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EFFECTS OF pH ON THE ADSORPTION OF Cd(II), Pb(II) AND Fe(III) IONS ON UNMODIFIED AND MODIFIED RAPHIA PALM FRUIT(*RAPHIA HOOKERI*)

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ABSTRACT

The biosorption of Cd (II), Pb(II) and Fe(III) ions from dilute aqueous solution using unmodified and modified raphia palm fruit (*Raphia hookeri*) as an adsorbent was carried out through pH –dependent studies. The results from the pH study showed that the biosorption was pH dependent and optimum pH ranged from 8 to 11. The result of the pH study on the unmodified biomasses showed that adsorption increased with increase in pH up to a maximum for all the metal ions on all biomasses considered. The maximum adsorption capacities for Pb (II) in the unmodified biomasses were 99.66% for unmodified epicarp (UEP), 99.89% for unmodified endocarp (UEN) and 94.06% for unmodified mesocarp (UMS). The maximum adsorption capacities for Fe (III) were 99.8% for UEP at pH = 11, 99.5% for UEN at pH = 8 and 99.78% for UMS at pH =11.The maximum adsorption capacities for Cd (II) in the unmodified biomasses were 99.69% for UEN, 98.84% for UEP and 98.86% for UMS, all at the pH of 11. Adsorption expressed as percent adsorption showed that sorption of Pb (II) increased gradually to a maximum at pH = 8 for all hydroxylamine treated mercaptoacetic acid (NH_2OH-MAA) modified raphia palm fruit biomasses. The maximum sorption capacities for Pb (II) were 97.17% for MMXY, 98.78% for MENXY and 99.76% for MEPXY. Percent sorption for Fe (III) showed that maximum adsorption for all NH_2OH-MAA modified biomasses occurred at pH = 8. The maximum capacities for Fe (III) were 96.68% for MMXY, 99.34% for MENXY and 99.27% for MEPXY. For iron (III), adsorption increased very slightly to the maximum after the initial pH of adsorption. Sorption of Cd (II) on to the NH_2OH-MAA modified biomasses followed a peculiar pattern for all the three biomasses considered except a single deviation for MENXY at pH = 8; all other maxima occurred at pH = 11 for Cd(II).

Key words: pH, Biosorption, Biomass, Unmodified epicarp, Unmodified endocarp, Unmodified mesocarp, Raphia palm fruit.

INTRODUCTION

The subject of biosorption of aqueous pollutants is one that has received much attention by researchers over the few decades. Despite the volume of findings in this area of research, much leaves to be desired, because, on the social angle, there are still hues and cries about environmental pollution occasioned by industrial processes; on the industrial angle, no medium has been found better than the aqueous for end-of-pipe effluent discharges which invariably results in the pollution of the environment; and on the intellectual and real time dimension, cost-effective and environmentally friendly materials and methods must be sought to remove or remediate the aqueous pollutants. For these and other possible reasons the surge of research in this area has not diminished and many more findings would be added. Adsorption by vegetable and agricultural by-products. Some reported materials include cassava waste (Abia *et al*. 2003) maize cob and husk (Abia and Igwe 2003, 2005, 2007; Opeolu *et al*., 2009), tree fern (Ho, 2003), fluted pumpkin waste (Horsfall and Spiff, 2005),wild cocoyam (Horsfall and Spiff, 2005) nipah palm shoot (Wankasi *et al*., 2006), pineapple stem (Hameed et al; 2009) maize tassel (Zvinowanda *et al*., 2009), orange barks(Azouaou *et al*.,2013), sugarcane bagasse, wheat husk, mango sawdust, neem sawdust (Vinodhini and Das 2009, 2010), sawdust of spruce (*Picea abies*) (Urik *et al*., 2009), *Pinus sylvestris* sawdust (Kaczala *et al*., 2009), luffa cylindrical fibre (Saueprasearsit *et al*., 2010), cocoa pod husk (Igwe *et al*., 2011a), coconut fibre (Igwe *et al*., 2011b), modified sugar beet pulp (Zolgharnein *et al*. 2011), to mention but a few. Some of the adsorbents have been modified with acids and chelating agents such as EDTA to increase the sorption capacity of the adsorbents. Horsfall et al ;(2004) reported the use of mercaptoacetic Acid (MAA) modification of cassava *(Manihot esculenta* Cranz*)* waste biomass on the adsorption of Cu^{2+} and Cd^{2+} from Aqueous Solution. Chen *et al*., (2011) reported the use of Ferric-impregnated volcanic ash (FVA) for the adsorption of arsenic from contaminated water. The pH of a solution affects the surface charge of the adsorbents, degree of ionization and solution composition (metal speciation).

