

## Sorption of Lead (II) and Copper (II) ions from Aqueous Solution by Acid Modified and Unmodified Gmelina Arborea (Verbenaceae) Leaves

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### Abstract

*Gmelina arborea* leaves of tropical origin were modified with citric acid as esterifying agent and was used to selectively removed Pb(II) and Cu(II) ions from aqueous solution by batch adsorption method. The concentrations of the metal ions adsorbed were determined by atomic absorption spectroscopic (AAS) method. The citric acid had a strong significant effect on the removal of metal ions from solution because of an increase in the carboxyl groups introduced into the biosorbent. The amount of metal ions removed from solution was found to depend on the metal ion-substrate contact time, ion concentration and ion type. The results indicated that after 90 minutes contact time, the amount of adsorbed metal ion increased with increase in the initial metal ion concentration up to 20 mg/cm<sup>3</sup>. This also varied with the cellulosic materials in the order Pb(II)>Cu(II). The acid modified *Gmelina arborea* leaves adsorbed more metal ions than when unmodified. The equilibrium data fitted well to the Freundlich adsorption isotherm. The *Gmelina arborea* leaves were better adsorbents of Pb(II) ion than Cu(II) ion.

**Keywords:** sorption, lead, copper, gmelina arborea leaves, aqueous solution

### INTRODUCTION

Environmental pollution with heavy metals has become a global phenomenon as a consequence of industrial and metallurgical process which introduce majority of toxic chemicals into the environment (Lone *et al.*, 2003; Faisal and Hasnain, 2004; Sadeghi *et al.*, 2006; Igwe and Abia, 2006 and Jimoh, 2010).

The heavy metals of widespread concern to human health are lead, copper, mercury, cadmium, arsenic, chromium, as well as zinc (Lazarova *et al.*, 2005). These are stable metals that cannot be destroyed or degraded in the environment and get passed up in the food chains to humans. At present, these toxic metals have polluted our atmosphere, our water, our soil and our food chain, and have been reported to be slightly toxic even at low concentration (Nedelkoska and Doran, 2000; Chehregani *et al.*, 2005). For instance, exposure to Lead causes anaemia, disease of the liver and kidney, brain damage and ultimately death, while, prolonged inhalation of Cu(II) spray is claimed to cause an increase in the risk of lung cancer (Aydin *et al.*, 2008). However, extensive research has been conducted on the discharge of metal ion contained in industrial effluents because of the presence and accumulation of toxic effects on living species. The recent Lead poisoning in Zamfara State, Nigeria between March and June, 2011 which claims thousands of lives clearly attests to the detrimental

effect of this metal in environment (The Punch Newspaper, June 15, 2011).

Some conventional methods used to remove heavy metals include chemical precipitation, ion exchange, electro dialysis, membrane separations, reverse osmosis, and solvent extraction (Feng *et al.*, 2000; Matlock *et al.*, 2002; Mohammed *et al.*, 2005). But these methods are often prohibitively costly, having inadequate efficiencies at low metal concentration. These constraints have caused the search for alternative methods that would be efficient for metal sequestering. Such a possibility offers a method that uses sorbents of biological origin for removal of heavy metals from aqueous solution based on metal binding capacities of various biological materials of little or no cost (Cimino *et al.*, 2000; Babarinde and Oyedipe, 2001; Babarinde *et al.*, 2002; Aksu, 2002; Abia *et al.*, 2003; Annadurai, *et al.*, 2003; Bansode, *et al.*, 2003; Demirbas, 2003; Feng and Aldrich, 2004; Ajmal *et al.*, 2005 and Jimoh, 2010). Now attention have directed towards the use of modified agricultural waste and by-products for the removal of heavy metals from industrial effluent. Okuo and Oviawe, (2007) demonstrated the use of cassava fiber modified with citric acid to selectively remove heavy metal ions from aqueous solution containing Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> ions. In a recent work, Egila *et al.*, (2010) showed that nitric acid modified *Amaranthus hybridus* L. stalk wastes could bind

substantial amount of Cobalt ion and that the amount of metal ion adsorbed per gram of the cellulose substrate increased with increased initial metal ion concentration.

