



## GRAFT COPOLYMERIZATION OF ACRYLAMIDE ONTO *Hyphaene thebaica* FIBER AND ITS PERFORMANCE FOR REMOVAL OF HEAVY METALS IONS FROM AQUEOUS SOLUTIONS

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### ABSTRACT

Microwave assisted preparation of *Hyphaene thebaica* fibre grafted with polyacrylamide (Cell-g-PAA) was carried out using microwave radiation and ammonium persulfate as initiator. The preparation was optimized in terms of percentage grafting by varying the microwave irradiation time, monomer (acrylamide) concentration and initiator concentration. The grafted product has been characterized using the following techniques; FTIR spectroscopy, SEM morphology study and X-ray diffraction (XRD). The application of the grafted product as adsorbent for removal of some metal ions from aqueous solutions has been investigated. Equilibrium data revealed that Langmuir isotherm model fitted better than Freundlich isotherm model. The adsorption capacities were 186 mg/g, 63 mg/g and 52 mg/g for lead, copper and cadmium ions respectively. The adsorbent could be used for removal  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  from aqueous solutions.

**Keywords:** *Hyphaene thebaica*, polyacrylamide, microwave, ammonium persulfate, adsorbent

### INTRODUCTION

Industrial, agricultural or domestic waters are often contaminated by toxic pollutants (Gurgel and Gil, 2009). For instance, effluents released from these sources are rich in toxic and non-biodegradable metal ions such as lead, cadmium, chromium, Irons, zinc, copper, arsenic etc (Fu and Wang, 2011). These metal ions circulate in the food chain causing severe effect to aquatic organisms and humans (Zhu *et al.*, 2015). Decontamination of water loaded by metal ions can be achieved by either of the following; chemical precipitation, ion-exchange, membrane filtration, evaporation, electrochemical treatment technologies (Arias *et al.*, 2002).

Numerous agricultural products and by-products such as wood sawdust, wheat straw, corncobs, rice husk, millet husk, jute, sugarcane bagasse etc are natural sources of cellulose (Hubbe *et al.*, 2008). In addition to cellulose, these biomass also contain hemicellulose, lignin, waxes, lipids, proteins etc and many of them have been studied as adsorbent for metal ions (Raji *et al.*, 1998, Orlando *et al.*, 2002, Chen *et al.*, 2013, Abdelwahab *et al.*, 2015). Cellulose is considered as the most abundant and renewable biopolymer in nature. It is a linear polymer consisting of  $\beta$ -1,4-glycosidic glucopyranose units joined together by  $\beta$ -1,4 glycosidic linkages (Fig 1). (Qin *et al.*, 2008, Faruk *et al.*, 2012). *Hyphaene thebaica* is among the huge lignocellulosic agricultural waste generated in

the northern part of Nigeria during early preparation of farming activities and burned on spot. Rather than burning which leads to environmental pollution, alternatively these material could be utilize as an adsorbent. In order to improve sorption performance of cellulosic fibers, several chemical modifications have been reported such as esterification (Chand *et al.*, 2014), etherification (Fox *et al.*, 2011), oxidation (Batmaz *et al.*, 2014), alkali treatment (Memon *et al.*, 2007), grafting polymers (Kumar *et al.*, 2017) etc. among these methods, grafting polymers onto the surface of cellulosic fibers is the most attractive, as different polymers can anchor to form graft copolymers for wide applications (Sen and Pal, 2009). Graft copolymerization reaction can be achieved by free radical polymerization or ionic polymerization initiated by various initiating systems such as redox, thermal or irradiation (Salisu *et al.*, 2016). Grafting induced by microwave radiation offers unique advantages over the conventional grafting techniques. Because the reaction is simple, rapid, clean, energy saving and benign (Mishra *et al.*, 2012). In the present work, grafting of acrylamide has been carried out onto alkali pre-treated *Hyphaene thebaica* cellulosic fiber by microwave assisted method. The effect of different reaction variables such as monomer concentration, initiator concentration and time on the grafting yield was studied. The graft copolymer was evaluated for the removal of some heavy metal ions from aqueous solutions.