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Also, the level of dissociation of functional groups on the adsorbent surface, solubility of metal ions and concentration of the counter ions in solution are affected by pH (Nomanbhay and Palanisamy, 2005; Antunes et al., 2003; Terker et al., 1999 in Onwu and Ogah, 2010). It is therefore necessary to ascertain the pH range at which optimum adsorption can occur on a given adsorbent surface. This research looks at the effect of pH on the adsorption of Cd (II), Pb(II) and Fe(III) ions from dilute aqueous solution using unmodified and modified raphia palm fruit (*raphia hookeri*) as an adsorbent.

MATERIALS AND METHODS

Preparation of Adsorbent

The adsorbent used in this work is raphia palm fruit (*Raphia hookeri*). Raphia palm fruit is commonly found in West Africa and is abundant in southern Nigeria. The composition is reported to contain: moisture10.6%, protein 7.8%, carbohydrate 63%,fibre 8.1% and ash 9.2% (Edem et al., 1984). Raphia palm fruit bunches were collected from the swamp forest of Ogu village in Yenagoa Local Government Area of Bayelsa State of Nigeria. The fruits were separated from the bunches and left for about a week. The epicarp, mesocarp and endocarp were separated, washed and air dried. The endocarp (nut) of raphia palm fruit was ground by ball mill abrasion at Rivers State University of Science and Technology (RSUST), Port Harcourt after drying in the oven. Four sizes of ground endocarp were obtained by passing sample through the 75,150, 300 and 600µm sieves. The sample sizes were soaked in 0.1M HCl for about two days and washed in distilled water until a constant pH was obtained. The washed samples were dried in the oven at 68ºC for 2 days. The pretreated samples were stored for further use. The air-dried epicarp peels and mesocarp were separately soaked in 0.05MHCl for about three days and washed in distilled water repeatedly for over three times. The washed epicarp peels and mesocarp were oven-dried at 55ºC for five days. The oven-dried epicarp peels and mesocarp were ground and sieved into four sizes of 75, 150 300 and 600µm. The pretreated samples were stored for further use.

Modification of biomass

150g of unmodified raphia palm fruit endocarp, epicarp and mesocarp were respectively soaked in 0.5M mercaptoacetic acid (MAA) solution for 24 hours. The mixtures were copiously washed with distilled water and filtered. The residues were air-dried and sieved. The same process was repeated with the addition of 0.1M hydroxylamine solution to the soaked mixture. After one hour the NH_2OH –MAA mixture was washed with distilled water, filtered and air-dried. The unmodified biomasses were labelled as UEN for unmodified endocarp, UEP for unmodified epicarp and UMS for the unmodified mesocarp. The modified samples were labelled as MENXY for the hydroxylamine treated mercaptoacetic acid (MAA) modified endocarp, MEPXY for the modified epicarp and MMXY for the modified mesocarp. In all, six samples of raphia palm fruit were used in the study.

Adsorbates/Instruments

Adsorbates for experiments were obtained from the following: Iron (III) ions from iron (III) chloride; Lead (II) ions from lead (II) nitrate and cadmium (II) ions from cadmium (II) acetate. Agitation of solutions was carried out with Barnstead|Labline maxQ 2000 Variable Speed shaker (20-500rpm). Centrifuging work was done with B.Bran Scientific & Instrument Co. 80-1 Electric Centrifuge and temperature maintenance was with the aid of Thermo Electron Corporation Precision water bath. Analysis of supernants was done with Unicam Photon Atomic Absorption Spectrophotometer

EXPERIMENTAL METHODS

Effect of pH

10 ml of 40mg/l of Pb(II), Fe(III) and Cd(II) solutions were equilibrated by shaking at 325rpm for one hour with 0.2g of biomass at the pHs of 2,5,8 and 11 respectively The mixtures were centrifuged at 3000 rpm for five minutes and decanted. The supernatants were store for AAS analysis. The pH adjustments of the metal ion solutions were done with 0.1M HCl and 0.1M NaOH. This experiment was carried out for UEN UEP,UMS MEN MEP and hydroxylamine treated mercaptoacetic acid (MAA) modified biomasses.

