the CP's surface. This observation is consistent with previous report on sorption of toxic metal ions in aqueous environment using electrospun polystyrene fibres incorporating diazole ligands [23]. Fig.7 shows the relationship between the pH value of metal ion solution

and adsorption capacity of CP for Cu^{2+} and Ni^{2+} . A range of initial pH values of the solution from pH 2 to 8 was used. The adsorption of the metal ions increased rapidly with the increase in the solution pH until it reached equilibrium where no significant observed change with pH. The optimal pH for adsorption was found to be 6.0, which indicated that the maximum removal percentage took place in moderately and slightly acidic medium. The adsorption curves and the optimal pH values obtained in the work are similar to those observed in the previous studies. For example, Onwu and Ogah found the pH of 6 as the optimal for quantitative recovery of Cd^{2+} [24].

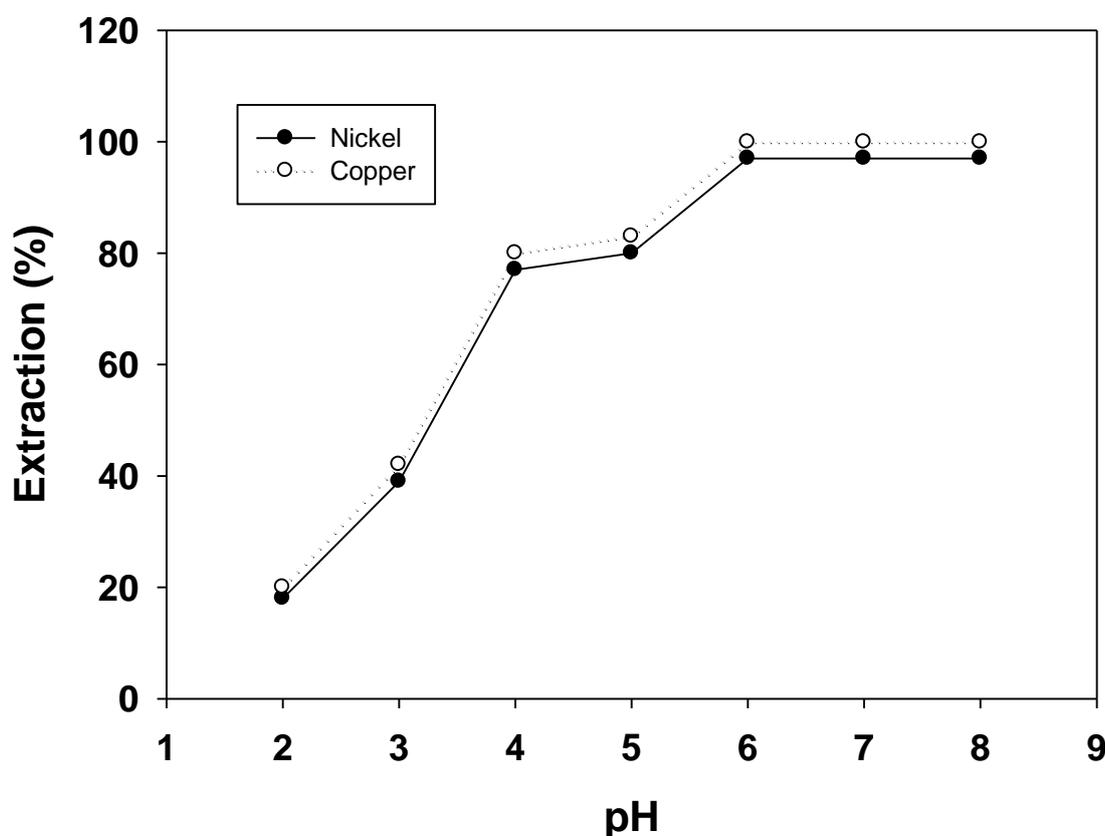


Fig. 7. Effect of pH on ions removal

CONCLUSIONS

In this research, feasibility of CPs in the removal of metal ions (with potential toxicity) from aqueous solutions was reported. The results showed that CPs can be successfully used for the extraction of Cu (II) and Ni (II) ions from aqueous system. CPs provide a good heterogeneity characteristics and a strong van der Waals binding energy. In addition, the adsorption of the metal ions on the biosorbent increased with increase in adsorption pH, and then leveled off at precisely pH 6. SEM, TGA and FTIR results indicate that binding of metal ions unto CP biosorbent has impact on the surface morphology, thermal properties and molecular structure of the biosorbent. Work to verify the effect of crosslinked breadfruit starch

(*Artocarpus altilis*) on the adsorption of porphyrins from organic media is currently underway.

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