

Full Length Research Paper

Desorption of Pb²⁺ and Cu²⁺ from Nipa palm (*Nypa fruticans* Wurmb) biomass

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The desorption of Pb²⁺ and Cu²⁺ from *Nypa fruticans* Wurmb biomass originally loaded with these two metals in a batch adsorption experiment was investigated using acidic, basic and neutral desorption solutions. The metal-loaded biomass was treated with 0.1 M HCl, 0.1 M NaOH and distilled water at varying contact time. The data shows that desorption in all the reagent increased with increase in contact time, reaching 75.3 and 63.7% in acid reagent, 18.9 and 14.06% in basic reagent and 3.35 and 2.44% in distilled water for Pb²⁺ and Cu²⁺, respectively, at a contact time of 140 min. The desorption kinetic showed that the release constant, k_{des} , for both metal ion in acidic system was faster (6.3×10^2 and $7.9 \times 10^2 \text{ min}^{-1}$ for Pb²⁺ and Cu²⁺) than other desorption reagents.

Key words: Desorption, adsorption, heavy metals, Nipa palm, industrial effluent.

INTRODUCTION

Regeneration and recovery of spent adsorbents and metals respectively is very important as it will reduce the cost of remediation of heavy metals and other contaminants in our environment. The increasing industrialization has led to the presence of heavy metals in the environment, which has become a major threat to plant, animal and human lives due to their bio-accumulating tendencies and toxicity. There is, therefore, the need for the removal of these toxic metals from municipal and industrial effluents before discharge.

In a recent study (Wankasi, 2004), Nipa palm biomass was used in an adsorption experiment to remove several metal ions from aqueous solution. It was observed that Nipa palm (*Nypa Fruticans* Wurmb) possesses some chemical characteristics that make it suitable for the possible removal and recovery of metals from wastewater

without disintegration during the process. Also a number of studies have demonstrated the feasibility of using plant biomass to remove heavy metals ions from aqueous solutions (Abia et al., 2003; Horsfall et al., 2004; Quek et al., 1998; Gardea-Torresdey et al., 1998). However, in the literature, information on desorption of adsorbed metals from biomass is scanty (Horsfall et al., 2004; Zhou et al., 1998; Chu and Hashim, 2001).

Due to the paucity of information, this project was aimed at studying the desorption of metals adsorbed by the biomass with a focus on reduction of by-products and cost implication. This paper reports the study on the ability of acidic, basic and neutral solutions in recovering Pb²⁺ and Cu²⁺ already adsorbed by Nipa palm biomass.

MATERIALS AND METHODS

Biomass preparation

The shoots of Nipa plant were obtained from the brackish waterfronts of the Niger Delta Area of Nigeria. The shoots were cut

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into smaller sizes and washed with deionized water. The samples were then oven dried at 90°C for seven days. Dried samples were ground and passed through the 100-mesh screens using a Wiley mill. These particle sizes of biomass were 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 twice again with deionized water to remove acid and then oven dried at 70°C to constant weight.

Batch adsorption experiment

Batch experiments were first conducted to load the Nypa biomass with metal ions separately. In this experiment 250 mg of the biomass was weighed and placed in pre-cleaned test tubes in triplicates. Several metal ion solutions with standard concentrations of 20, 40, 60, 80, and 100 mg/L were made from spectroscopic grade standards of Pb^{2+} (from $Pb(NO_3)_2$) and Cu^{2+} (from $CuSO_4$). The two metals solutions made separately were adjusted to pH 5.0 with conc. HCl. 50 mL of each metal solution were added to each tube containing the biomass and equilibrated for 2 h by shaking at 29°C.

The biomass suspensions were centrifuged for 5 min at 3000 rpm. The supernatants were analyzed as stated in metal analysis. The amount of metal uptake was computed using equation 1.

Batch desorption experiment

250mg of metal-laden Nypa biomass were placed in several flasks containing 50 ml of 0.1 M HCl, 0.1 M NaOH or distilled water. The flasks were shaken for 20, 40, 60, 80, 100, 120 and 140 min at 29°C. At the end of each time interval the suspensions were centrifuged at 2500 rpm for 5 min. The supernatants were measured for metal ion concentration using atomic absorption spectroscopy (AAS).