Determination of pH point of zero charge (pH_{PZC})

The determination of the pHpzc of adsorbents was carried out by the method described by Nomanbhay and Palanisamy, (2005). 20 cm^3 of 0.01M NaCl solutions were placed in various plastic vials. Their pH was adjusted to different values between 2 and 12 by the addition of 0.1M HCl or 0.1MNaOH solutions. 0.2 g of unmodified and modified adsorbents were respectively added to each vial and shaken for one hour on a shaker. The final pH of the solutions was measured with their corresponding zeta potential values after 48 hours. The pHpzc is the point where the curve zeta potential (ζ) versus pH intersects the pH axis of the plot.

RESULTS AND DISCUSSION

Effect of pH on the sorption of the metal ions

The results of the effect of pH on adsorption of Pb(II), Fe(III) and Cd(II) ions by raphia palm endocarp, epicarp and mesocarp are represented in plots of relevant variables in the figures shown. The results of the pH study on the unmodified biomasses showed that adsorption increased with increase in pH up to a maximum for all the metal ions on all biomasses considered. Higher adsorption values were observed for higher pH values for Cd (II) and Fe (III) than for Pb (II) in UEP. Higher optimal values are also observed for Cd (II) in all the three unmodified biomasses. There appeared to be a general pattern of dependence for Pb (II) which had a constant optimal pH of 8 for all the unmodified biomasses. The maximum adsorption capacities for Pb (II) in the unmodified biomasses were 99.66% for UEP, 99.89% for UEN and 94.06% for UMS. The maximum adsorption capacities for Fe(III) were 99.8% for UEP at pH = 11, 99.5% for UEN at pH = 8 and 99.78% for UMS at pH =11.The results indicated that Fe(III) was on the average more adsorbed than the other metal ions as pH was increased for unmodified biomass adsorption. The results also indicated the high level of affinity of the biomasses for the metal ions under the conditions of increasing pH. A pattern of dependence on pH was shown by all three metals for all the biomasses considered as shown from Figure 1 to 12.

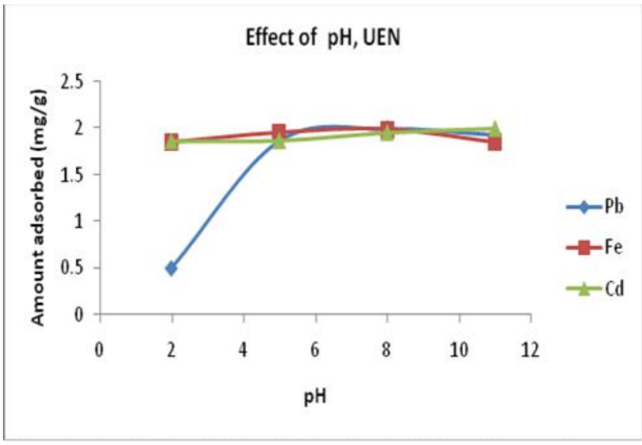

Figure 1. Plot of the effect of pH on the adsorption of Pb(II),Fe(III) and Cd(II) ions by unmodified raphia palm fruit endocarp(UEN)

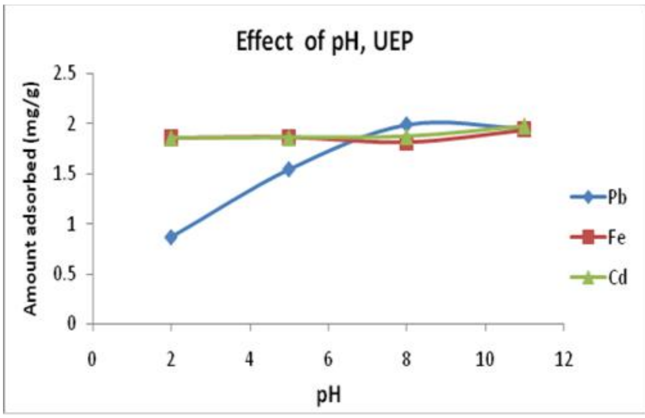

Figure 2. Plot of the effect of pH on the adsorption of Pb(II), Fe(III) and Cd(II) ions by unmodified raphia palm fruit epicarp (UEP)

