

*Full Length Research Paper*

# Studies on the effect of pH on the sorption of cadmium (II), nickel (II), lead (II) and chromium (VI) from aqueous solutions by African white star apple (*Chrysophyllum albidium*) shell

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The cleaning of our environment should be carried out with the use of natural products instead of chemicals so as to reduce pollution. This study investigates the potential of an agricultural waste in scavenging heavy metal ions from aqueous solution. The role of pH in the removal of cadmium (II), nickel (II), lead (II) and chromium (VI) from aqueous solution by bio-sorption using African white star apple was examined. The adsorption process was found to be highly pH-dependent and the results indicate that the optimum pH for sorption of Cd (II) and Ni (II) was 6.0 while Pb (II) was 7.0 and maximum percentage removals recorded were 64.69 and 76.88% for Cd (II), 61.04 and 72.28% for Ni (II) and 55.60 and 67.44% for Pb (II) for the two adsorbents, UAWA and MAWA. Cr (VI) exhibited a different pH dependence having the optimum pH for its removal as 2.0 for both adsorbents. Maximum percentage removals recorded were 69.00 and 77.40% by the two adsorbents presented in the original order. The results from this study showed that chemically modified and unmodified African white star apple can be a good sorbent for these heavy metal ions.

**Key words:** Adsorption, heavy metals, *Chrysophyllum albidium*, sorption, biosorbent, mercaptoacetic acid.

## INTRODUCTION

As a result of the great concern for heavy metal pollution and the potential adverse health effect on the public, a great effort has been made to clean our lands and waters containing toxic metal ions. Conventional methods that have been previously employed have proved to be costly and less efficient particularly for low-level waste remediation. Adsorption is now considered as an alternative technique because of its simple design, sludge-free and low investment in terms of initial cost and land requirement (Viraraghavan and Dronamraju, 1993). As a result of high capital involved in heavy metal remediation using

conventional adsorbents, a great deal of attention has now been diverted to the use of alternative sorbents which have been found to be more cost effective and are readily available. Biosorbents of both living and non-living biological materials have been extensively employed in the economical remediation of these toxic metal ions from industrial wastewaters and mining effluents (Carvalho et al., 1994; Volesky et al., 1995; Madwick, 1991; Wieder, 1990). Unlike typical synthetic ion-exchange resins, plant-based biosorbents do not require the use of toxic chemicals in their preparation.

Some of the raw agricultural and natural wastes that have been employed as cheap adsorbents for water and wastewater treatment include microbial biomass, peat, compost, leaf mould, palm press fibre, coal, straw, wool fibre, rice milling by-products, etc (Singh and Rawat, 1997). Not all of these are effective. Therefore, it is still important to identify suitable low cost adsorbents for heavy metal removal. The potential of some of these agricultural by-products to remove heavy metals from

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**Abbreviations:** UAWA, Unmodified African white star apple; MAWA, mercaptoacetic acid modified African white star apple; MBT, methylene blue absorption test; MB, methylene blue; SSA, specific surface area.

aqueous solutions and wastewater has been reported in literature and some of them include: Sorption of lead onto waste tea leaves (Tan and Rahman, 1988), the sorption of lead onto china clay and wollastonite (Yadava et al., 1991) and sorption of lead onto corn (*Zea mays*) cobs modified with thioglycolic acid solution (Okieimen et al., 1988). Removal of nickel from aqueous solutions by sorption process has been done using various sorbents which include sewage sludge (Gao et al., 1997) and *Medicago sativa* (Alfalfa) (Gardea-Toresdey et al., 1995). Studies on removal of copper (II) and cadmium (II) from aqueous solution using cassava peel (Horsfall et al., 2004) had been done. De Vasconcelos and Beca (1992) had investigated the feasibility of using pine bark for the decontamination of wastewaters from heavy metal ions such as lead (II), Cd (II) and chromium (III). In addition, chemical modification of these agricultural by-products has been found to contribute to better removal of these metal ions thus providing wider applications of these sorbents to a range of metal ion removal.

The aim of this research is to develop inexpensive and effective metal ion adsorbents from abundant sources of natural waste (by-product) of plant material. African white star apple (*Chrysophyllum albidum*), which is the sorbent used in this study is primarily a forest tree crop found in the forest zones of South Eastern and Eastern States of Nigeria. Its natural occurrences have also been reported in diverse ecozones in Uganda, Niger Republic, Cameroun and Cote d' Ivoire (Odo et al. 2005). The fruit is a largely berry containing four (4) to five (5) seeds or sometimes fewer due to seed abortion. Both young and old people relish the fleshy pulp of the fruit. This is because of its high vitamins, iron and flavours. In most areas, the seeds are usually discarded while in some other localities, they are used for local games and plays as anklets in dancing indicating that there is little or no significant end use of the seed. This study is therefore designed to evaluate the potentials of *C. albidum* shell as biosorbent for metal ion removal from aqueous solutions.