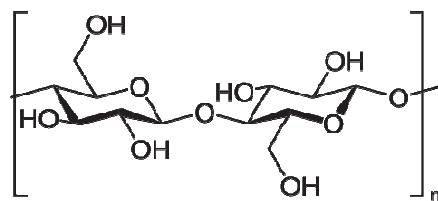


Figure 1:Chemical repeat structure of cellulose

## MATERIALS AND METHODS

Acrylamide, acetone, methanol and ammonium persulfate (APS) were purchased from Zayo-Sigma-Aldrich (Nigeria).  $Pb(NO_3)_2$  and  $Cu(NO_3)_2 \cdot 3H_2O$  salts were purchased from Loba Chemie (England). Stock solutions of  $Pb^{+2}$  and  $Cu^{+2}$  ions (1000mg/L) were prepared by dissolving 3.880 g of  $Cu(NO_3)_2 \cdot 3H_2O$  and 1.599 g of  $Pb(NO_3)_2$  salts in separate beakers (250 cm<sup>3</sup>) with deionized water respectively. The prepared stock solutions were transferred to a 1.0 litre volumetric flask each was followed by the addition of 100 mL of 0.1M  $HNO_3$  and they were made to mark. Desired concentrations of the metal solutions were prepared by serial dilution of the stock solutions using deionized water. Other chemical reagents were of analytical grade and used as received.

### Sample Collection and Pretreatment

**Collection of *Hyphaene thebaica* fiber**  
Fresh stalk of *Hyphaene thebaica* was collected from the local fields near Kayauki village, along Daura road Katsina State, Nigeria. The stalk (300g) was pulverized and soaked in distilled water at room temperature for 24 hrs. Thereafter the fibers were removed out and washed thoroughly with distilled water and dried in hot air oven at 50 °C.

### Mercurization of *Hyphaene thebaica* fiber

In this process, the fibers were pre-treated with 5% (w/v) aqueous sodium hydroxide (500 ml) for 24 hrs in a 1000 ml beaker at room temperature. This treatment removes lignin, wax and oil and also increases hydrophilicity (fiber wetting). The alkali treated fibers were washed thoroughly with distilled water until the pH of wash water becomes neutral. The fibers were dried in hot air oven at 50 °C

### Graft copolymerization of acrylamide onto *Hyphaene thebaica* fiber

Mercurized *Hyphaene thebaica* fiber (0.5 g) was immersed in 100ml distilled water in a 500ml Bomex beaker for 24 hrs before graft

copolymerization in order to actuate the reaction site on the fiber surface. Required amount of acrylamide and APS were added and mixed well. The reaction vessel was placed at the center of a rotating ceramic plate in the domestic microwave oven (ModelWMO20L-MGSB, Skyrun Calabar municipal, Nigeria). The reaction vessel was then exposed to microwave radiation at 900 W power for desired time. Periodically, the microwave irradiation was paused and the reaction mixture cooled by placing the reaction vessel in cold water. Reaction parameters such as monomer concentration, initiator concentration and microwave exposure time were optimized. The viscous polymer was precipitated by adding excess acetone and kept in the solvent for 5 hours to remove unreacted acrylamide. The graft sample thus obtained was dried in hot air oven at 50 °C.

The percentage grafting was determined using equation (1) below.

$$(\%) \text{Grafting} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where  $W_1$  is the initial weight of the fiber sample,  $W_2$  is the weight of the grafted sample after extraction of unreacted polymer (Gupta and Sahoo, 2001).

### Characterization of the Grafted Sample

Fourier Transform Infrared analysis was conducted using FTIR VERTEX 70/70v spectrophotometer (Agilent Technologies, USA).

The scanning electron microscope (SEM) micrograph of the bead and its surface morphology was examined using PHENOM PRO X (Netherland).

