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Chemical Modification of Kola-Nut (Cola Nitida) Testa for Adsorption of Cu2+, Fe2+, Mg2+, Pb2, and Zn2+ from Aqueous Solution

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Chemical Modification of Kola-Nut (Cola Nitida) Testa for Adsorption of Cu²⁺, Fe²⁺, Mg²⁺, Pb², and Zn²⁺ from Aqueous Solution

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Abstract

In this study, kola-nut testa samples were modified with 0.1 M acetic acid and 0.1 M EDTA at room temperature. The modified Kola-nut testa samples were then characterized with respect to their pH at point of zero charge, melting point, specific gravity, Fourier-transform infrared (FTIR) spectra, and solubility. The characterization results of the modified Kola-nut testa (MKT) revealed that it was sparingly soluble in water, ethanol, and acetone but insoluble in n-hexane. The MKT had a specific gravity of 0.992 ± 0.020 and exhibited various pH values of 4.50 ± 0.50 and 12.00 ± 0.50 at the point of zero charges. The FTIR spectra of the MKT indicated the presence of −OH and −NH groups at 3310.97 cm⁻¹, alkyl groups at 2928.53 cm⁻¹, and aromatic rings at 1612.27−1529.81 cm⁻¹. The results of the adsorption studies at various time intervals indicated that MKT had the capacity to adsorb Fe^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, and Pb^{2+} as follows: 1.90 ± 0.30 mg/g, 1.80 ± 0.20 mg/g, 1.40 ± 0.20 mg/g, 0.10 ± 0.01 mg/g, and 0.05 ± 0.01 mg/g, respectively. Thus, Fe^{2+}, Mg^{2+}, and Zn^{2+} were quantitatively removed from the aqueous solutions, whereas Cu^{2+} and Pb^{2+} were not. The adsorption of Fe^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, and Pb^{2+} by MKT from the aqueous medium was dependent on certain factors such as pH, temperature, adsorbent dosage, contact time, and initial metal-ion concentration.

Keywords: modified kola-nut testa, agro waste, adsorption, heavy-metal ions, EDTA

Introduction

The utilization of agro-waste materials in the remediation of wastewaters containing heavy metals has generated a lot of interest from researchers because of the availability of these materials at no cost and their biodegradability [1]. Agro-wastes have been found to be effective in the treatment of effluents laden with heavy metals [2-3]. Agro-waste materials like tur-dal husks, tamarind husks, and Bengal gram husks could be used as adsorbents for the decontamination of effluents laden with Hg^{2+}, Fe^{3+}, Ni^{2+}, and Cr^{6+}.[3] Other researchers have utilized agro-waste materials in the adsorption of heavy metals from aqueous solution [4-7]. The versatility of agro-waste in water treatment processes has received equal attention [2].

However, the utilization of agro-waste materials for other purposes may have cost implications because some agricultural products generate relatively high volumes of agro-waste at the point of processing [1]. Examples of these produces include sugarcane, kola nuts, groundnuts, oranges, mangos, watermelons, grains, and blood and bones from slaughter houses. The cost implication, however, is minimal compared to the gain derived from the end use of the agro-waste

material. For example, urban waste facilities in Nanyang, China supply over twenty thousand homes with biogas [8]. In other regions of the world, specifically the United States, some farmers convert their agro-wastes into biogas (methane) to generate all the fuel they need to run their farms in situ [9]. The entire process is cost-effective and the agro-waste generated can be endlessly recycled and reused, thereby greatly minimizing their environmental burden and associated health hazards. These applications of agro-wastes greatly reduce the disease burden of pollutants in the environment.

Anthropogenic sources are largely responsible for the contamination of natural water supplies with heavy metals [5], and researchers have expressed grave concern about the consequences of heavy metals in the environment [4, 10-16]. Long-term exposure to heavy metals is known to be deleterious to human health [17]. The physical properties of heavy metals, i.e., good electrical conduction, strength, rich hue, durability, and good optical properties [18], have led to their presence in virtually all aspects of contemporary life [19]. To negate their impact on the environment, the need to remove them from wastewaters has gained much attention from both 'town and gown' communities

around the world. The shortcomings of conventional methods in the removal of heavy metals from aqueous solution, including their non-biodegradability and high cost and energy requirements, necessitates research to identify low-cost biodegradable materials [20-21].

