

## Sorption kinetics of Pb<sup>2+</sup> and Cu<sup>2+</sup> ions from aqueous solution by Nipah palm (*Nypa fruticans* Wurmb) shoot biomass

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The sorption kinetics of Pb<sup>2+</sup> and Cu<sup>2+</sup> ions in aqueous solution by unmodified and mercaptoacetic acid modified biomass of *Nypa fruticans* shoot has been investigated. The equilibrium sorption capacity of Pb<sup>2+</sup> and Cu<sup>2+</sup> was determined from the Langmuir equation and found to be 15.59 mg/g and 21.85 mg/g for unmodified biomass and 52.86 mg/g and 66.71 mg/g for modified biomass at 30°C. The time dependent studies showed relatively rapid sorption of 5 - 10 min to reach equilibrium for both metal ions. A batch sorption model, based on the assumption of the pseudo-second-order mechanism, was applied to predict the rate constants (g mg<sup>-1</sup> min<sup>-1</sup>), which were found to be 3.59 x 10<sup>-4</sup> (Pb<sup>2+</sup>) and 1.85 x 10<sup>-4</sup> (Cu<sup>2+</sup>) and 2.82 x 10<sup>-2</sup> (Pb<sup>2+</sup>) and 3.67 x 10<sup>-2</sup> (Cu<sup>2+</sup>) on unmodified and mercaptoacetic acid modified biomass respectively. The activation energy of the sorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> on Nypah palm reveals an endothermic process.

removal of heavy metals from wastewater are relatively expensive involving either elaborate and costly equipment or high costs of operation with ultimate disposal problems (Cheng-Shlun and Shang-Da, 1994). In view of these reasons, development of a more cost effective remediation process using biological system for removal of heavy metal ions from wastewater is necessary. Biomaterials previously investigated include sago waste (Quek et al. 1998), *Cyanidium caldarium* (Lucido et al. 1991), sunflower (Sun and Weixing, 1998), *Spagnum* peat moss (Gardea-Torresdey et al. 1996), cassava waste (Horsfall et al. 2003), Fluted pumpkin waste (Horsfall and Spiff, 2005a) and *Caladium bicolor* (Horsfall and Spiff, 2005b) for the removal of metal ions from aqueous solutions, just to mention a few. However, the necessity of investigating more biomaterials is still important in order to obtain the best biomaterial for industrial application.

Therefore, the aim of this project is to assess the potential ability of Nipah palm shoot biomass as adsorbent for the removal of metal ions from aqueous solutions. In this paper we report the sorption kinetics of Pb<sup>2+</sup> and Cu<sup>2+</sup> on unmodified and mercaptoacetic acid (MAA) modified biomass of Nipah palm (*Nypa fruticans* Wurmb) shoot.

Due to the increasing environmental concern regarding heavy metal contamination, there has been an abundance of interest in the removal of heavy metals from contaminated waste streams. Techniques presently in existence for

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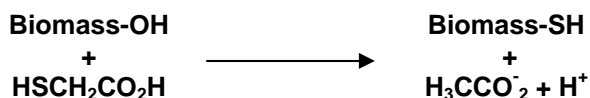
## MATERIALS AND METHODS

### Biomass preparation

The shoots of Nipah plant were obtained from the brackish waterfronts of the Niger Delta Area of Nigeria. The shoots were cut into smaller sizes and washed with deionised water. The samples were then oven dried at 90°C for seven days. Dried samples were ground and passed through the 100 µm mesh to obtain fine biomass. The biomass was then washed twice with 0.01 M HCl to remove any metals and debris that might be in the biomass prior to experimental metal ion exposure. The acid washed biomass were washed severally with deionised water until wash solution attained a pH of 7.1 and then oven dried at 40°C to constant weight. The dried biomass was then stored for further experimentation.

### Mercaptoacetic acid modification

25 grams of part of the pretreated biomass was mixed with 250 ml of 1.0 M MAA solution and mechanically stirred for 6 hrs at 30°C while maintaining a pH of 7.1. The mixture was allowed to settle overnight and then centrifuged at 2500 rpm for 10 min. The supernatant discarded and the paste washed with deionised water and then re-suspended in 0.1 M-hydroxyl amine to remove all o-acetyl groups. To remove all other soluble materials, the biomass was washed with deionised water and centrifuged at 2500 rpm for 5 min and supernatants discarded and the paste air-dried.