## MATERIALS AND METHODS

### Adsorbent preparation

The African white star apple (*C. albidum*) fruits were basically sourced from local market, Abakaliki in Ebonyi state of Nigeria. The edible fruits were eaten while the seeds were washed and air-dried and finally oven-dried for 12 hours at a temperature of 80°C in preparation for the adsorption analysis. The air-dried African white star apple shells were crushed with manual blender to smaller particles and sieve analysis was performed using the sieve screen to obtain final sample size of 180 µm. 200 g of the screened (180 µm) adsorbent was further soaked in 500 mL 0.3 M HNO<sub>3</sub> solution for 24 h. It was then filtered through a Whatman No. 41 filter paper and washed copiously with deionised water until a pH of 6.9 was obtained. The rinsed adsorbent was later air-dried for 6 h. The treatment of the adsorbent with 0.3 M HNO<sub>3</sub> solution aids in the removal of any debris or soluble biomolecules that might interact with the metal ions during the sorption process and also to open-up the micropores of the adsorbent thereby making them ready for

adsorption. This process is called chemical activation of the adsorbent. The air-dried activated adsorbent was divided into two parts. 100 g of the first portion labelled "A" was left untreated and labelled unmodified African white star apple (UAWA) while 100 g of the second portion labelled "B" was acid treated by dissolving it in excess of 1.0 M mercaptoacetic acid (HSCH<sub>2</sub>COOH) solution, stirred for 1 h and left to stand for 24 h at 30°C and called mercaptoacetic acid modified African white star apple (MAWA). After 24 h, the mixture was filtered using Whatman No. 41 filter paper. The residue in the filter paper was then soaked in 1.0 M hydroxylamine (NH<sub>2</sub>OH) for 1 h to remove all O-acetyl groups. After which they were filtered and rinsed copiously with deionised water until a pH 6.8 was obtained. The washed residues were air-dried and stored in an air-tight container. The mercaptoacetic acid modification led to the thiolation of the hydroxyl groups of the biosorbent by the following reaction (Horsfall et al., 2005).



The degree of infusion of thiol (-SH) group was further estimated by reacting 0.5 g of acid treated biosorbent with 20 mL of iodine solution at pH 7.3, followed by back titration of the unreacted iodine with standard thiosulphate solution. The extent of thiolation was evaluated to be 2.27%.

### Adsorbent characterization

The specific surface area and the pH point of zero charge (pH<sub>pzc</sub>) were used to characterize the surface of the two adsorbents.

### Characterization of the adsorbents

The specific surface area of the two adsorbents (UAWA and MAWA) was determined using the methylene blue absorption test (MBT) method described in Santamarina et al. (2002). The step-to-step procedure was carried out as follows: 2.0 g of each adsorbent was mixed with 200 mL of deionized water. Methylene blue (MB) solution was prepared by dissolving 1.0 g of the powder in 200 mL of deionized water. 10 ppm of the MB solution was added to the adsorbent solution and the suspension was agitated in a shaker for 2 h. It was then kept for 24 h to attain equilibrium. After which 10 mL aliquot was taken and centrifuged. The centrifuged aliquot was analyzed in a visible spectrophotometer (model 722S Spectrophotometer) at a wavelength of 665 nm to determine the amount of MB absorbed. Higher concentrations (20-70 ppm) of the methylene blue solution were added sequentially and the previous steps repeated for the adsorbents.

A graph of concentration of MB added versus the amount of absorbed MB was used to identify the point of complete cation replacement. The specific surface area was calculated from the amount of absorbed MB at the optimum point as follows:

$$\text{Specific Surface Area (SSA)} = \frac{m_{\text{MB}}}{319.87} A_v A_{\text{MB}} \frac{1}{m_s}$$

Where, m<sub>MB</sub> is the amount of MB absorbed at the point of complete cation replacement, m<sub>s</sub> is the mass of adsorbent, A<sub>v</sub> is the Avogadro's number -6.02 × 10<sup>23</sup>, A<sub>MB</sub> is the area covered by one MB molecule (typically assumed to be 130 × 10<sup>-20</sup> m<sup>2</sup>) (Santamarina et al., 2002).