Powder X-ray diffraction patterns were recorded on ARL X'TRA X-ray Diffractometer (Thermoscientific, Switzerland) using graphite monochromatic  $CuK\alpha_1$  (1.5406Å) and  $K\alpha_2$  operated at 40 kV and 30 mA. Percentage crystallinity and crystallinity index (C.I) were calculated using equation (2) and (3) respectively (Sarghavi *et al.*, 2013).

$$\% X_c = \frac{I_c}{I_A + I_C} \times 100 \quad (2)$$

$$C.I = \frac{I_C - I_A}{I_C} \times 100 \quad (3)$$

Where  $I_c$  is the intensity of crystalline phase,  $I_A$  is the intensity of amorphous phase,  $X_c$  is the percentage of crystallinity, C.I. is the crystallinity index.

### Batch Equilibrium Studies

The adsorption experiments were performed by batch equilibrium method. The experiments were carried out in 250ml conical flasks by mixing 0.5g of the grafted fiber with 50ml of each metal ion solutions of concentrations, 50, 100, 150, 200, 250, and 300mg/L and pH= 6.0 at room temperature using a shaker operating at 300rpm. The sample solutions were taken out from the conical flask on the shaker at certain time intervals and the residual metal ions in the solutions were separated by filtration and the filtrates were analyzed by using flame atomic absorption spectrophotometer (Shimadzu, 6800, Japan, 210) to determine the equilibrium metal ion concentrations. All the experiments were conducted in duplicate and averages of duplicate readings were presented. The percentage removal of metal ions and the amount of metal ions adsorbed on the grafted fiber at equilibrium ( $q_e$ ) were calculated using equations (4) and (5) respectively:

$$\text{Percentage removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (4)$$

$$q_e \text{ (mg/g)} = (C_0 - C_e) \frac{V}{M} \quad (5)$$

where  $C_0$  is the initial metal ions concentration (mg/L), and  $C_e$  is the equilibrium concentration of metal ions in solution (mg/L),  $V$  is the

volume of metal ions solution used (L) and  $M$  is the mass of the grafted fiber used (g). The equilibrium data obtained were tested using the linear forms of Langmuir and Freundlich isotherm models, as shown in equations (6) and (7), respectively, (Langmuir, 1918; Freundlich, 1906).

$$\frac{C_e}{q_e} = \frac{1}{q_m Q_L} + \frac{C_e}{q_m} \quad (6)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

### RESULTS AND DISCUSSION

Under influence of microwave radiation persulphate initiator- $K_2S_2O_8$  when heated in aqueous medium, it decomposes to  $SO_4^{\cdot-}$  and  $\cdot OH$  free radicals. These generated free radicals abstract H atom from the cellulose fiber chains and the cellulose free radicals are formed. Then they react with monomers- acrylamide (AA) to initiate graft copolymerization. Subsequent addition of monomer molecules to the cellulose fiber increases the size of the branched chain. When the two radicals react, the graft copolymerization is terminated. The percentage grafting under optimized conditions is shown in Table 1.

**Table 1:** Optimization of monomer, initiator concentration and exposure time for Cell-graft-poly(acrylamide) (Cell-g-PAA)

S/N	wt of fiber (g)	wt of acrylamide (g)	wt of APS (g)	Time of irradiation (min)	% grafting
1	0.5	5	0.2	1	23
2	0.5	5	0.3	3	28
3	0.5	5	0.4	5	31
4	0.5	10	0.4	7	18
5	0.5	2.5	0.4	5	-
6	0.5	7.5	0.4	5	24
7	0.5	5	0.5	5	15