Metal Analysis: The metal analysis was performed by AAS using a Buck scientific Atomic Absorption/Emission spectrophotometer 200A (AAES). Controls of one of the metal solution were run to detect any possible metal precipitation or contamination.

Data Analysis: The amount of metal uptake was computed using the following formula (equation 1):

$$q_e = v/m(C_o - C_e) \quad (1)$$

with q_e as metal uptake capacity (mg/L biomass at equilibrium), C_e is metal ion concentration in solution (mg/L) at equilibrium, C_o the initial metal ion solution (L) and M the dry weight of biomass used in (g).

Under the experimental conditions employed, metal ion loading of 50.13 Pb^{2+} mg/g and 49.63 Cu^{2+} mg/g biomass was obtained which was used in all the desorption study.

The amount of metal ion remaining on the biomass as a function of time were estimated using a mass balance equation as shown in equation 2:

$$q_t = q_e - c_t(v/m) \quad (2)$$

where q_t and q_e are the biomass phase metal ion concentration (mg/g) and C_t solution phase metal ion concentration (mg/L) at time t (min) respectively.

Kinetic of desorption was described by a pseudo-first order rate equation previously described by Chu and Hashim (2001)

equation previously described by Chu and Hashim (2001) and expressed as follows (equation 3):

$$\frac{q_t}{q_o} = \exp(-k_{des}t) \quad (3)$$

where q_t is the metal concentration in the biomass phase (mg/g biomass) at time t (min). q_o is the total desorbable metal concentration in the biomass at the beginning (mg/g biomass) and k_{des} is the pseudo first-order desorption rate constant (min^{-1}). k_{des} can also be said to be the release constant.

To account for the fraction of bound metal ion resistant to desorption by recovery reagents, equation 3 was modified as follows (equation 4):

$$\frac{q_t}{q_o} = \theta \exp(-k_{des}t) + (1 - \theta) \quad (4)$$

where θ is a desorption fraction of the initial metal loading (q_o) and $(1 - \theta)$ is fraction resistant to desorption.

The linear form of equation 4 can be obtained by taking natural logarithm of equation 4 as given below in equation 5:

$$\ln \frac{q_t}{q_o} = \ln \theta - k_{des}t + (1 - \theta) \quad (5)$$

The pseudo first-order kinetic of desorption k_{des} and values of desorbable fraction θ and fraction resistant desorption $(1 - \theta)$ can

be obtained from a plot of $\ln \frac{q_t}{q_o}$ against time (min).

RESULTS AND DISCUSSION

Desorption studies help in the elucidating the mechanism of metal ion removal and recovery from metal-loaded adsorbent and also for the regeneration and recycling of spent adsorbents, which in turn may reduce operational cost and protect the environment. In order to assess the recyclability of the Nipa palm biomass, desorption reagents of acid, basic and neutral systems were tried at varying contact times with the biomass. The data in Figure 1 gives the percent desorption of the Pb^{2+} and Cu^{2+} as a functions of contact time. The figure showed that the longer the contact time between the metal loaded biomass and the recovery reagent, the higher the amount of metal ion recovered from the biomass. It was also noticeable from the figure that desorption in the acidic media for both metal ions were more rapid than in basic and neutral media. At the end of the study time of 140 min, it was noticed that over 70 and 60% of Pb^{2+} and Cu^{2+} were recovered from the biomass by the acidic reagent, which increased from 40.2% at 20 min to reach 75.3% at 140 min for Pb^{2+} and 28.9% at 20 min to 63.7% at 140 min for Cu^{2+} . In the case of desorption in basic