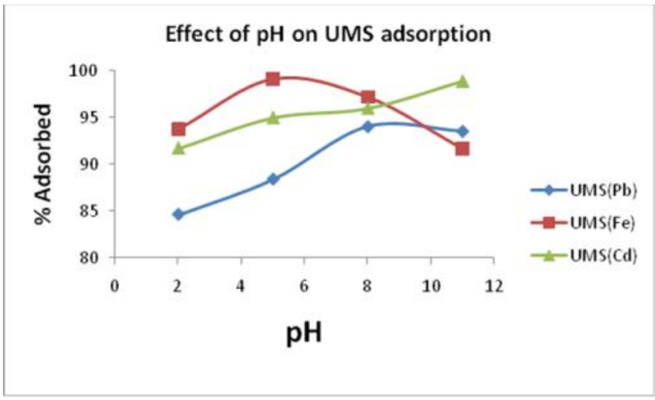

Figure 3. Plot of the effect of pH on the adsorption of Pb(II), Fe(III) and Cd(II) ions by unmodified raphia palm fruit mesocarp (UMS)

Adsorption expressed as percent adsorption showed that sorption of Pb^{2+} increased gradually to a maximum at pH = 8 for all NH_2OH-MAA modified biomasses. The maximum sorption capacities for Pb (II) are 97.17% for MMXY, 98.78% for MENXY and 99.76% for MEPXY. Percent sorption for Fe^{3+} showed that maximum adsorption for all NH_2OH-MAA modified biomasses occurred at pH = 8. The maximum capacities for Fe^{3+} were 96.68% for MMXY, 99.34% for MENXY and 99.27% for MEPXY.

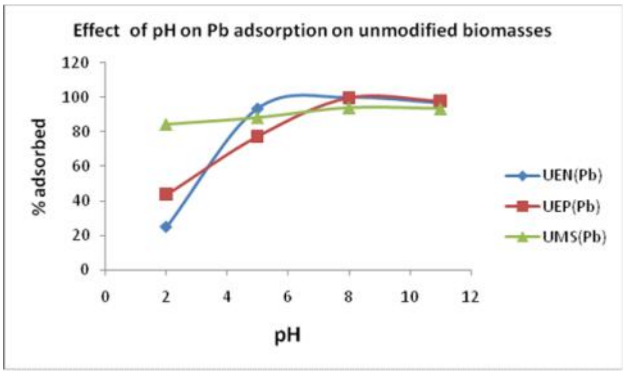

Figure 4. Comparison of pH effects on the adsorption of Pb (II) ion on unmodified raphia palm fruit biomasses

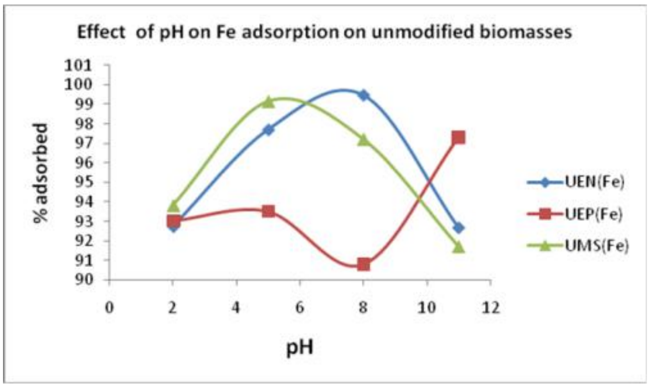

Figure 5. Comparison of pH effects on the adsorption of Fe(III) ion on unmodified raphia palm fruit biomasses