*Gmelina arborea* otherwise called White teak, locally known as Gamhar, is a fast growing deciduous tree. It is native to India and Burma, but is now planted in many tropical areas due to its good form and growth. It grows on different localities and prefers moist fertile valleys with an annual rainfall between 750 and 4500mm and annual mean temperature of 25-38<sup>0</sup>C. It does not thrive on ill-drained soils and remains stunted on dry sandy or poor soils. The *Gmelina arborea* tree attains a moderate height up to 30 m with girth of 1.2 to 4. Flowering takes place during February to April when the tree is more or less leafless whereas fruiting starts from May onwards up to June (Ogbonnaya *et al.*, 1992). *Gmelina arborea* leaves however, littering the environment are thus gathered and used as biomaterial in this study.

Several researchers were able to show that chemical modification improved metal ion binding capacity of the substrate and that it increased the metal ion uptake rate. It was even suggested that the modification process involved the reduction of the molecular size of the substrate molecules through hydrolysis and the introduction of the carboxyl group on the substrate.

The objective of this study was to compare the adsorptive capability of citric acid modified and unmodified *Gmelina arborea* leaves for the removal of Lead and Copper ions from aqueous solution.

## MATERIALS AND METHODS

### Sample Collection

The *Gmelina arborea* leaves were collected from different spots in Federal University of Technology, Minna, Bosso campus. A composite sample of the collected leaves were made and representative samples were taken for sorption studies.

### Sample Pretreatment

The waste leaves were rinsed with deionised water to remove sand debris and sun-dried for about seven days and ground to fine powder by mortar and pestle. The sample was then sieved through a 300  $\mu\text{m}$  mesh size. The sample was divided into two parts and a part of it was modified using citric acid. The modification process was done by adding 30cm<sup>3</sup> of 0.5 mg L<sup>-1</sup> solution of citric acid into the sample and was stirred until the acid mixes properly with the sample to form slurry, it was then kept for about an hour and then dried in the oven 60<sup>0</sup>C.

### Preparation of Aqueous Solution

The aqueous solution containing cobalt was prepared from Cu (NO<sub>3</sub>)<sub>2</sub> .3H<sub>2</sub>O and Pb (NO<sub>3</sub>)<sub>2</sub>. A 1000 mg L<sup>-1</sup>

stock solution of the salts was prepared. Other concentrations (5, 10, 20, 30, 40 and 50 mg L<sup>-1</sup>) were obtained from this stock solution by serial dilution.

## SORPTION EXPERIMENT

### The Effect of Contact Time

The effect of contact time was studied using an initial concentration of 5 mg L<sup>-1</sup>. The time intervals chosen for this experiment were 30, 60, 90, 120, and 150 minutes.

### Procedure

0.5g of modified and unmodified sample was separately mixed with 20cm<sup>3</sup> solution of initial concentration 5 mg L<sup>-1</sup>. the mixture was shaken constantly in a shaker at 420rpm speed for the time period of 30, 60, 90, 120, and 150 minutes each. At the end of each contact time, the mixture was filtered and the concentration of the filtrate was determined using FAAS, model Pye Unicam SP-9 Cambridge, UK.

### The Effect of Initial Metal Ions Concentration

The effect of initial metal ion concentration on adsorption was studied as well at equilibrium time of 90minutes and varying the concentration from 10, 15, 20, 25 and 30 mg L<sup>-1</sup>.

### Procedure

0.5g of modified and unmodified sample each were separately mixed with 20cm<sup>3</sup> solution of initial concentration of 10, 10, 15, 20 25 and 30 mg L<sup>-1</sup>. The mixture were shaken constantly using a rotary shaker at 420 rpm for 90 minutes for both Cu (II) and Pb (II) ions. At the end of the 90 minutes, the mixture was filtered and the concentration determined using the Flame Atomic Absorption spectrophotometer (AAS). The difference between the initial concentration and the final concentration was recorded as the amount adsorbed for each concentration.