### Determination of pH<sub>pzc</sub>

The pH<sub>pzc</sub> of each of the adsorbents (UAWA and MAWA) was

carried out as described by Onyango et al. (2004). 50 mL of 0.01 M NaCl was placed in different closed Erlenmeyer flasks. The pH of each solution in the flasks was adjusted to values of 2.0, 4.0, 6.0, 8.0 and 10.0 by adding 0.1 M HCl or 0.1 M NaOH solutions. Then 0.5 g of each of the adsorbents was added and agitated in a shaker for 1 h and allowed to stay for 48 h to reach equilibrium at 30°C. A graph of zeta potential (mV) versus initial pH ( $pH_{initial}$ ) was used to determine the  $pH_{pzc}$ .

### Phytosorption experiments

All reagents used were of analytical reagent grades and double distilled deionized water was used in the sample preparation. 100 ppm stock solutions of cadmium (II) from  $CdSO_4 \cdot 8H_2O$ , Cr (VI) from  $K_2Cr_2O_7$ , Ni II from  $(NiSO_4 \cdot 6H_2O)$  and lead (II) from  $PbCl_2$  were prepared at a pH 5.0 and temperature of 30°C. From the stock solutions, 25 ppm working solution of each of the adsorbates was obtained by dilution. The effect of pH on the adsorption of the metal ions was studied by transferring 100 mL of the 25 ppm solutions into different 250 ml Erlenmeyer flasks and then adjusting the pH of the solutions to the different pH of 2, 4, 5, 6, 7 and 8 using 0.1 M HCl or 0.1 M NaOH. Then 0.2 g of each of the adsorbents was weighed and put into the flasks, corked and labelled. The flasks were placed in a rotary shaker and agitated for 2 h to attain equilibrium. Thereafter, the content of each flask was filtered, centrifuged and the residual metal ion concentrations (Ce) were analyzed using buck scientific Atomic Absorption Spectrophotometer (AAS) model 210 VGP. The concentrations of the metal ions adsorbed at the different pH were calculated by difference.

## RESULTS AND DISCUSSION

### Determination of specific surface areas of the adsorbents

The specific surface area (SSA) of an adsorbent is the ratio of its surface area to its mass. Specific surface considers the combined effects of particle size and slenderness in a measurement that is independent and complementary to grain-size distribution. There is a considerable effect of particle size on specific surface area; as the particle size decreases, the specific surface area increases (Santamarina et al., 2002). The high rate of adsorption by adsorbents with smaller particle sizes had been attributed to the availability of more specific surface areas on the adsorbent. According to Karthikeyan et al. (2004), the breaking of larger particles tend to open tiny cracks and channels on the particle surface of the material resulting in more accessibility to better diffusion, owing to the smaller particle size.

Figure 1 displays the plot of concentration of MB added versus the amount of absorbed MB used to identify the point of complete cation replacement. The specific surface areas calculated were 81.96 and 119.88  $m^2/g$  for UAWA and MAWA, respectively.

The obtained results revealed that the specific surface area increased slightly with acid modification of the adsorbent. Since the specific surface area varies inversely with the particle size, it can therefore be concluded that the chemical modification of the adsorbent reduced the

particle size thereby increasing the number of binding sites on the modified surface, which may result to better adsorption than the unmodified surface. Dermibas et al. (2002) observed an increase in specific area with a chemical modification of an agricultural waste using tetraoxosulphate VI acid.

### The $pH_{pzc}$ of the adsorbents

The  $pH_{pzc}$  is defined as the pH of the suspension at which the surface acidic (or basic) functional groups of an adsorbent no longer contribute to the pH value of the solution (Nomandhay and Palanisamy, 2005). The  $pH_{pzc}$  of each adsorbent, UAWA and MAWA, was assessed from the graph of zeta potential (mV) versus initial pH ( $pH_{initial}$ ) as displayed in Figure 2.

From the graph, it is seen that each adsorbent was positively charged at pH less than 6. However, above pH 6.0, there was a charge reversal. The  $pH_{pzc}$  of MAWA was found to be 6.6 and 7.3 for UAWA.