The use of rice husks [22], the barks of dead biomass [23], peanut testa [6, 24], onion skins [7, 25], and several other agro-waste materials[26] have been reported in the removal of heavy metals from aqueous solutions. However, there is no documentation of reports on the use of kola-nut waste in the removal of heavy metals. In Southern Nigeria, the processing of kola nuts generates a tremendous amount of waste, which is indiscriminately discarded in the environment and constitutes a nuisance [27]. Were it to be fully harnessed, this "nuisance" could offer a potential solution to water pollution problems. Phytochemical analysis of the kola-nut reveals that it contains tannins, alkaloids, saponins, glycosides, volatile oils, and steroids [28], which provides a scientific basis for its various uses. According to numerous reports, the chemical modification of agro-waste can greatly enhance the sorption capacity for heavy metals in aqueous solutions [6, 7, 23, 25, 29, 30]. Thus, in this work; we explore the potential of unmodified and chemically modified kola-nut testa in the adsorption of some heavy metals.

Methods

Sample preparation. In this experiment, we used analytical-grade reagents obtained from BDH. Fresh samples of kola nuts were obtained from the Omuma community in the state of Rivers, Nigeria and were properly identified at the University of Port Harcourt herbarium. The kola nuts were hulled and their testas were washed, sun-dried, and sieved to particles 63 μm in size for subsequent treatment with acetic acid and EDTA.

Modification and characterization of kola-nut testa. The method reported by Abdullahi [31] was adopted with slight modification. We equilibrated 100 g of kola-nut testa (63-μm particle size) with 0.1 M acetic acid for 24 hours. The mixture was filtered after 24 hours and washed several times with deionized water. The residue was then oven dried at 100 °C for 3 h and further equilibrated with 0.1 M EDTA for 24 hours. Finally, the mixture was filtered, and the residue was sun-dried. The dried residue was kept in a clean plastic bag and labeled as modified kola-nut testa (MKT). The MKT was then characterized to determine its specific gravity, solubility, melting point, pH at point of zero charge, and infrared spectra.

The melting point, solubility, and specific gravity were determined using methods described in the literature.[31, 32] The functional groups of MKT were determined using a table-top Alpha Fourier-transform infrared (FTIR)

spectrophotometer (Brucker: 12028429). The pH was measured using a Hanna pH meter (Model H12211), and the pH at point of zero charge was determined according to the method described in the literature [31-32].

Preparation of metal ion solutions. A concentration of 100 ppm was prepared for each of the following metal-ion solutions (Pb^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, and Mg^{2+}) by determining the appropriate masses of their salts using a Radway Analytical Balance (Model AS220/C/2). The following amounts of metal salts were obtained: A 0.1598 g of $Pb(NO_3)_2$, 0.3357 g of $(CH_3COO)_2Zn.2H_2O$, 0.3174 g of $CuSO_4.5H_2O$, 0.6448 g of $(NH_4)_2SO_4.FeO_4.6H_2O$, and 0.6905 g of $MgCl.6H_2O$. Each of these metal salts was dissolved in 1000-ml volumetric flasks with deionized water.

Adsorption studies. The capacity of MKT to adsorb the heavy-metal ions (Pb^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+} and Mg^{2+}) from aqueous solution was investigated under different equilibrium conditions (temperature, pH, contact time, initial metal-ion concentration, and adsorbent dose). Five (5) ml of each metal-ion stock solution was used to make up 50 ml with deionized water in 250-ml Erlenmeyer flasks. The pH of each metal solution in the flasks (working solution) was set to 6.0 using appropriate buffer solutions.