## RESULTS

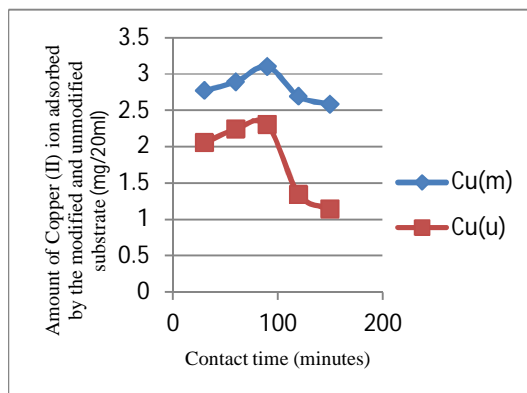


Figure 1: Effect of variation of contact on the adsorption of Copper(II) ion on modified and unmodified sample. The contact time was established at 90 minutes for both modified and unmodified sample

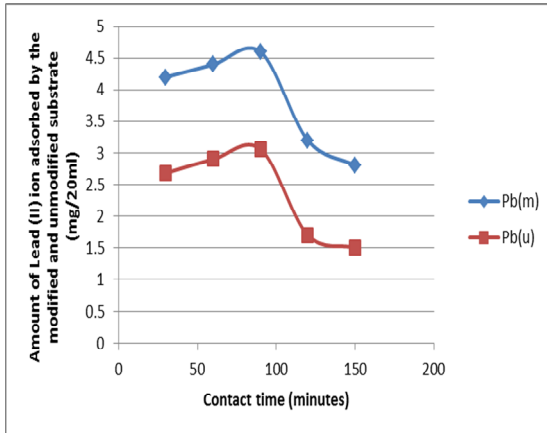


Figure 2: Effect of variation of contact on the adsorption of Lead(II) ion on modified and unmodified sample. The contact time was established at 90 minutes for both modified and unmodified sample

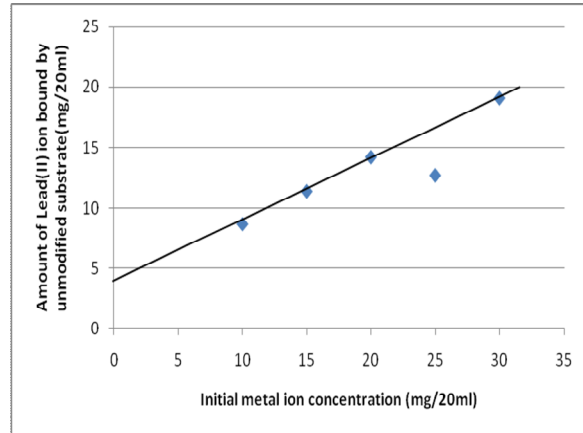


Figure 5: The effect of varying Lead(II) ion concentration on the adsorption of unmodified sample at 33°C for 90minutes. There was an increase in the amount of metal ions sorbed as the concentration increases from 10 to 30 ( mg/20ml).

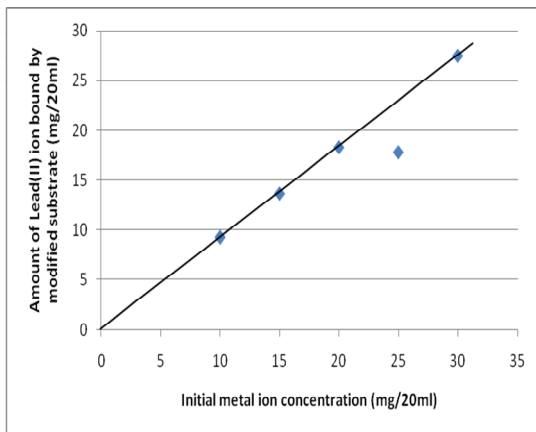


Figure 3: The effect of varying Lead(II) ion concentration on the adsorption of modified sample at 33°C for 90minutes. There was an increase in the amount of metal ions sorbed as the concentration increases from 10 to 30 ( mg/20ml)