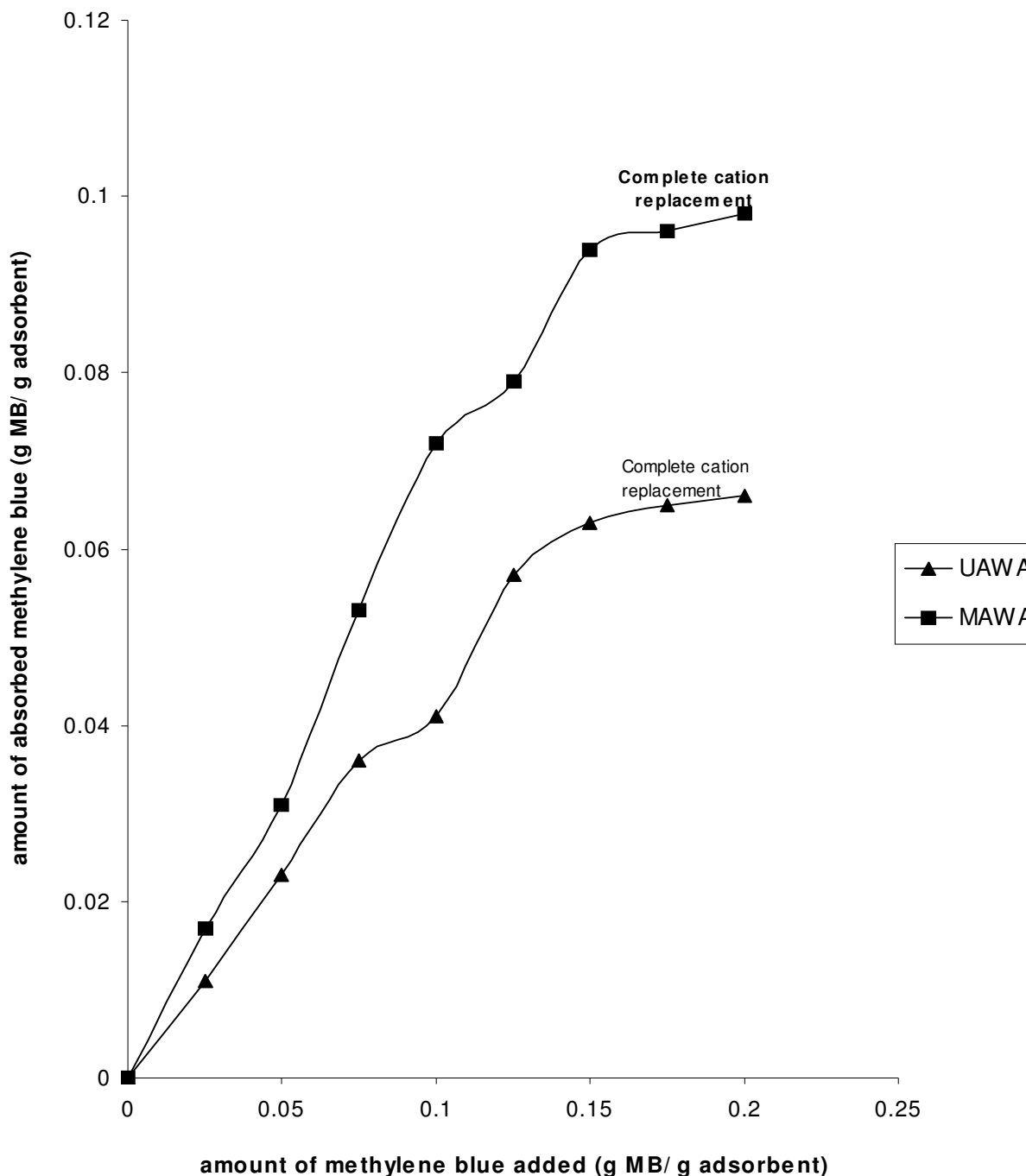
It has been reported by earlier researchers (Anirudvan and Krishnan, 2004) that the  $pH_{pzc}$  of an adsorbent decreases with increase in acidic groups on the surface of the adsorbents. From the results, it can be concluded that acid modification of the adsorbent gave a positive (acidic) surface charge for the adsorbent since the  $pH_{pzc}$  for the modified was found to be lower than that of the unmodified surface. The relationship between  $pH_{pzc}$  and adsorption capacity is that cations adsorption on any adsorbent will be expected to increase at pH value higher than the  $pH_{pzc}$  while anions adsorption will be favourable at pH values lower than the  $pH_{pzc}$  (Nomanbhay and Palanisamy, 2005).

The reduction in the value of the  $pH_{pzc}$  for the modified adsorbents caused by thiol enrichment is significant and would be expected to alter the sorption properties of the thiolated adsorbents due to electrostatic effects.

Thus, it can be concluded that chemical modification of the adsorbent surface with mercaptoacetic acid ( $CH_2SHCOOH$ ) reduced the  $pH_{pzc}$  of the adsorbent from pH 7.3 to 6.6 for MAWA. In a related study, Anirudvan and Krishnan (2003) reported the decrease in  $pH_{pzc}$  of steam activated sulphurized carbon prepared from sugar cane bagasse pith from pH 5.8 to 5.5, 4.7 to 4.3, respectively, by the loading of 2.3, 6.8 and 8.9% sulphur content. This indicated that the surface of the steam activated carbon might have been modified after activation in the presence of sulphur IV oxide ( $SO_2$ ) and hydrogen sulphide ( $H_2S$ ).