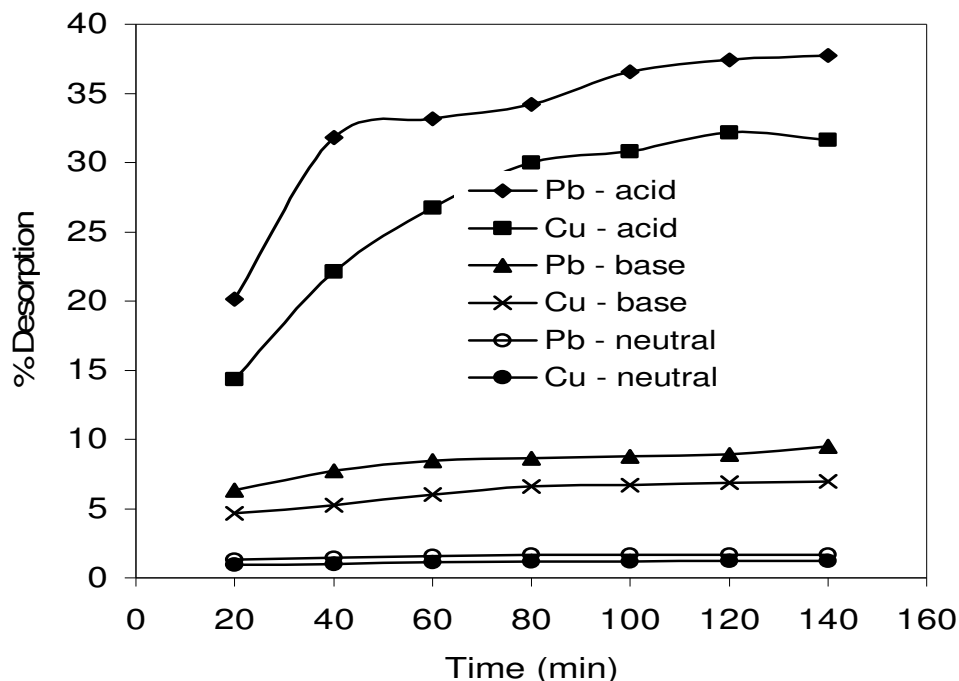


Figure 1. Effect of desorption media on the recovery on Pb^{2+} and Cu^{2+} from metal loaded Nipa palm biomass.

media (0.1 M NaOH), less than 20% of both metal ions (18.9% for Pb^{2+} and 14.06% for Cu^{2+}) were recovered from the metal-laden biomass at the end of study time. Insignificant level (less than 4%) of desorption was recorded for distilled water (neutral media). The highest metal recovery from the metal-laden biomass was observed in acid medium. This is because in acidic medium the carboxyl, carbonyl or hydroxyl groups in the biomass become protonated and does not attract the positively charged metal ions, and so the protons replace the bound metal ions. The poor desorption of less than 20% observed in basic medium may be due to the coordinating ligands being deprotonated hence bound-metal ions find it difficult to be detached from the biomass.

Comparatively, desorption of bound metal ions from the biomass is greater for Pb^{2+} than Cu^{2+} in all the desorption media tested. This observation may be due to the formation of stronger metal-biomass bond with Cu^{2+} as a result of smaller ionic radius.

The concentration decay profiles of the biomass phase expressed in terms of the ratio of metal concentration remaining on the biomass to metal concentration initially loaded (q_t/q_0) is shown in Figure 2. The decay profiles indicate that both the extent and the rate of desorption increased with increasing hydrogen ion or hydroxonium ion concentration. Although complete desorption were not

achieved, it is clear from the results that the HCl acidic medium is a better recovery agent than the NaOH basic medium. The data also indicates that desorption is a time dependent variable. It may be possible to obtain 100% desorption if the contact time is extended. However, the reusability of the biomass must be considered, because the longer the biomass get in contact with the desorption reagent the faster the biomass may be and lose its reusability.

It is necessary to consider the kinetics of desorption to assess the overall performance of desorbing reagent. The pseudo-first order kinetics of desorption, k_{des} , was used to evaluate the release constant. k_{des} is a measure of the degree of desorption. The larger the value of k_{des} ,

the greater the desorption. A plot of $\ln \frac{q_t}{q_0}$ against time

was made and the plot is shown in Figure 3. The release constant, k_{des} , and values of desorbable fraction θ for both metal ions as obtained from regression lines of Figure 3 is presented in Table 1.