The mercaptoacetic acid modification process led to the thiolation of the hydroxyl groups of the cellulosic biomass by the following reaction (Horsfall et al. 2004).

The degree of incorporation of -SH groups was further

determined by reacting 0.5 g of acid treated biomass with 20 ml of iodine solution, followed by back titration of the un-reacted iodine with standard thiosulphate solution. The degree of thiolation was *ca.* 95%.

### Sorption experiments

Batch experimental procedure was applied to determine the contact times required for equilibrium sorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> by putting 0.2 g samples of the 100 µm mesh sized samples of unmodified and MAA modified biomass into several flasks. 10 ml of 37.5 mg/l Pb<sup>2+</sup> (from Pb(NO<sub>3</sub>)<sub>2</sub>) and 40.0 mg/l Cu<sup>2+</sup> (from CuSO<sub>4</sub>) solutions respectively were added and equilibrated by rocking at a mixing speed of 200 rpm for each time intervals of 5, 10, 20, 40 and 60 min. The suspensions were maintained at a fixed pH of 5.5 and kept at a constant temperature of 30°C in a water bath. At the end of each time interval, the suspension was allowed to settle followed by centrifugation at 2500 rpm for 5 min and then decanted. The supernatants were analyzed for Pb<sup>2+</sup> and Cu<sup>2+</sup> using a Buck Scientific Atomic Absorption/Emission spectrophotometer 200A (AAES). The calibration was performed within the range for each metal. Controls of one of the metal solution were run to detect any possible metal precipitation or contamination. The confidence level of the result was 95%. The difference between the initial metal concentration and the remaining concentration in supernatants was assumed to sorbed. Triplicate determinations were made for each determination and their mean values computed for quality assurance.

## RESULTS AND DISCUSSION

### Sorption isotherm

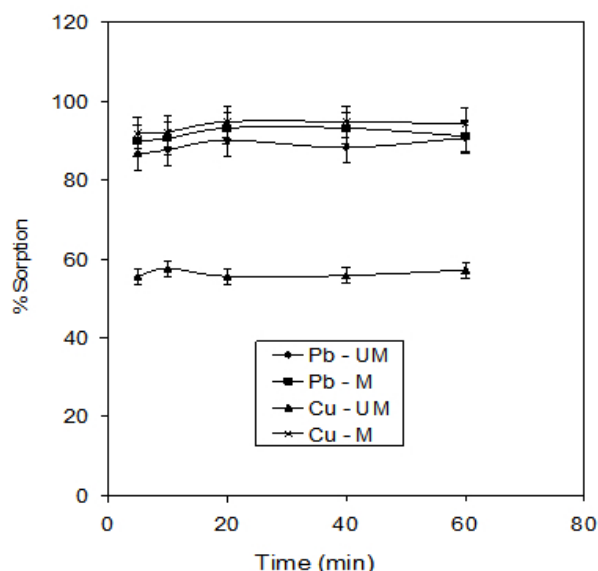
The time course profile as percent sorption for the sorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> from 37.5 mg/l Pb<sup>2+</sup> and 40.0 mg/l Cu<sup>2+</sup> solutions respectively using unmodified and mercaptoacetic acid modified Nipah palm shoot biomass are shown in Figure 1. The data showed that as the contact time increased from 5 to 60 min, there was only a slight increase

**Table 1. Comparison of Pb<sup>2+</sup> and Cu<sup>2+</sup> sorption capacities of different biomaterials.**

Material	*Sorption capacity, mg/g		Reference
	Pb <sup>2+</sup>	Cu <sup>2+</sup>	
Tree fern	39.8	10.6	Ho et al. 2002
Peat	24.7	12.4	Ho et al. 2000
Sago waste	46.6	12.4	Quek et al. 1998
Flute pumpkin waste	9.54	10.74	Horsfall and Spiff, 2005
Groundnut husk	39.3	*	Okiemen et al. 1991
Tea leaves	78.7	*	Tan and Khan, 1988
<i>Penicillium chrysogenum</i>	116	*	Niu et al. 1993
<i>Cladophora crispata</i>	251	*	Ozer et al. 1994
Oil-palm fibres	*	1.98	Low et al. 1993
<i>Aspergillus oryzae</i>	*	6.9	Huang et al. 1998
Cassava waste	*	127.3	Horsfall et al. 2004
Nypa palm shoot biomass <sup>+</sup>	15.59 <sup>+</sup> 52.86 <sup>++</sup>	21.85 <sup>+</sup> 66.71 <sup>++</sup>	This Study