To each metal solution, we added 0.2010 g of MKT and the mixtures were agitated for 2 h at room temperature. Then, we filtered the mixtures through Whatmann No. 13 filter paper and collected the filtrates in sterile plastic containers. The final metal-ion concentration in each filtrate was determined using a Buck Atomic Absorption Spectrophotometer (AAS, Model: 210/211 VGP). The capacity of MKT to adsorb each of the heavy metals from aqueous solution was then evaluated using Equation 1.

The effect of temperature on the adsorption of the heavy metals by MKT from aqueous solution was determined by varying the temperatures from 40–80 °C. Each metal salt solution (10 ppm) was prepared from its stock solution, to which 0.2010 g of MKT was added. The mixture was agitated several times and then transferred to a thermostat water bath pre-set to the respective temperature (40–80 °C) for 10 min. At 10-min intervals, the mixture at that particular temperature was removed from the water bath, agitated, and filtered through the Whatmann No. 13 filter paper. The filtrate was collected and the metal-ion concentration determined using the Buck AAS. The amount of heavy-metal ions adsorbed by MKT at each temperature was calculated using the following mass balance equation [34]:

$$Q_e = \left[\frac{Co - Ce}{m}\right] \times V \qquad (1)$$

where Qe is the amount of heavy-metal ions adsorbed, (mg/g), Co and Ce are respectively the initial and final equilibrium metal-ion concentrations (ppm), m is the mass of MKT (g), and V is the volume of the metal-ion solution (L). The amount of heavy-metal ions adsorbed by MKT was also expressed in terms of the percentage removal, %R, which we calculated using Equation 2:

$$\%R = \left[\frac{(Co-Cf)}{Co}\right] \times 100 \qquad (2)$$

where Co and Cf are the initial and final metal ion concentrations of the adsorbate in ppm, respectively [35-37].

We also determined the effect of varying pH (2.0–10.0) on the adsorption of heavy metals by MKT, following a procedure similar to that described above. In addition, we studied the adsorption of the metal ions (Pb^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+} and Fe^{2+}) by MKT for different contact-time intervals. To do so, we varied the contact time of the adsorbent (MKT) and adsorbate (metal-ion solution) from 20–100 min (i.e., 20 min, 40 min, 60 min, 80 min, and 100 min) at room temperature. Finally, we investigated the influence of the initial metal-ion concentration and adsorbent dose on the adsorption of heavy metals by MKT at room temperature. The equilibrium adsorption of the heavy metals by MKT under these conditions was evaluated using Equation 1, as described by other authors [32, 38]. The experiments were performed in triplicate to ensure accuracy and their average values are reported here.

Results and Discussion

Characterization of MKT. MKT was found to be sparingly soluble in water, ethanol, and acetone but insoluble in n-hexane. The specific gravity result obtained for MKT was 0.992 ± 0.020. These results indicate that MKT is relatively dense relative to water. The pH values at the point of zero charge were found to be $4.50 \pm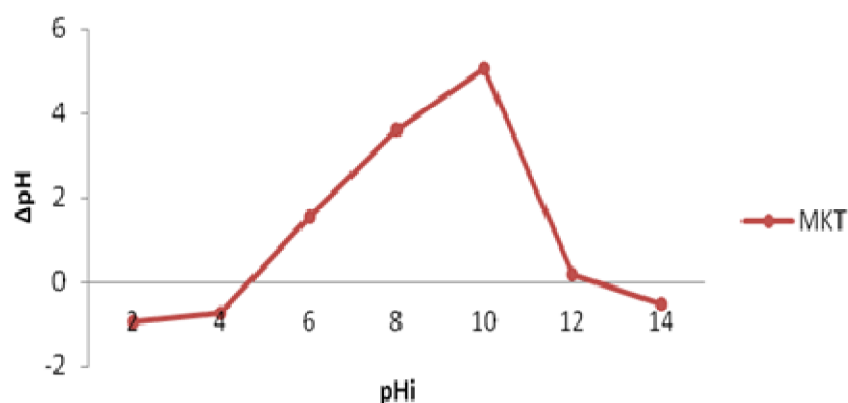 0.50$ and 12.00 ± 0.50, as shown in Figure 1, which are the neutral charges (i.e., zero charge) at which MKT is expected to effectively adsorb metal ions from aqueous solution [24, 32-33]. The sum of the charges on the surface of MKT are neutral (net charge is zero) at these initial pH (pHi) values because at these points the ΔpH is zero. Similar results have been reported in the literature [24, 32-33].