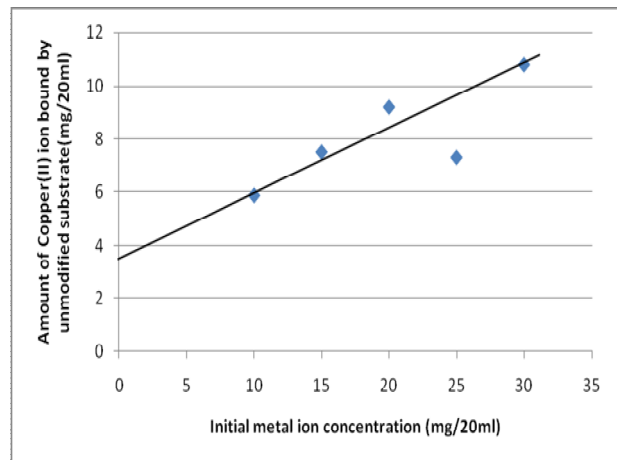


Figure 6: The effect of varying Copper(II) ion concentration on the adsorption of unmodified sample at 33°C for 90minutes. There was an increase in the amount of metal ions sorbed as the concentration increases from 10 to 30 ( mg/20ml).

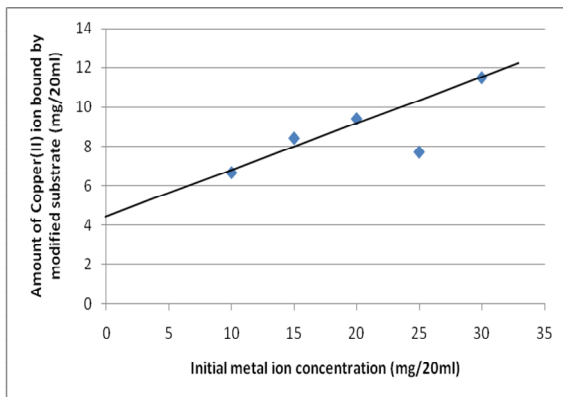


Figure 4: The effect of varying Copper(II) ion concentration on the adsorption of modified sample at 33°C for 90minutes. There was an increase in the amount of metal ions sorbed as the concentration increases from 10 to 30 ( mg/20ml).

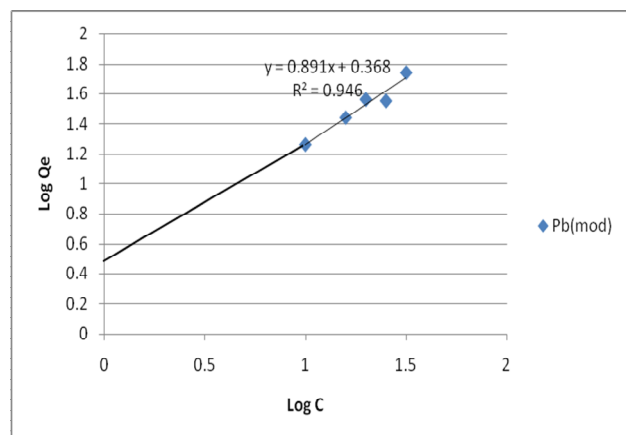


Figure 7: Freundlich adsorption isotherm plot of modified substrate on adsorption of Lead(II)ion

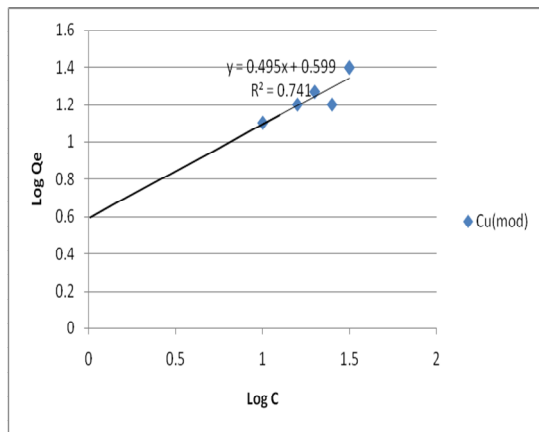


Figure 8: Freundlich adsorption isotherm plot of modified substrate on adsorption of Copper(II)ion