\*Data not available in original text; <sup>+</sup> = unmodified; <sup>++</sup> = chemically modified.

in the amount of metal ion removed by both unmodified and chemically modified biomass, until a contact time of *ca.* 20 min was reached. After 20 min, metal ion removal remained approximately constant. These data indicate that the removal of Pb<sup>2+</sup> and Cu<sup>2+</sup> by Nipah palm shoot biomass is very rapid for unmodified and chemically modified biomass. Within the first 5 - 10 min, both unmodified and chemically modified biomass were capable of removing over 55.6 - 92.2% of both metal ions. According to Poots and co-workers as reported by Gardea-Torresday et al. 1998 and Ho et al. 1995, a short contact time necessary to reach equilibrium in adsorption studies indicates that the predominant mechanism of reaction is chemisorption. The relatively short contact times of 5 to 10 min for the sorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> onto both the unmodified and MAA modified biomass as shown in Figure 1 indicates that chemisorption is probably important. This implies that biomass regeneration will be difficult; however, since the biomass is relatively cheap, the use of spent biomass for energy purpose is possible.



**Figure 1.** Effect of contact time on the removal of dissolved metal ions by unmodified (UM) and chemically modified (M) biomass of *Nypa palm* shoot.

### Comparison analysis

The sorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> from aqueous solutions by a range of adsorbents which has been studied previously are compare with Nipah and are presented in Table 1. Ho et al. (2000) have reported that the sorption capacity of Pb<sup>2+</sup> and Cu<sup>2+</sup> by peat were 24.7 mg/g and 12.4 mg/g respectively at 20°C using 2.0 g/250 ml peat dose. Ho et al. (2002) in another adsorption study also used tree fern for the sorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> in and reported that the maximum sorption capacity for fern adsorbent were 39.8 mg/g and 10.6 mg/g of Pb<sup>2+</sup> and Cu<sup>2+</sup> at 20°C and a dose of 0.25 g/50 ml tree fern. Quek et al. (1998) examined the maximum sorption of

Pb<sup>2+</sup> and Cu<sup>2+</sup>. Using 4 g/l of sago waste at 25°C, they found 46.6 mg/g for Pb<sup>2+</sup> and 12.4 mg/g for Cu<sup>2+</sup>. Fluted pumpkin waste had a maximum sorption capacity of 9.54 mg/g for Pb<sup>2+</sup> (Horsfall and Spiff, 2005a) and 10.74 mg/g for Cu<sup>2+</sup> (Horsfall and Spiff, 2005b). Other adsorption studies show that the maximum sorption capacities of ground nut husk (Okieimen et al. 1991), tea leaves (Tan and Khan, 1988), *Penicillium chryogenum* (Niu et al. 1993) and *Cladophora crispata* (Ozer et al. 1994) for Pb<sup>2+</sup> were 39.3 mg/g, 78.7 mg/g, 116 mg/g and 251 mg/g, while oil-palm fibre (Low et al. 1993), *Aspergillus oryzae* (Huang et al. 1998) and Cassava waste (Horsfall et al. 2004) were respectively 1.98, 6.9, 10.1 and 127.3 mg/g for Cu<sup>2+</sup>. Although the comparison of the adsorption characteristics of different adsorbents tested under different condition could be misleading, it has come to stay as a procedure which is done frequently. The comparison of Nipah palm shoot biomass with other biomaterials used as adsorbent indicates that the biomass of Nipah palm shoot is also a good source of adsorbent for remediation of metal ion polluted effluent and that were more effective for some of the inorganic materials.

**Table 2.** Pseudo-second order rate constants for the sorption of Pb<sup>2+</sup> and Cu<sup>2+</sup> by unmodified (UM) and mercaptoacetic acid modified (M) biomass of Nipah palm.