The complex nature of MKT became more evident in its IR spectrum (Figure 2). The sharp and broad absorption band at 3310.97 cm^{-1} can be attributed to the –OH and N-H stretching modes of alcohols and amines [39]. The intense sharp peak at 1612.27 cm^{-1} is attributable to the –C=C- bonds of aromatic rings [39]. The C-H stretching mode of the alkyl groups (CH_3, C_2H_5, C_3H_7, etc.) exhibited weak absorption at 2928.53 cm^{-1}. MKT also exhibited different absorption bands at the finger print region (1600–800 cm^{-1}) [39]. The absorption band at 1300–1150 cm^{-1} was probably due to the C-O stretching modes of the acids (RCOOH), esters (RCOOR), or anhydrides (RCOOCOR') [39]. A strong out-of-plane bending vibration arose from the terminal alkenes RCH=CH_2 between 800–1000 cm^{-1} and the sharp band at 1100.17 cm^{-1} is due to secondary alcohols, ROH [39]. These MKT absorption frequencies differed slightly from the IR spectrum of unmodified kola-nut testa (UKT), which is shown in Figure 3.

The melting point of MKT was inconclusive because there was no change in physical state (i.e., from solid to liquid) during the melting-point investigation (the thermometer scale range was 0–360 °C). The color of the MKT changed in the temperature range of 70–90 °C during the melting point investigation. In addition, the MKT contained different mixtures of substances that are rich in carbon, some of which are susceptible to thermal degradation and therefore difficult to melt in a mixture. The implication of this MKT behavior is that it contained a complex mixture of materials with different melting points and other properties (chemical and physical).
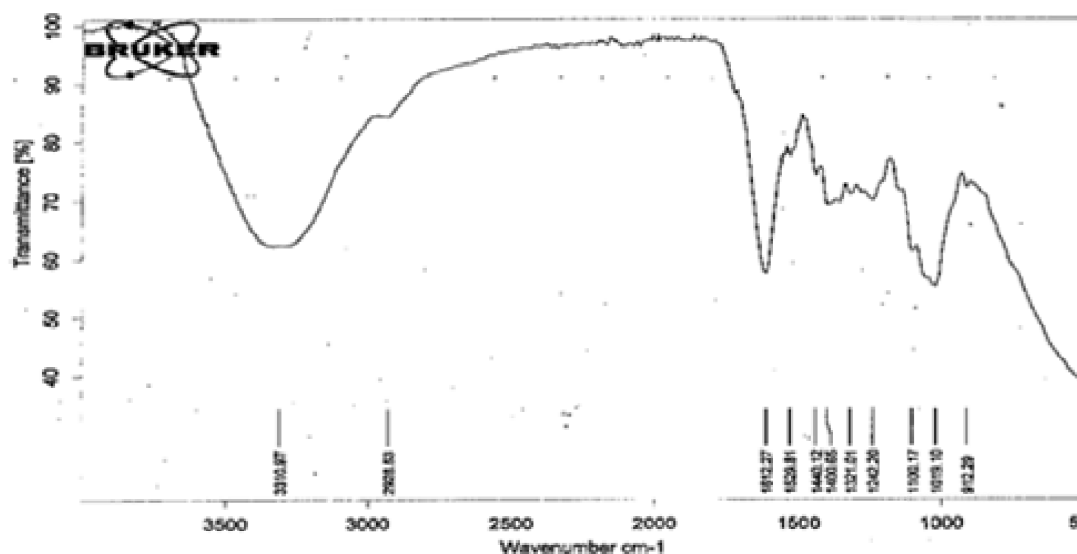