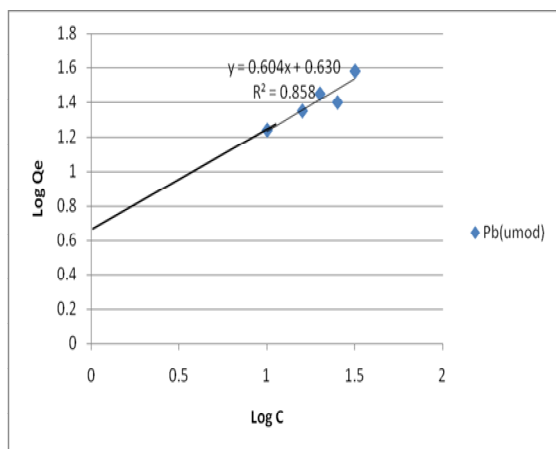


Figure 9: Freundlich adsorption isotherm plot of unmodified substrate on adsorption of Lead(II)ion

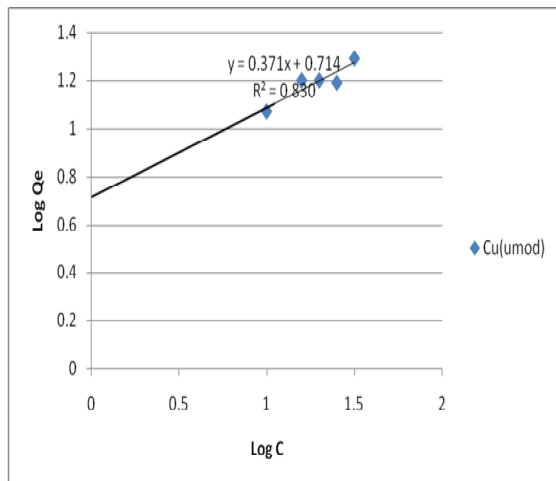


Figure 10: Freundlich adsorption isotherm plot of unmodified substrate on adsorption of Copper(II)ion

## DISCUSSION

### Effect of Contact Time on Adsorption

The results for the effect of contact time on adsorption of Pb(II) and Cu(II) ion as shown in Figure 1 to 2. The results shows that for an initial metal ion concentration of 5 mg L<sup>-1</sup> for Pb(II) and Cu(II) ions, there was a progressive increase in the amount of metal ions bound as the contact time increased for both modified and unmodified substrate. After the contact time of 90minutes, as the time increased further, the amount adsorbed reduces. This means that equilibrium was reached at 90 minutes, and the adsorption sites became saturated to maximum uptake capacity. Similar results have been reported in literature for the removal of Pb (II) and Cu(II) ions from aqueous solution by plant leaves (Saeed *et al.*, 2005), Neem leaves (Obloh *et al.*, 2009), water leaves (Oyebamiji *et al.*, 2009).

This study also showed that *Gmelina arborea* leaves was more efficient adsorbent for the removal of Pb (II) ions than Cu (II) ions, according to the results shown in figure 1 and 2, although they both reached equilibrium at the same contact time of 90 minutes, the amount of Pb (II) ions bound was more at every given contact time and even at their equilibrium. This is because ions with smaller sizes are heavily hydrated and make the size larger and bulkier than the less hydrated like Pb (II) ion. This will significantly enhance their chances of being adsorbed to the reactive sites present in the adsorbents because the heavily hydrated ions migrate slowly in aqueous solutions. This might be the reason why more of Pb (II) ion was able to adsorbed than Cu (II) ion.

Furthermore, a comparison of the Figures 1 to 2 shows clearly that Figure 2 gave better result than Figure 1, this probably means that the citric acid modified substrate could removed more of Pb (II) ion than Cu (II) ion. Also, the modified substrate was able to adsorbed more than the unmodified substrate. This was because the citric acid donated proton and made the adsorbent surface become protonated and upon contact with the metal ions, it adsorbed more rapidly. Thus, acid modification increases the binding capability of the substrate to the metal ion on adsorption.