### Effect of pH on the sorption of the metal ions

The effect of pH on the removal efficiency of the metal ions Cr (VI), Cd (II), Ni (II) and Pb (II) by unmodified (UAWA) and modified (MAWA) adsorbents was examined by varying the solution pH from 2.0–8.0 using initial metal



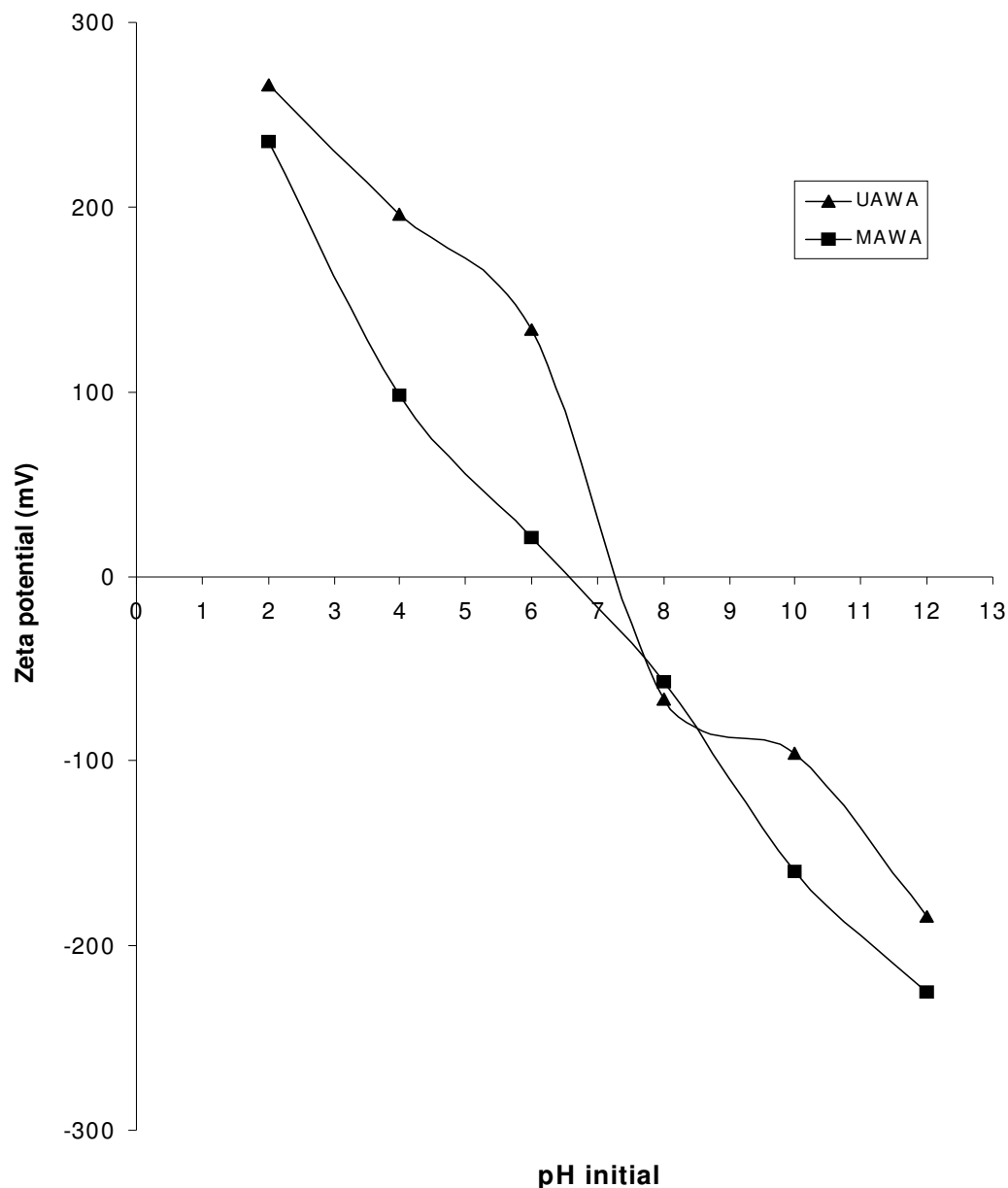
**Figure 1.** Plot of the amount of methylene blue added (g/g) vs amount of methylene blue absorbed by the adsorbents.

ion concentration of 25 ppm at temperature of 30°C. Figures 3 and 4 display the variation of solution pH on the sorption capacity of the metal ions from the solution by the adsorbents.