Metal ion		$q_e$ , mg/g	$k_2$ , g/mg min	$h$ , mg/g min	$R^2$
Pb <sup>2+</sup>	UM	15.59	$3.59 \times 10^{-3}$	0.89	0.9996
	M	21.85	$1.85 \times 10^{-4}$	0.09	0.9996
Cu <sup>2+</sup>	UM	52.86	$2.92 \times 10^{-2}$	81.59	1.000
	M	66.71	$3.67 \times 10^{-2}$	159.86	0.9996

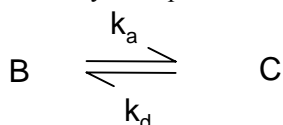
Examination of the maximum sorption capacity for both metals by unmodified and chemically modified biomass indicated that, mercaptoacetic acid modified Nipah palm shoot biomass have a greater sorption capacity than unmodified biomass. This improved sorption capacity of MAA modified biomass may have resulted from the relative ease of exchanging H<sup>+</sup> of the - SH groups with metal ions and also probably due to the presence of empty 3d orbital in sulphur atom. Similar observations have been made by other workers (Ho et al. 1995; Horsfall et al. 2004).

The sorption capacity for Pb<sup>2+</sup> and Cu<sup>2+</sup> are 15.59 mg/g and 21.85 mg/g respectively for unmodified biomass and 52.86 mg/g and 66.71 mg/g for modified biomass. The data revealed that the sorption capacity of the Nipah palm shoot biomass towards Cu<sup>2+</sup> was greater than that of Pb<sup>2+</sup>. Differential sorption of metal ions from aqueous solutions by adsorbents have been generally ascribed to three principal processes: (1) differences in ionic sizes of the metal ions, (2) differences in the affinity of the metal ions for active groups on the adsorbent and (3) nature of anions of the salt of the metal ion. The differential sorption behaviour could be explained in terms of ionic radii of the

metal ions ( $Pb^{2+} = 1.20 \text{ \AA}$ ;  $Cu^{2+} = 0.69 \text{ \AA}$ ). Generally, the element with smaller ionic radius will compete faster for exchange sites than those of larger ionic radius (Ho et al. 1995). This may have influenced the greater sorption ability of  $Cu^{2+}$  on the biomass than  $Pb^{2+}$ .

### Sorption kinetics

The rate of adsorption of a molecule onto a surface is an essential parameter when designing batch sorption systems, consequently it is essential to establish the time dependence of such systems under various process conditions. In an attempt to describe the sorption rate and confirm the reaction mechanism of  $Pb^{2+}$  and  $Cu^{2+}$  onto Nipah palm shoot biomass, two kinetic models were applied to the experimental data. The first model was based on the assumption that sorption of metal ions onto the biomass was reversible and followed a first order rate kinetics. The hypothetical reaction may be expressed as



where  $k_a$  and  $k_d$  are the adsorption and desorption constants respectively.

The concept developed by Vinod and Anirudhan (2002) was applied to confirm the first-order model. The equation is expressed as (equation 1):

$$\ln(1 - \alpha) = kt \quad [1]$$

where  $(1 - \alpha)$  is the fraction of metal ion in solution at equilibrium and  $k$  is the overall rate constant.  $\alpha$  is the fraction of metal ion adsorbed by the biomass at equilibrium, and it is the ratio of the amount of metal ion ( $q_t$ ) removed from solution at time  $t$  to that removed at equilibrium ( $q_e$ ). This model was tried without success. Hence, the experimental data were further evaluated based on the pseudo-second order kinetic rate model proposed by Ho et al. (1995). The pseudo-second order equation kinetic model is usually expressed as in equation 2:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad [2]$$

where  $h = k_2 q_e^2$  can be described as the initial rate constant as  $t$  approaches zero.  $q_t$  is the amount of metal ion on the biomass surface (mg/g) at any time  $t$ .  $q_e$  is the amount of metal ion sorbed at equilibrium (mg/g);  $k_2$  is the pseudo-second order rate constant (g/mg min). If the pseudo-second-order kinetics is applicable, the plot of  $t / q_t$  vs.  $t$  will give a linear plot, which allows the

computation of  $q_e$ ,  $k_2$  and  $h$  without having to know any parameter before hand.