### Characterization

#### Fourier transforms infrared spectroscopy

FTIR spectra of mercerized fiber and grafted sample were depicted in Figure (2 and 3) in the wave number ranging from 600 to 4000  $\text{cm}^{-1}$ . In Figure 2, the absorption peak at  $3335\text{cm}^{-1}$  could be due to the presence of -OH group in the cellulose fiber (Boufi and Alila, 2011). The bands at  $899\text{ cm}^{-1}$  and  $1033\text{cm}^{-1}$  may be due to  $\beta$ -glucosidic linkage and C-O stretching vibrations. In case of the grafted sample (Figure. 3),

additional absorption bands which appeared at  $3331\text{cm}^{-1}$  and  $3193\text{cm}^{-1}$  were attributed to N-H stretching of the grafted chains. The other two intense bands at  $1655\text{cm}^{-1}$  and  $1603\text{cm}^{-1}$  were assigned to C=O stretching (primary amide) and scissor vibrations in polyacrylamide, respectively. The appearance of these bands successfully confirmed the grafting chemical modification of *Hyphaene thebaica* cellulosic fiber with acrylamide.

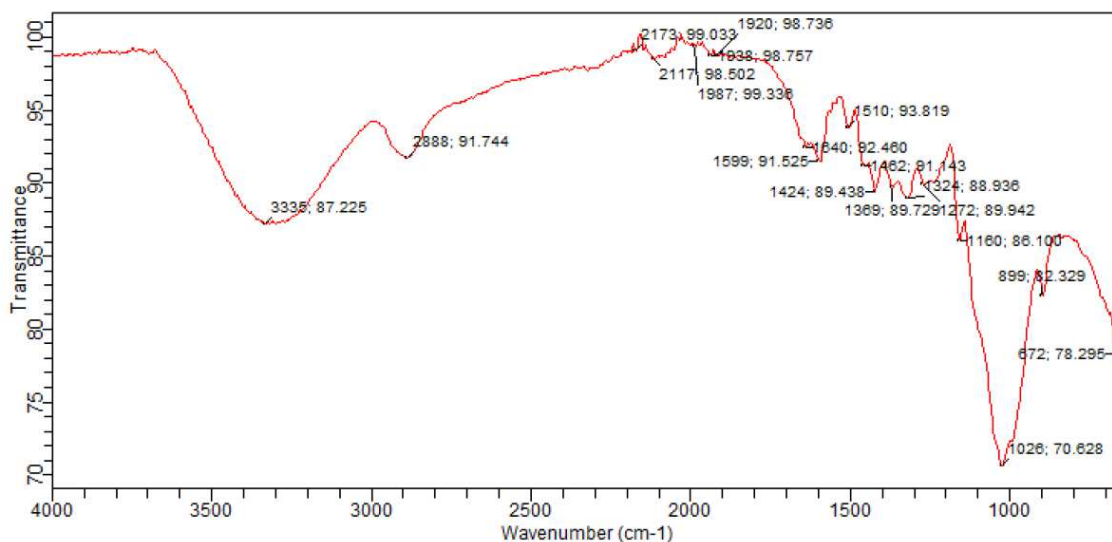


Figure 2: FTIR Spectrum of mercerized fiber

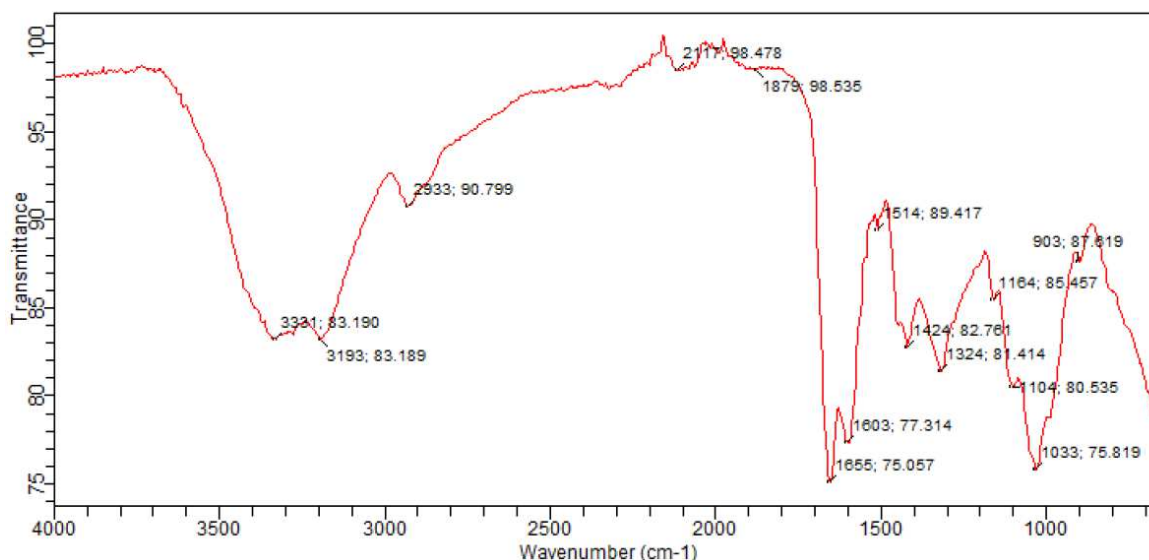


Figure 3: FTIR Spectrum of grafted fiber (Cell-g-PAA)