Estimating the optimum pH for metal removal is vital since the pH of a solution affects the surface charge of the adsorbents, degree of ionization and solution composition (metal speciation). 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).

With the exception of Cr (VI), the other three metal ions, Cd (II), Ni (II) and Pb (II) behaved in a similar fashion. From Figures 3 and 4, it is observed that the uptake (removal) of the metal ions depends on pH, where optimal metal removal efficiency of Cd (II) and Ni (II) occurred at a pH 6.0 while that of lead occurred at pH



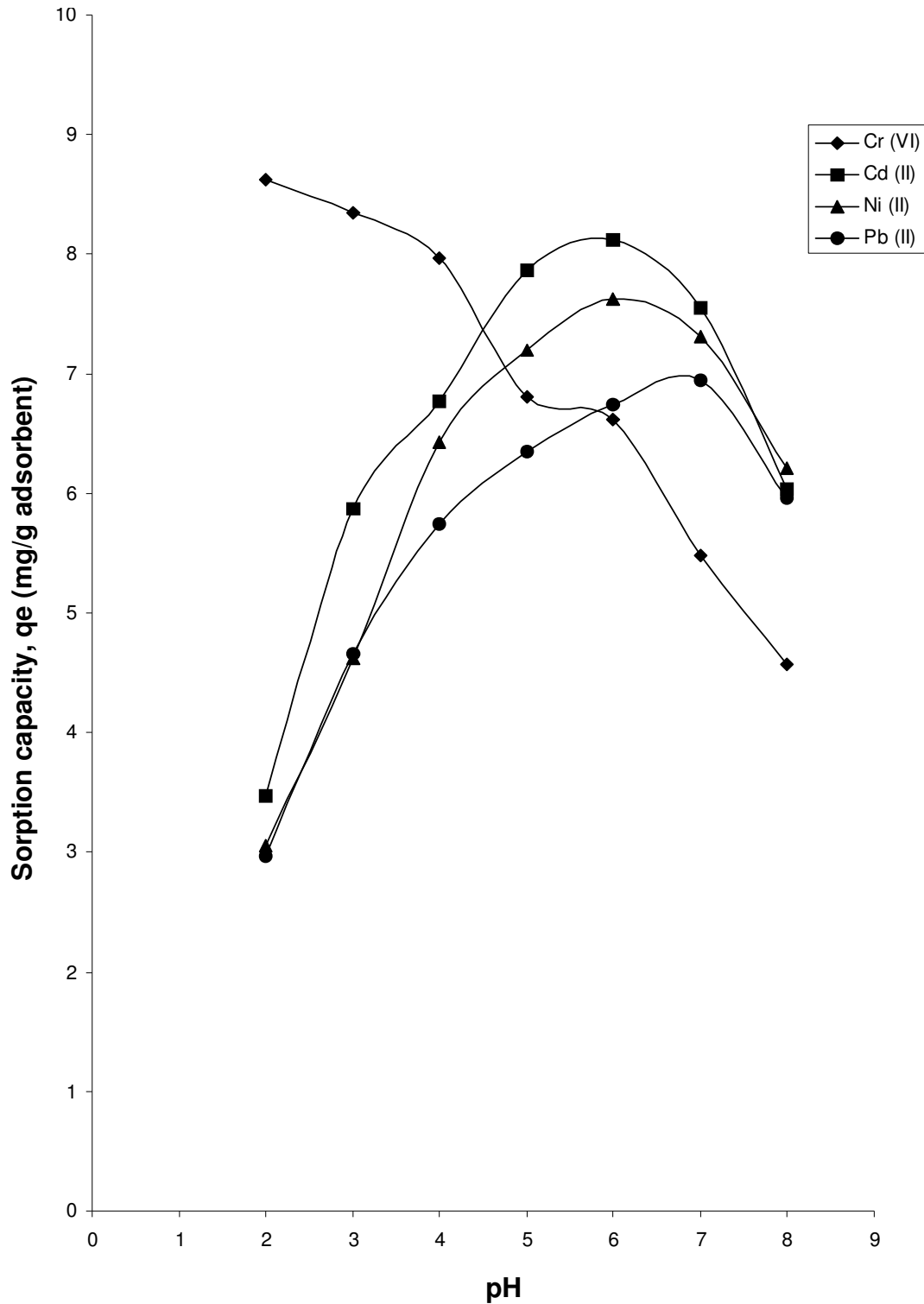
**Figure 2.** Plot of zeta potential (mV) vs initial pH for determination of pH point of zero charge of adsorbents.