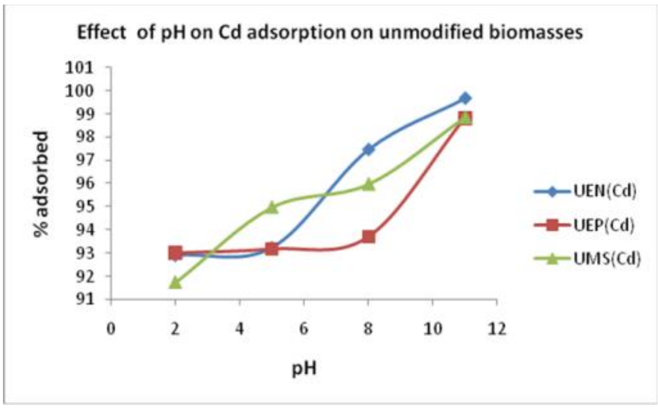

Figure 6. Comparison of pH effects on the adsorption of Cd (II) ion on unmodified raphia palm fruit biomasses

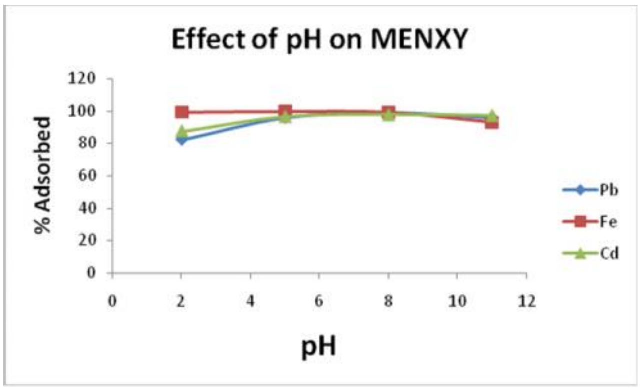

Figure 7. Plot of the effect of pH on the adsorption of Pb(II), Fe(III) and Cd(II) ions on hydroxylamine treated MAA modified raphia palm fruit endocarp (MENXY)

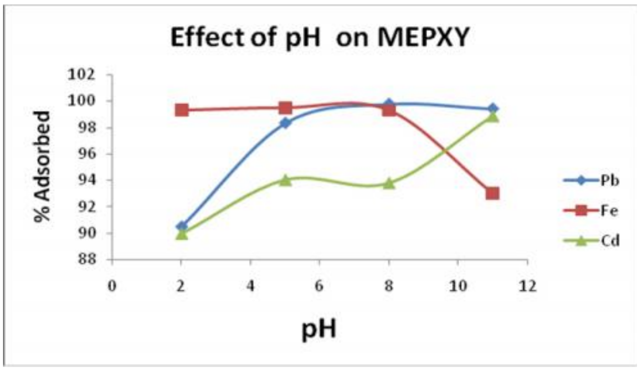

Figure 8. Plot of the effect of pH on the adsorption of Pb(II),Fe(III) and Cd(II) ions on hydroxylamine treated MAA modified raphia palm fruit epicarp (MEPXY)

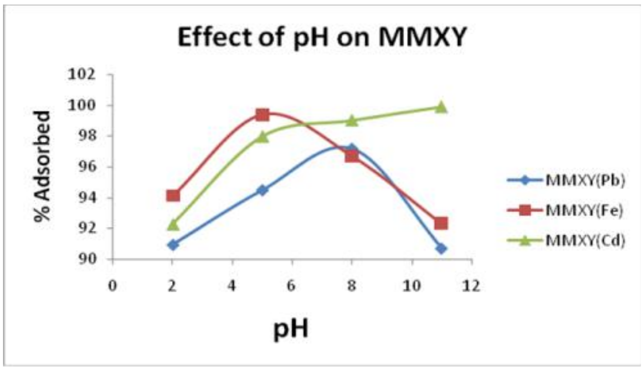

Figure 9. Plot of the effect of pH on the adsorption of Pb(II), Fe(III) and Cd(II) ions on hydroxylamine treated MAA modified raphia palm fruit mesocarp (MMXY)