#### Scanning electron microscopy (SEM)

Surface morphological study was carried out. Figure 4 (a) and 4(b) showed the SEM images of mercerized fiber and grafted sample at same magnification. It was observed that considerable amount of polyacrylamide was

deposited onto fiber backbone upon grafting which brought about changes in the morphological appearance of the fiber (Figure 4(b)). Furthermore, the surface of fiber became rough after grafting of the acrylamide.

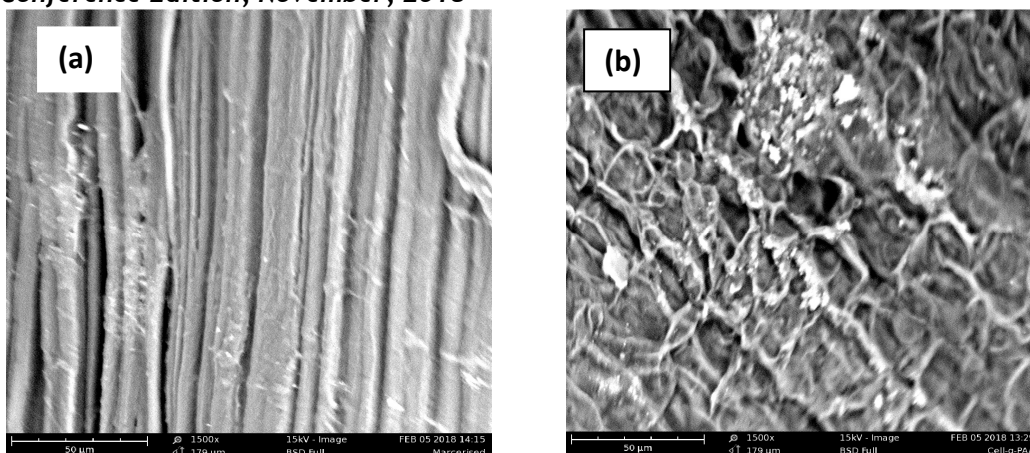


Figure 4: SEM images of (a) mercerized fiber and (b) grafted sample.

### X-ray Diffraction Study (XRD)

The XRD pattern of mercerized fiber and grafted sample is depicted in Figure 5. The characteristics peaks of mercerized fiber were observed at 23.70 and 17.16 with relative intensities at 1012 and 406 respectively. The peaks of grafted sample were found at 22.20 and 18.80 with relative intensities of 556.8 and 314.1 respectively. This showed that grafting has resulted in the decrease in the peak

intensity of grafted sample. It was observed that the grafting of acrylamide to the backbone disrupted the crystallinity of the fiber. The lower value of crystallinity index (Table 2) in case of grafted fiber indicated the poor order of cellulose crystals in the fiber. Furthermore, the grafted fiber showed broadening of the peak after grafting due to convergence of the fiber toward amorphous phase (Sharma *et al.*, 2013).