The data further confirmed that acidic medium constitutes the best desorption reagent as it has the potential highest desorbable fraction. Furthermore, the release constant of the acid reagent was observed to be

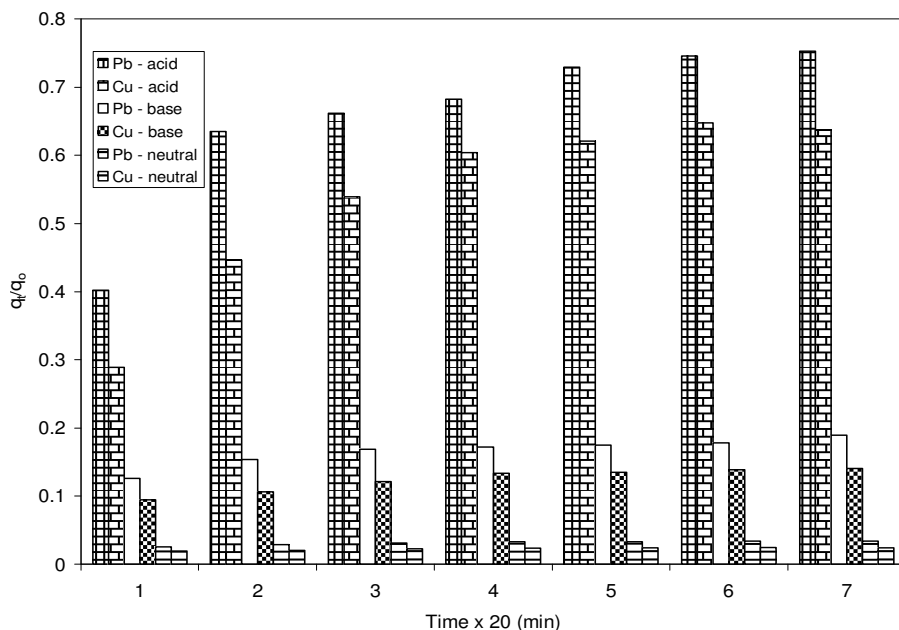


Figure 2. Concentration decay profile of Pb²⁺ and Cu²⁺ from Nipa palm by the desorption media.

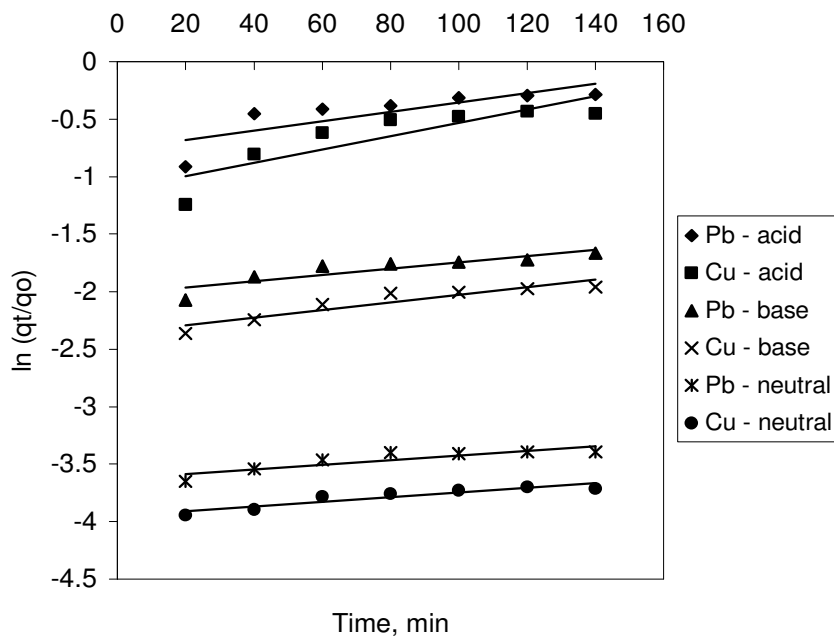


Figure 3. Pseudo-first order desorption kinetic plots on the recovery on Pb²⁺ and Cu²⁺ from metal loaded Nipa palm biomass.

twice greater than the other reagents, making it a potentially better reagent than the basic medium.