According to Ho et al. (1995), if the plot is linear, then the sorption process may be described as chemisorption. The experimental data were fitted into equation 2 and a plot of  $t / q_t$  vs.  $t$  made (Figure 2) and a linear relationship was observed. The values of the sorption capacity of the biomass,  $q_e$ , the pseudo-second order rate constant,  $k_2$ , the initial sorption rate constant,  $h$ , and the coefficients of determination,  $r^2$ , were evaluated from the plot (Figure 2) and the data presented in Table 2. The data showed that, modification of the raw biomass by mercaptoacetic acid enhanced the equilibrium sorption capacity of the biomass towards both metal ions. The rate constants decreased (from  $3.59 \times 10^{-3}$  to  $1.85 \times 10^{-4} k_2, \text{ g/mg min}$ ) from unmodified to modified biomass towards  $Pb^{2+}$ , while an increase (from  $2.92 \times 10^{-2}$  to  $3.67 \times 10^{-2} k_2, \text{ g/mg min}$ ) was observed for  $Cu^{2+}$ . The initial rate is also dependent on the chemical modification of the biomass, which indicates that removal of  $Pb^{2+}$  and  $Cu^{2+}$  from aqueous solution may be achieved much easily and more rapid onto chemically modified biomass. Furthermore, the coefficient of determination,  $r^2$ , from the pseudo-second order rate model showed that,  $r^2$  values are greater than 0.990 for both metals with or without modification. The coefficient of determination values indicates that the biomass in its natural or modified form is an excellent biomaterial for the removal of metal ion from aqueous solution.

The sorption rate constant was employed to evaluate the activation energy, using an Arrhenius form equation expressed by the following relationship (Ofomaja and Ho, 2005):

$$k = k_o \exp\left(-\frac{E_a}{RT}\right) \quad [3]$$

where  $k$  is the sorption equilibrium constant,  $k_2, \text{ g/mg min}$ ,  $k_o$  is initial rate constant,  $E$  is activation energy,  $R$  is the gas constant (8.314 J/k mol) and  $T$  is absolute temperature (K).  $k_o$  may be related to  $h$ , hence equation 3 may be rewritten as:

$$k = h \exp\left(-\frac{E_a}{RT}\right) \quad [4]$$

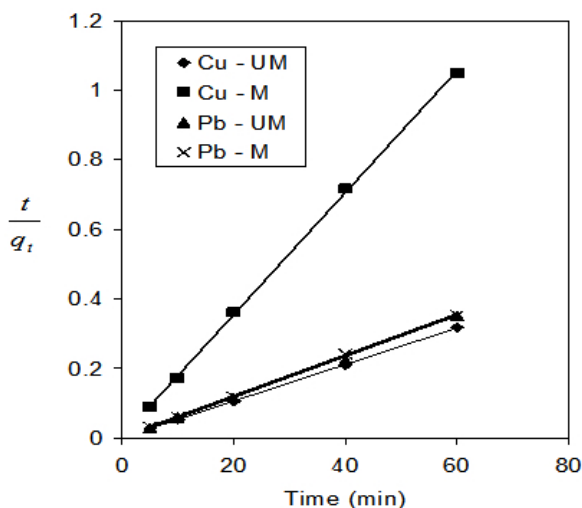
The linear form of the Arrhenius expression was applied to our experimental data (equation 5):

$$\ln k = \ln h - \frac{E_a}{RT} \quad [5]$$

The parameters  $k$  and  $h$  were experimentally determined from the intercept and slope of a plot of  $t / q_t$  vs.  $t$  and the values of  $E$  computed from equation 5 at ca. 30°C.

The activation energies are positive indicating an endothermic reaction, meaning that small amount of energy is required by the sorption system and that temperature increase may not enhance the sorption process.

**Figure 2. Determination of pseudo-second order rate constants on the removal of dissolved metal ions by unmodified (UM) and chemically modified (M) biomass of Nypa palm shoot.**



## CONCLUDING REMARKS

Sorption of the Pb<sup>2+</sup> and Cu<sup>2+</sup> onto the MAA modified and unmodified Nipah palm biomass was found favourable. The kinetic data has provided information on the suitability of Nipah palm biomass as an excellent biosorbent for Pb<sup>2+</sup> and Cu<sup>2+</sup> in aqueous effluents. The acid modification process enhanced the sorption capacity of the biomass. The results from these studies will be useful for a novel phytofiltration technology, which is effective and environment friendly to remove and recover heavy metal ions from aqueous solution.

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