Figure 1. pH at Point of Zero Charge for MKT (n = 3)

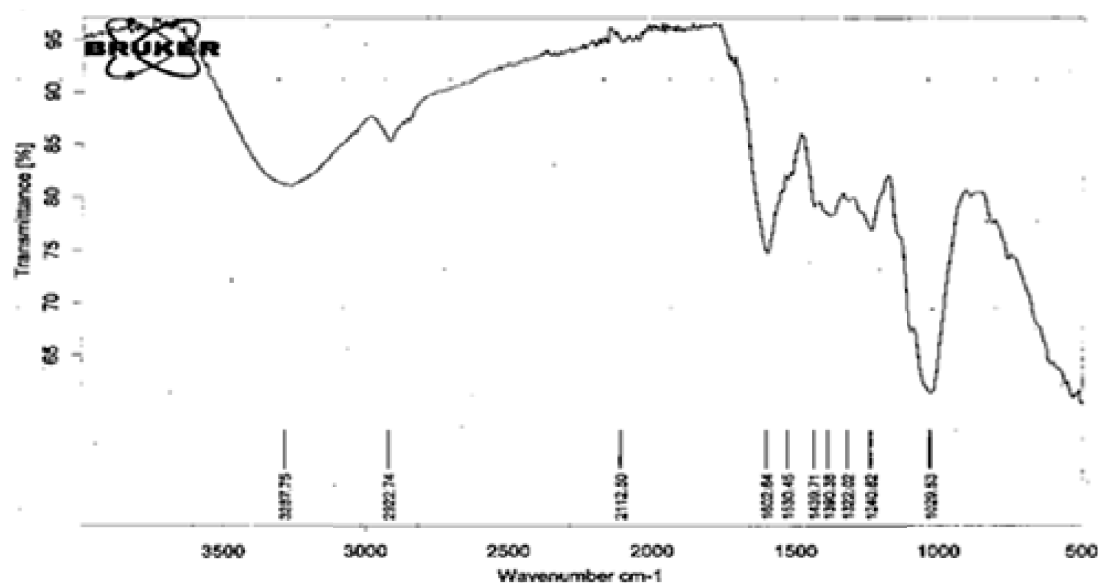**Figure 2. FTIR Spectrum of Modified Kola-nut Testa (MKT)**

Figure 3. FTIR Spectrum of Unmodified Kola-nut Testa (UKT)

Adsorption of heavy metals. MKT was found to have the capacity to take up metal ions (Pb^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, and Fe^{2+}) from an aqueous medium. However, the amounts of copper and lead adsorbed were relatively poor. The highest adsorption capacity of MKT for each of the following metals, Fe^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+} and Pb^{2+}, at various contact-time intervals is as follows: 1.90 ± 0.30 mg/g, 1.80 mg/g ± 0.20, 1.40 mg/g ± 0.20, 0.10 ± 0.01 mg/g, and 0.05 ± 0.01 mg/g, respectively, as presented in Table 1.

The pertinent question to ask at this point is: why was MKT ineffective in adsorbing some heavy-metal ions from aqueous solution considering the fact that EDTA is a good complexing agent for the heaviest metal ions.

These deviations could be accounted for by reconsidering the chemical treatment and studying the nature of the heavy metals. It could be argued that the chemical treatment was not entirely successful due to stearic hindrances between the chelate (EDTA) and high-molecular-weight substances (bulky groups) likely present in the kola-nut testa. It is likely that only a limited fraction of EDTA was present in the MKT.