One property of an adsorbed molecule that is intimately related to desorption kinetics is the surface residence

time (τ). This is the average time that a molecule will spend on the surface under a given set of conditions before it desorbs into the aqueous phase. The residence time is very essential because the higher the residence

Table 1. Values of release constant (k_{des}) and desorbable fraction (θ) of Pb^{2+} and Cu^{2+}

Desorption reagent	Pb^{2+}		Cu^{2+}	
	k_{des}, min^{-1}	θ	k_{des}, min^{-1}	θ
0.1 M HCl	6.3×10^{-2}	0.92	7.3×10^{-2}	0.86
0.1 M NaOH	3.6×10^{-2}	0.33	3.0×10^{-2}	0.18
Distilled water	2.4×10^{-2}	0.002	1.7×10^{-2}	0.002

Table 2. Values of surface residence time (τ) computed from the release constants for Pb^{2+} and Cu^{2+} desorption in different media at 29°C.

Desorption reagent	Pb^{2+}		Cu^{2+}	
	$k_{des} (\text{min}^{-1})$	τ (sec)	$k_{des} (\text{min}^{-1})$	τ (sec)
0.1 M HCl	6.3×10^2	0.095	7.3×10^2	0.082
0.1 M NaOH	3.6×10^2	0.167	3.0×10^2	0.200
Distilled water	2.4×10^2	0.250	1.7×10^2	0.353

time, the longer the contact between the desorption reagent and the metal loaded biomass. Hence, residence time must be relatively small in order to protect the deterioration of the biomass and enhance its recyclable life time.

For a pseudo-first order process, the average surface residence time prior to the desorption process occurring may be given as in equation 6:

$$\tau = \frac{1}{k_{des}} \quad (6)$$

The surface residence times of the two metals ions in the recovery media were computed and are presented in Table 2. The data observed in this study was very short, which is an essential requirement for wastewater in a sorber system and may result in a higher operational efficiency of the sorber. This relatively short residence time is also essential for regeneration of spent biomass. It was observed that acidic media had the shortest residence time indicative of its potential in preserving the biomass for further use.

The negative values of ΔH_0^{des} suggest that lower solution temperatures will favour desorption of Pb^{2+} and Cu^{2+} from the *Nypa* biomass and the desorption mechanism is an exothermic process.

The applicability of plant biomass for metal ion recovery from waste streams requires that the biomass be regenerated efficiently so that the bound metal can be recovered in concentrated form and the biomass reused. Although a single cycle of adsorption- desorption

equilibrium studies is not enough to sufficiently access the desorption capacity of a desorption reagent, the study has demonstrated that the selection of an eluent may be influenced by the consideration of the reusability of the biomass as well as the desorption kinetics. The results of this investigation are quite useful for further researches especially in trying concentration gradients to obtain optimum working concentration for the acid media. The study will be beneficial to small and medium scale industries.

REFERENCES

- Abia AA, Horsfall M Jnr, Didi O (2003). The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from solution. *Bioresour. Technol.* 90 (3): 345-348.
- Chu KH, Hashim MA (2001). Desorption of Copper from Polyvinyl alcohol immobilized seaweed biomass. *Acta Biotechnol.* 21(4): 295-306.
- Gardea-Torresdey J L, Gonzalez JH, Tiemann JL, Rodinguez O, Gamez G (1998). Phytosorption of cadmium, chromium, lead and zinc ions by biomass of *Medicago sativa* (Alalfa). *J. Hazard. Mater.* 57: 29 - 39.
- Horsfall M, Spiff AI, Abia AA (2004). Studies on the influence of Mercaptoacetic acid (MAA) modification of Cassava (*Manihot Sculenta* Cranz) Waste Biomass on the Adsorption of Cu^{2+} and Cd^{2+} from Aqueous Solution. *Bull. Korean chem. Soc.* Vol. 25 No. 6
- Quek SY, Wase DAJ, Forster CF (1998). The use of sago waste for the sorption of lead and copper. *Water SA* . 24 (3): 251-256.
- Wankasi D (2004). Kinetics of heavy metal phytosorption using unmodified and chemically modified biomass of *Nypa palm* (*Nypa fruticans* Wurmb). PhD Thesis. University of Port Harcourt, Nigeria.
- Zhou JL, Huag PL, Lin RG (1998). Sorption and desorption of Cu and Cd by macroalgae and microalgae. *Environ. Pollut.* 101: 6 – 75.