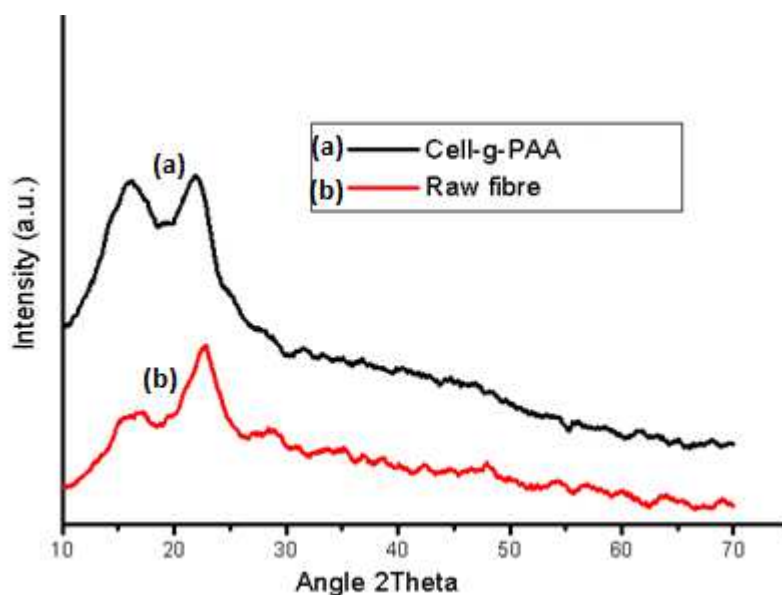


Figure 5: X-ray diffraction pattern of (a) mercerized fiber and (b) grafted sample

### Adsorption Study

The effect of contact time on adsorption of metal ions were investigated under optimized dose of adsorbent (0.5 g), metal ions concentration (100 mg/L), and pH solution of 6. It was revealed that the adsorption gradually increased with time and attained equilibrium after 80 minutes. The rapid intake initially could be due to the availability of the more surface sites on the adsorbent for adsorption.

The plot of  $C_e/q_e$  versus  $C_e$  gave straight lines with correlation coefficients of 0.995, 0.997 and 0.993 for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  respectively which indicate that the adsorption of the metal ions onto the adsorbent fitted the Langmuir isotherm well than Freundlich isotherm equation. The maximum adsorption capacity of each metal ion, constants and correlation coefficients were represented in Table 2.

Table 2: Langmuir and Freundlich isotherms constants and correlation coefficients

Metal ion	Freundlich isotherm			Langmuir isotherm			
	(K <sub>F</sub> ) (mg/g)	(n) (g/L)	(R <sup>2</sup> )	(Q <sub>L</sub> ) (L/mg)	(q <sub>e</sub> ) (mg/g)	R <sub>L</sub>	(R <sup>2</sup> )
Pb	94	0.12	0.880	0.012	186	0.5	0.995
Cu	26	0.67	0.818	0.016	63	0.7	0.997
Cd	35	0.72	0.896	0.003	52	0.4	0.993

## CONCLUSION

The grafting of acrylamide onto *Hyphaene the baica* fiber was confirmed by FTIR, SEM and XRD analysis studies. X-ray diffraction results indicated the decreased in crystallinity in the grafted sample. Moreover the optimum conditions obtained for the removal of metal ions from aqueous solutions were pH of 6, metal ion concentration (200 mg/L), adsorbent dose (0.5 g) and contact time (80 min.). The adsorption equilibrium was found to gradually increase with increase in contact time and

finally reached the equilibrium after 80 minutes. Among the metal ions tested, maximum adsorption capacity was in the following order of Pb (186 mg/g) > Cu (63 mg/g) > Cd (52 mg/g). The adsorption equilibrium data were satisfactorily fitted Langmuir isotherm equation better than Freundlich isotherm equation. Thus, it can be concluded that the adsorbent could be used in the treatment of toxic metals effluents polluted with Pb, Cu and Cd ions.

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