Secondly, the ligand (EDTA is a hexadentate ligand, i.e., it has six lone pairs of electrons that can fill the vacant orbitals in the metals) might have been associated with other groups present in the MKT through chemical interaction (hydrogen bonding, ionic or covalent interaction), thereby limiting the ability of

MKT to effectively adsorb heavy metals from aqueous solution. To this end, relative success was recorded for the adsorption of Zn^{2+}, Mg^{2+}, and Fe^{2+}, whereas the adsorption of Cu^{2+} and Pb^{2+} was very poor, as shown in Table 1. The poor adsorption of the metal ions Cu^{2+} and Pb^{2+} may be due to the bulky nature (size) of lead and copper, which may be difficult for MKT to adsorb because of the limited number of sites available for the adsorption of these metals. In summary, the increasing order of adsorption for the metal ions by MKT is as follows: $Pb^{2+} < Cu^{2+} < Zn^{2+} < Mg^{2+} < Fe^2$.

Adsorption studies in different equilibration conditions. The results obtained regarding the adsorption of the metal ions (Pb^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, and Fe^{2+}) under different equilibrium conditions indicated that temperature influenced the adsorption of these heavy metals, as presented in Figure 4. An increase in temperature from 40 °C to 80 °C had little or no effect on the general percentage removal of the metal ions. Fe^{2+} recorded the highest percentage removal with an average of $73.56 \pm 0.6\%$, followed closely by Mg^{2+} with $71.96 \pm 1.0\%$ and Zn^{2+} with $46.20 \pm 0.4\%$. For the metal ions Cu^{2+} and Pb^{2+}, adsorption by MKT was very low (below 20.00% for Cu^{2+} and 3.00% for Pb^{2+}). The results further revealed that each metal ion has a unique optimum temperature at which its adsorption from aqueous solution by MKT is favorable. The response of each metal-ion solution during interaction with the adsorbent (MKT) varied greatly, which is probably because the aqueous solution was a single-metal ion solution in which competition with other metal ions was minimal.

Table 1.   Adsorption Capacities for Some Heavy-metal Ions by MKT at Room Temperature and Constant pH 6.0

Metal ion (M^{2+})	Adsorption capacity (mg/g) *Values for MKT*
Pb^{2+}	0.05 ± 0.01
Cu^{2+}	0.10 ± 0.01
Zn^{2+}	1.40 ± 0.20
Mg^{2+}	1.80 ± 0.20
Fe^{2+}	1.90 ± 0.30
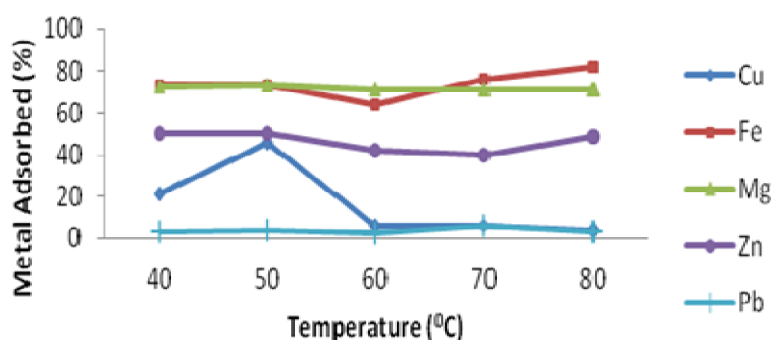
Figure 4. Effect of Temperature on the Percentage of Metal Adsorbed Using MKT at Constant pH 6.0
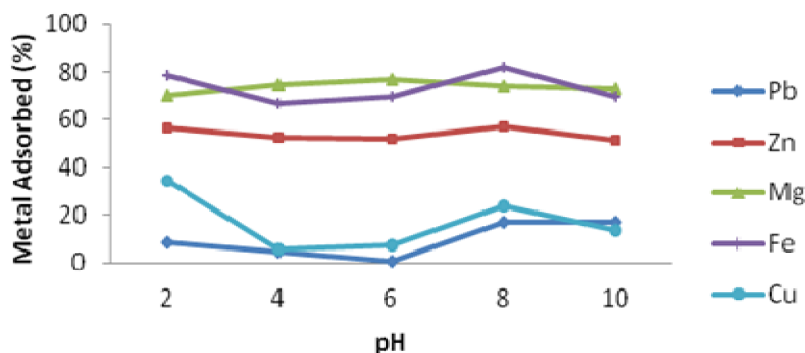
Figure 5. Effect of pH on the Percentage of Metal Adsorbed Using MKT at Room Temperature
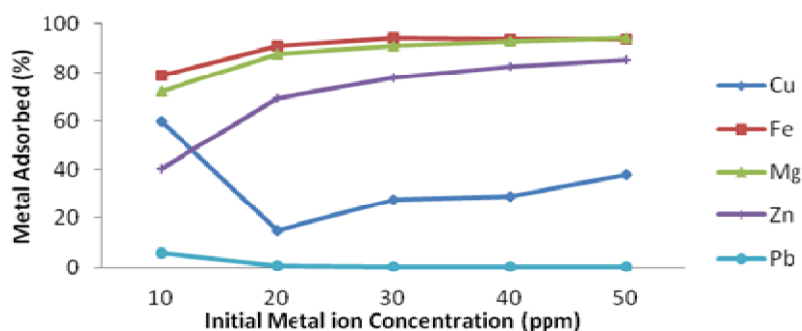
Figure 6.   Effect of Initial Metal Ion on Percentage of Metal Adsorbed by MKT at Room Temperature and Constant pH of 6.0
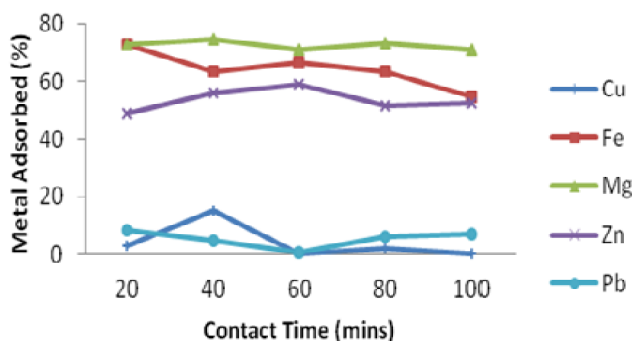