7.0. Percentage removal for Cd (II) increased from 27.76 to 64.96% for pH increase from 2.0–6.0 and decreased to 48.20% at pH 8.0; for Ni (II), the removal efficiency varied from 24.44 to 61.04% for pH 2.0–6.0 and decreased to 49.68% at a pH 8.0; for Pb (II), there was an increase from 23.72 to 55.60% from pH 2.0 to 7.0 and decreased to 47.64% at a pH 8.0, all for sorption onto the unmodified surface (UAWA).

A similar trend was observed for the removal of the metal ions by the thiolated surface. Cd (II) increased from 29.88 to 71.40% for pH range 2.0 - 6.0 and decreased to 59.56% at a pH 8.0; Ni (II) increased from 27.32 to 70.12% for pH range 2.0 - 6.0 and decreased to 53.32%

at pH 8.0 while Pb (II) increased from 25.00 - 64.12% for pH 2.0 - 7.0 and decreased to 50.84% at pH 8.0 all for adsorption onto MAWA.

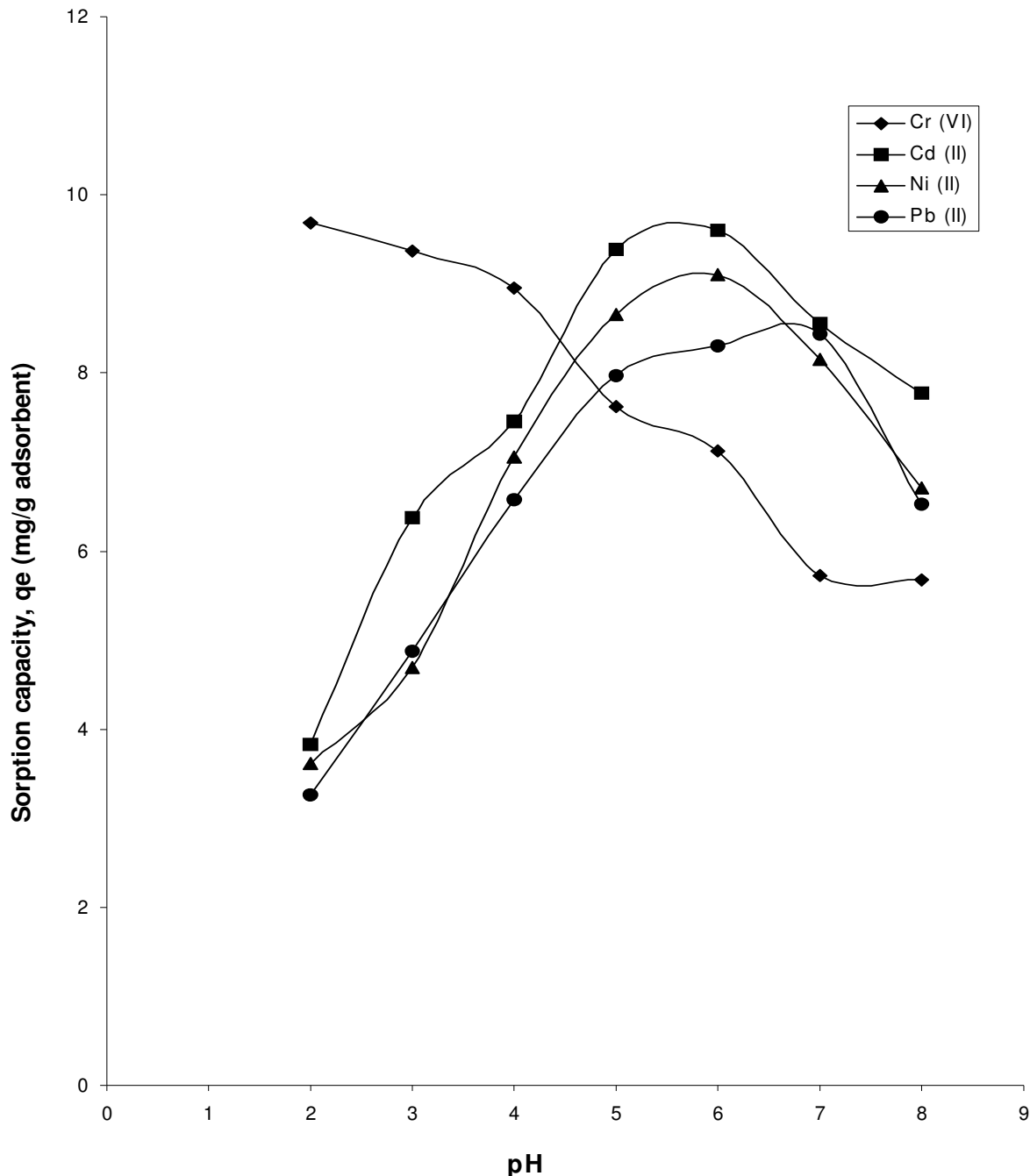
The plots show that the amount of metal ions removed from the solutions by the adsorbents increased as the pH of the metal ion solution is increased from pH 2.0 to 6.0 for Cd II and Ni II and pH 2.0 to 7.0 for Pb II. This shows that the optimum pH for the sorption of the metal ions, Cd II and Ni II is 6.0 while Pb II is 7.0. The decrease in uptake at higher and lower pHs may be attributed to the formation of precipitates of the metal hydroxides at higher pH and formation of more H<sup>+</sup> ions at lower pH, which might compete with the metal ions for active sites on the