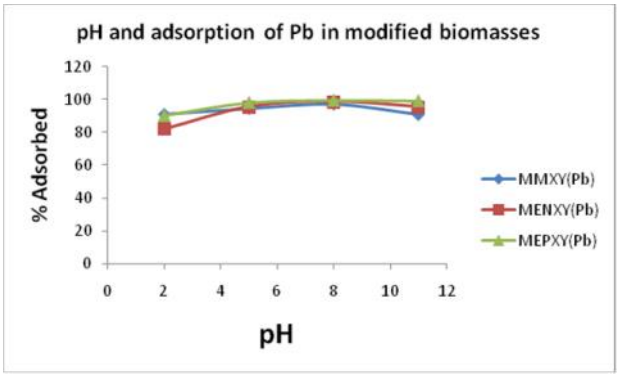

Figure 10. Comparison of pH effects on the adsorption of Pb(II) ion on hydroxylamine treated MAA modified raphia palm fruit biomasses

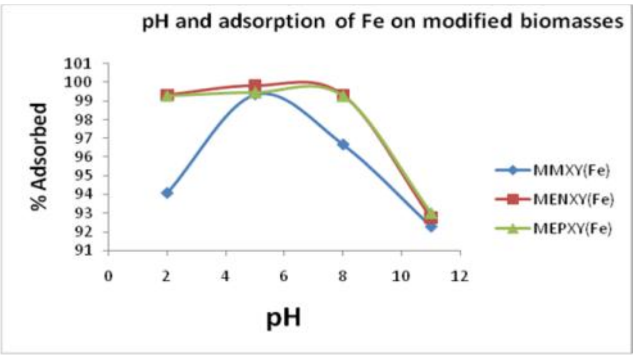

Figure 11. Comparison of pH effects on the adsorption of Fe(III) ion on hydroxylamine treated MAA modified raphia palm fruit biomasses

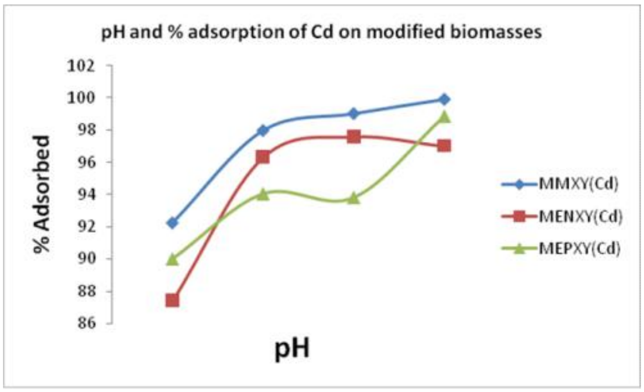

Figure 12. Comparison of pH effects on the adsorption of Cd(II) ion on hydroxylamine treated MAA modified raphia palm fruit biomasses

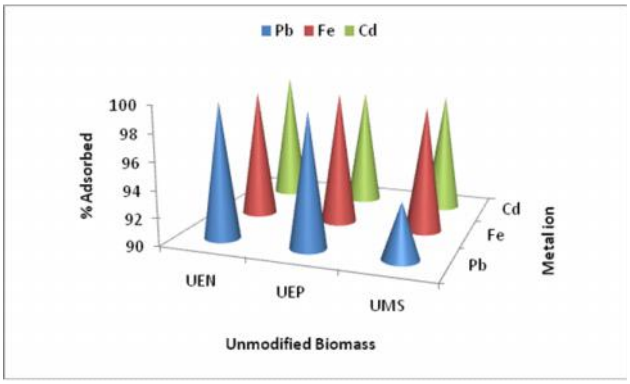

Figure 13. Percent maximum sorption capacities for Pb(II),Cd(II) and Fe(III) on unmodified biomasses

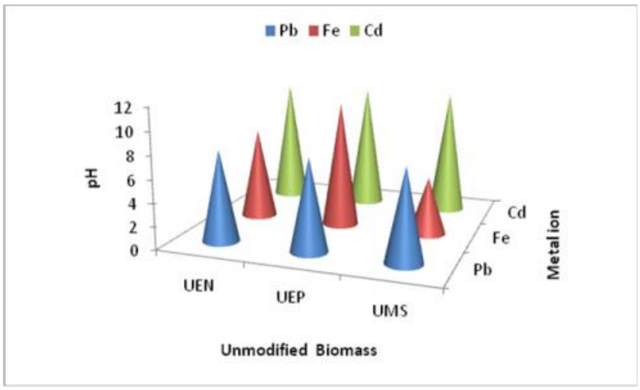

Figure 14. Maximum sorption pH for Pb(II),Cd(II) and Fe(III) on unmodified biomasses