Figure 7. Effect of Contact Time on Percentage of Metal Adsorbed by MKT at Room Temperature and Constant pH of 6.0

pH has a profound effect on the extraction of heavy-metal ions from aqueous solutions [40-41]. Figure 3 shows the results for the adsorption of the metal ions at different pH values (1.0–10.0). From the figure, we can see that Fe^{2+} had the highest percentage removal of 81.80% at pH 8.0, closely followed by Mg^{2+} with 76.70% at pH 6.0, and Zn^{2+} with 56.90% at pH 8.0. Once again, the lead and copper ions were least adsorbed throughout the pH range of this study. Generally, their adsorption was slightly more favorable at pH 8.0. The values reported for the metal ions in the basic region suggest that precipitation of the metal ions as insoluble hydroxides $M(OH)_2$ may have contributed to their extraction from the aqueous solution by other mechanisms, such as complexation, co-precipitation, or other routes [40-41]. The optimum pH for each metal ion differed considerably.

Figure 6 shows a graphical representation of the percentages of metal adsorbed at different metal ion concentrations by MKT. Increases in the metal-ion concentrations resulted in a corresponding increase in the percentages of metal ion adsorbed. Optimum values of 95.00% and 94.30% were recorded for Fe^{2+} and Mg^{2+}, respectively, at 50 ppm by MKT. These results were closely followed by Zn^{2+} with 85.2%. Interestingly, at the very low concentration of 10 ppm, Cu^{2+} had an optimum adsorption value of 60.1%, which subsequently dropped to 14.9% with further increases in concentration. The percentage removal of Pb^{2+} was abysmal, irrespective of the metal ion concentration.

The order of the percentage removal followed the same trend as above, with $Fe^{2+} > Mg^{2+} > Zn^{2+} > Cu^{2+}$ and Pb^{2+}.