### Effect of Initial Metal Ion Concentration on the Adsorption

The variation in the amount of metal ion on to the *Gmelina arborea* leaves with increasing initial metal ion concentration is illustrated in Figures 3 to 6. The result showed that the sorption capacity increased with increase in metal ion concentration for both modified and unmodified sample. Although modified substrates was able to bind more Pb(II) and Cu(II) ion than unmodified. This is as a result of the incorporation of carboxyl group by the citric acid on the adsorbent surface which enhances the binding

ability of the sorbent and as such increasing the number of binding sites. This phenomenon had been reported by several authors (Abia *et al.*, 2003; Annadurai, *et al.*, 2003; Bansode, *et al.*, 2003; Demirbas, 2003; Feng and Aldrich, 2004; Ajmal *et al.*, 2005 and Jimoh, 2010). This observation could also be explained in terms of progressive increase in the columbic interaction between the cationic species in water and the adsorbent sites. Moreover, more adsorption sites were being covered as the metal ions concentration increases. Besides, higher initial concentrations lead to an increase in the affinity of the metal ions towards the active sites and so at low concentrations, adsorption sites took up the available metal more quickly (Saifuddin *et al.*, 2005). Hence any further increase in the concentration of the metal ion will consequently lead to decrease in amount sorbed. The plausible reason for this might be attributed to the fact the adsorption sites of the adsorbent get saturated once it exhausts its binding capability. Similar results were observed by Han *et al.*, (2005) and Obboh *et al.*, (2009) who had independently reported the adsorption of copper (II) and lead (II) on chaff and Neem leaves from aqueous solution respectively.

Table 1: Freundlich isotherm constants for the adsorbent on Lead(II) and Copper(II) adsorption

Adsorbent /metal in solution	Equation of graph	$K_f$	1/n	N	$R^2$
Modified <i>Gmelina arborea</i> /Pb(II)	$Y=0.871x+0.368$	2.333	0.871	1.148	0.946
Modified <i>Gmelina arborea</i> /Cu(II)	$Y=0.495x+0.599$	3.971	0.495	2.020	0.741
<i>Gmelina arborea</i> /Pb(II) unmodified	$Y=0.604x+0.630$	4.266	0.604	1.656	0.858
<i>Gmelina arborea</i> /Cu(II) unmodified	$Y=0.371x+0.714$	5.176	0.371	2.695	0.830

**Adsorption Isotherm**

The Freundlich isotherm coefficients were determined by plotting  $\log Q_e$  against  $\log C$  and the results are shown in Table 1. The Freundlich model is used to estimate the adsorption intensity of the sorbent towards the adsorbate. The constants  $K_f$  and 1/n indicate the adsorption capacity and the adsorption intensity. The linearity of the plot showed the representative nature of adsorption on the adsorbents tested. The correlation regression coefficient  $R^2$  from the graphs showed that Lead (II) and Copper (II) ions adsorption was favorable. The values obtained were comparable to values of obtained from the previous studies on other adsorbents (Igwe *et al.*, 2005; Kurniawan, 2008). The

values of  $R^2$  and  $K_f$  from the plot indicates that adsorption was favorable. The value of 1/n which is less than 1 indicates that the metal ions are favourably adsorbed by the *Gmelina arborea* leaves. A value of  $1/n < 1$  indicates better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent (Patil *et al.*, 2006; Jimoh, 2010). This shows that *Gmelina arborea* leaves are better adsorbent for the metal ions.

**CONCLUSION**

The experiments showed that the adsorption process using *Gmelina arborea* leaves was dependent on both contact time and initial metal ion concentration. It was observed that the optimum binding of Cu (II) and Pb (II) ion to the powdered leaves occurred at a contact time of 90minutes. It was also observed that acid modified *Gmelina arborea* bind more metal ion than the unmodified adsorbent at every given time, and this attribute to the fact that citric acid increases its sorption capacities. The equilibrium data for both Cu(II) and Pb (II) metal ions fitted well into the Freundlich adsorption isotherm, and the linearity of the plot tested the representative nature of adsorption on the adsorbent, and the correlation regression coefficient showed that Cu(II) and Pb (II) ion adsorption was favorable using *Gmelina arborea* leaves

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