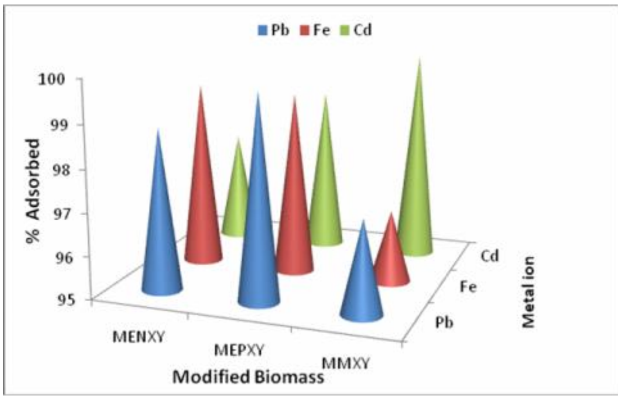

Figure 15. Percent maximum sorption capacities for Pb(II),Cd(II) and Fe(III) on NH_2OH-MAA modified biomasses

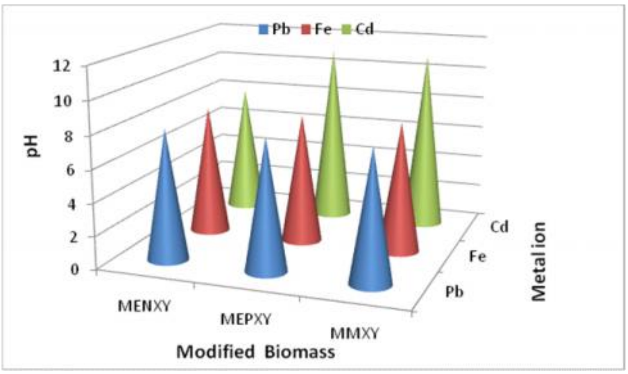

Figure 16. Maximum sorption pH for Pb(II),Cd(II) and Fe(III) on NH_2OH-MAA modified biomasses

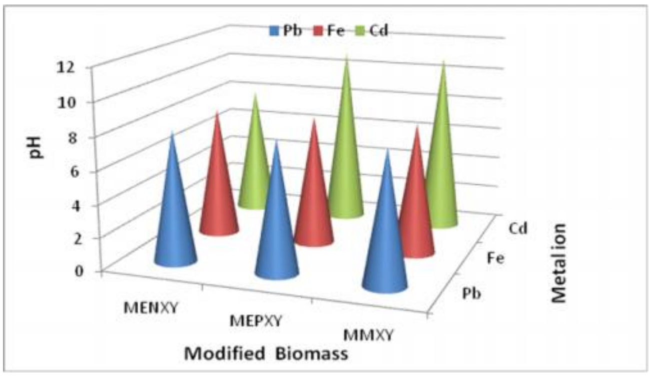

Figure 17. Determination of the pH point of zero charge of metal ion on unmodified adsorbents

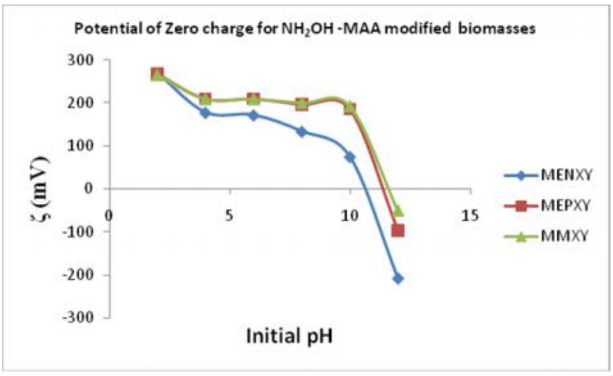

Figure 18. Determination of the pH point of zero charge of metal ion on NH_2OH – MAA modified adsorbents