**Figure 3.** Plot of sorption capacity vs initial pH for sorption of the metal ions onto the unmodified surface (UAWA).

adsorbent surface. According to Low et al. (1995), at low pH values, the surface of the adsorbents would be closely associated with hydroxonium ions ( $H_3O^+$ ) which might hinder the access of the metal ions, by repulsive forces, to

the surface functional groups and consequently decreasing the percentage metal removal. Therefore, the effect of low pH on the biosorption capacity may be interpreted to result from competition of the  $H_3O^+$  and metal ions for



**Figure 4.** Plot of sorption capacity vs initial pH for sorption of the metal ions on modified surface (MAWA).

binding sites. At low pH values, the ligands on the cell walls are closely associated with the hydroxonium ions thereby causing the surface of the adsorbents to be positively charged, but when the pH is increased, the hydroxonium ions are gradually dissociated and the positively charged metal ions are associated with the free binding sites on the adsorbent. This result also suggests that  $H^+$  ion concentration on these adsorbents affects the amount of metal ions adsorbed. The results further indicated that the levels of metal ion uptake by MAWA

surface were higher than the levels reported for the unmodified African white star apple.

Therefore, increased uptake of the metal ions at the higher pH (pH 6.0 and 7.0) for Cd, Ni and Pb may be attributable to the reduction in the amount of  $H^+$  in the solution and possibly the ionization of the  $-OH$  groups in the adsorbent matrix. The pH metal binding dependence of the African white star apple also suggests that the bound metals Cd II, Ni II and Pb II can be recovered by lowering the pH (reversing the reaction) of the medium.

Chromium (VI) on the other hand was found to exhibit different pH dependence with highest percentage removal occurring at a pH 2.0. Chromium exists mostly in two oxidation states, which are Cr (VI) and Cr (III) and the stability of these forms is dependent on the pH of the system (Ahalya et al., 2005; Cimino et al., 2000; Selomulya et al., 1999). Chromium (VI) displays different types of pH dependent equilibria in aqueous solution. As the pH is shifted, the equilibrium will also shift; in the pH range 2 - 6,  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions are in equilibrium. At lower pH values (pH < 2.0),  $\text{Cr}_3\text{O}_{10}^{2-}$  and  $\text{Cr}_4\text{O}_{13}^{2-}$  species are formed (Ahalya et al., 2005). The optimum initial pH for biosorption of hexavalent chromium on the adsorbents was observed at a lower pH, (pH 2.0). This reveals the formation of more polymerized chromium oxide species with decreased pH. Figures 3 and 4 reveal that 69.00 and 77.40% removal of Cr (VI) from a solution of 25 ppm of the adsorbates occurred at pH 2.0 for the adsorbents (UAWA and MAWA).

Conclusively, adsorption of metal ions depends on solution pH, which influences electrostatic binding of ions to corresponding active sites. At the optimum sorption pH 2.0, the dominant species of Cr (VI) ions in solution are  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Cr}_4\text{O}_{13}^{2-}$  and  $\text{Cr}_3\text{O}_{10}^{2-}$ . These chromate anions may interact very strongly with the positively charged ions on the adsorbents. Again, it has been reported (Krotochvil et al., 1998) that at lower pHs, Cr (VI) is reduced to Cr (III) by some biomasses. This might also explain the binding of Cr (VI) at low pH. It can therefore be concluded that African white star apple could be used to remove Cr VI, Cd II, Ni II and Pb II from aqueous solutions. The removal of the metal ions is pH dependent with each metal having a characteristic pH range within which it is mostly removed.

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