The percentages of metal adsorbed for different contact times (min) by MKT indicate that most of the Fe^{2+}, Mg^{2+} and Zn^{2+} ions were adsorbed throughout the time of the study (20 min to 100 min), as presented in Figure 7. Mg^{2+} recorded the highest average percentage of metal adsorbed ($72.58\% \pm 1.20$), followed by Fe^{2+} with an average of $63.82\% \pm 0.80$ and Zn^{2+} with average of $53.50\% \pm 1.00$. As usual, the amounts of copper and lead adsorbed by MKT were very low, which indicates that MKT is not an effective adsorbent for the removal of Pb^{2+} and Cu^{2+} ions from an aqueous medium. The adsorption capacity results of MKT for the metal ions presented in Table 1 above confirm this conclusion.

Finally, Figure 8 presents the percentage of metal adsorbed at different adsorbent doses (grams) by MKT. The dosages of the adsorbent ranged from 0.200 g to 1.000 g. The percentage removal of magnesium (II) metal ions was highest, with an average value of $73.82\% \pm 1.50$, followed by iron (II) metal ions with $75.16\% \pm 2.55$ and zinc (II) metal ions with $46.99\% \pm 2.32$. As anticipated, the copper (II) and lead (II) metal ions gave very poor average percentage removal values of $30.34\% \pm 2.74$ and $5.84\% \pm 2.37$, respectively. In all, in this experiment, a small quantity of MKT was needed to adsorb the metal ions Fe^{2+}, Mg^{2+}, and Zn^{2+} from aqueous solutions, whereas Pb^{2+} and Cu^{2+} ions could not be efficiently removed by the adsorbent MKT.
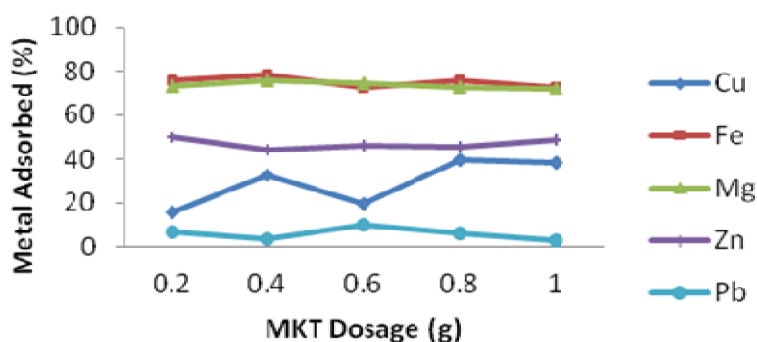
Figure 8. Effect of Adsorbent Dose (Grams) on Percentage of Metal Adsorbed by MKT at Room Temperature and Constant pH of 6.0

Conclusion

In this study, kola-nut testa modified with 0.1 M acetic acid and 0.1 M EDTA (MKT) showed the capacity to remove certain heavy-metal ions (Fe^{2+}, Mg^{2+}, Zn^{2+}) from aqueous solution. The order of adsorption of the metal ions by MKT was as follows: $Pb^{2+} < Cu^{2+} < Zn^{2+} < Mg^{2+} < Fe^{2+}$. The highest adsorption capacity of MKT for each of the following metal ions, Fe^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, and Pb^{2+} at various contact-time intervals is as follows: 1.90 ± 0.30 mg/g, 1.80 mg/g ± 0.20, 1.40 mg/g ± 0.20, 0.10 ± 0.01 mg/g, and 0.05 ± 0.01 mg/g, respectively. However, MKT was not a good adsorbent for the removal of Cu^{2+} and Pb^{2+} from aqueous solutions. These findings showed that the application of 0.1 M acetic acid and 0.1M EDTA in the modification of kola-nut testa for the adsorption of Fe^{2+}, Mg^{2+}, Zn^{2+} from wastewater is quantitatively effective. (Fe^{2+} had the highest percentage removal of 81.80% at pH 8.0, closely followed by Mg^{2+} with 76.70% at pH 6.0 and Zn^{2+} with 56.90% at pH 8.0.). The chemical modification was relatively successful, thereby making MKT a viable option in the treatment of wastewaters containing the metal ions Fe^{2+}, Mg^{2+}, Zn^{2+}.

Acknowledgments

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