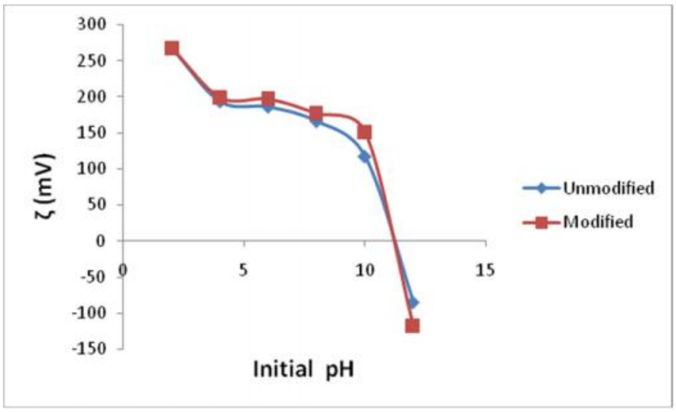

Figure 19. Plots of average zeta potentials of biomasses as a function of initial pH

For iron (III), adsorption increased very slightly to the maximum after the initial pH of adsorption. Sorption of Cd^{2+} on to the NH_2OH-MAA modified biomasses followed a peculiar pattern for all the three biomasses considered except a single deviation for MENXY at pH = 8; all other maxima occurred at pH = 11 for Cd^{2+}. The sorption capacity with pH change rose significantly after the initial pH for Cd^{2+}. Maximum capacities for Cd^{2+} were 99.92% for MMXY, 97.59% for MENXY at pH = 8 and 98.86% for MEPXY at pH = 11. Figures 13 to 16 are 3-D plots of percent adsorption and pH as functions of the biomasses and the metal ions. The results from fig. 13 showed that Cd (II) was the most adsorbed ion on UEN and UMS biomasses Pb(II) and Fe(III) were equally adsorbed on UEP. Cd(II) was still the most adsorbed ion on the modified biomass MMXY; Pb(II) and Fe(II) were the most adsorbed on MEPXY and MENXY respectively as shown in fig.15. The results of the plots of the sorption pH showed that Cd(II) ions attained the highest sorption pH for all unmodified and modified biomasses as shown in fig. 14 and 15.

The pH point of zero charge (pHpzc) of the adsorbents

The efficiency of adsorption depends on the solution pH (Janet et al., **2015**).The pH of a solution affects the surface charge of the adsorbent as well as the degree of ionization and speciation of different adsorbates. Change of pH affects the adsorption process through dissociation of functional groups on the active sites of the adsorbent surface. Due to this, there occurs a shift in reaction kinetics and equilibrium characteristics of the adsorption process. Adsorption of various anionic and cationic species on such adsorbents had been explained on the basis of competitive adsorption of H^+ and OH^- ions with adsorbates (Kumar, 2011). The results of the determination of the pH points of zero charge are shown in Figures 17 and 18. The pHpzc of each adsorbent was assessed from the graph of zeta potential (mV) versus initial pH as shown in figures 17 and 18. The results showed that the pHpzc of the adsorbents were between pH 10 and 12 implying that the adsorbent surfaces were positive for less than the values indicated. The pHpzc for the adsorbents were 10.4, 11.8, 12.0, 10.6, 11.4 and 11.6 for UEN, UEP, UMS, MENXY, MEPXY and MMXY respectively. At pH values above the pHpzc for each adsorbent, the surface possesses a negative charge. The average zeta potential (mV) of the unmodified and modified biomasses were separately calculated and plotted as a function of the initial pH as shown in fig.19. The results showed that the average zeta potential (mV) of both biomasses decrease with increase in initial pH. However, the modified potentials are on the average, shifted to higher values than the unmodified. This could only imply that the adsorbent surface charge was enhanced by modification.

Conclusion

The result of the pH study on the unmodified and the chemically modified biomasses showed that adsorption increased with increase in pH up to maximum of 99% for all the metal ions on all biomasses considered. The pH results indicated that optimum adsorption was attainable at values of pH ≥ 7 for Cd^{2+} and Pb^{2+} and at pH ≤ 8 for Fe^{3+}. It was concluded that high pH favoured the adsorption of the metals on raphia palm fruit. A maximum adsorption efficiency of

99.99% was obtained for the initial concentration of 20mg/l and 40mg/l of the NH_2OH –MAA treated biomass of the raphia palm fruit. It was also observed the modification of biomasses enhanced the surface charge of the biomasses.

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