INNSPUB

Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 16, No. 2, p. 1-8, 2020
https://www.innspub.net

RESEARCH PAPER OPEN ACCESS

Modified *Hyphaene thebaica* fiber for the sequestration of heavy metal ions from aqueous solution

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Article published on February 28, 2020

Key words: Adsorption, Fiber, Acrylonitrile, Grafting, Lignocellulose

Abstract

Lignocellulose biomass is an abundant and sustainable polymer in nature that can be modified for other useful products. The objective of this study is to modify *Hyphaene thebaica* fiber by grafting polyacrylonitrile via free radical polymerization in aqueous medium and determine its potential to sequester metal ions from aqueous solution. Fresh stalk of *Hyphaene thebaica* (300g) was pulverized and subjected to alkali pre-treatment (mercerization). The fiber was grafted with Polyacrylonitrile via microwave radiation using potassium persulphate (KPS) as chemical initiator. The graft copolymer synthesized was characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM). The graft copolymer was evaluated for sequestration of Pb^{2+} and Cu^{2+} ions from aqueous solution using batch adsorption method. The results showed that the highest grafting percentage 56% was achieved using acrylonitrile (5g), KPS (0.3g) and irradiation time (3 mins). The maximum adsorption capacity of the adsorbent was 84mg/g and 63mg/g for Pb^{2+} and Cu^{2+} respectively. The equilibrium data followed the Langmuir isotherm model, which assumed a monolayer coverage and uniform activity distribution on the adsorbent surface. The grafting of Polyacrylonitrile onto *Hyphaene thebaica* was successfully carried out and formation of the product was confirmed by FTIR, SEM and XRD analyses. The graft copolymer showed moderate performance in the removal of Pb (II) and Cu (II) in aqueous solution thus can be utilized as a low cost adsorbent material.

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Introduction

Cellulose is one of the most abundant, inexpensive, and renewable polymeric raw material that has found wide applications in many areas such as textile industry, composite materials, drug delivery systems, adhesives and catalysis (Malherbe and Cloete, 2002; Sannino and Demitiri, 2009). In addition to these applications, cellulose can also be used directly or in a modified form for the adsorption of heavy metal ions from aqueous solutions (Nishio, 2006). Huge agricultural waste materials contain lignocellulose fibers that remain un-utilized and most often are left to decompose naturally or burned, leading to environmental pollution. *Hyphaene thebaica* is one of the huge lignocellulose biomass found in most part of Sub-Saharan African countries. Many chemical modifications of cellulose such as oxidation, esterification, etherification and acetylation were reported (Fox *et al.,* 2011; Chand *et al.,* 2009). However, modification by grafting synthetic monomers changed the physical and chemical properties of cellulose and enhanced its functionality (Roy *et al., 2006).* Synthesis of graft copolymers via "grafting-from" technique were achieved through various initiating system such as redox (Shah *et al.,* 1995*)*, thermal (Isiklan *et al.,* 2010), microwave irradiation (Rani *et al.,* 2013). Among these methods, microwave irradiation is considered most environment friendly because of less energy consumption, less organic solvent, and shorter reaction time (Singh *et al.,* 2012). Industrial wastewater, domestic effluents and natural surface water (rivers, dams and lakes) in most cases are contaminated by toxic Inorganic and organic substances, causing deleterious effects of ecological environment (Kumar *et al.,* 2017). For example, heavy metals contamination in water is a serious problem due to their toxicity even at trace level, and affects the entire organisms in the food chain (Liu *et al.,* 2009). The methods of treatment of wastewater include; chemical precipitation, ion-exchange, membrane filtration, evaporation, electrochemical processes and adsorption. Doum palm (*Hyphaene thebaica*) is a desert palm plant with edible oval fruit, originally native to the Nile valley. It is also abundant in the northern part of Nigeria. The foliage is used in making important items for domestic uses such as mats, ropes, and hats (Hsu *et al.,* 2006). Hyphaene thebaica stalks biomass is not utilized maximally; majority of people in the region burned them on spot during clearing lands for farming activities, which results in severe environmental pollution and the waste of biomass resources, alternatively it could be utilize as an adsorbent. The present study is aimed to modify *Hyphaene thebaica* fiber by free radical polymerization and evaluate its adsorption performance to sequester lead and copper ions from aqueous solution.

Materials and methods

Materials

Acrylonitrile, acetone, methanol, dimethyl formamide (DMF) and potassium persulfate (KPS) were purchased from Zayo-Sigma-Aldrich (Nigeria). Other chemical reagents were of analytical grade and used as received. The research work was carried out in the Analytical Chemistry Laboratory, Umaru Musa Yar'adua University Katsina Nigeria.

Sample Collection

A Fresh stalk of Hyphaene thebaica was collected in June, 2017 from the local fields in Kayauki village, along Daura road Katsina State, Nigeria. Fresh stalks (300g) were 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.

Sample Pretreatment (Mercerization of the fiber)

In this process, the fiber was pre-treated with 5% (w/v) aqueous sodium hydroxide (500mL) for 24 hours in a 1000mL 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 acrylonitrile onto Hyphaene thebaica fiber

In this reaction, a procedure reported by Gupta *et al.* (2013) was adopted with little modifications. Mercerized *Hyphaene thebaica* fiber (0.5g) was immersed in 50mL distilled water in a 500mL Bomex beaker for 24 hours before graft copolymerization reaction in order to actuate the reaction site on the fiber surface. Required amount of acrylonitrile and KPS were added and mixed well. The reaction vessel was placed at the center of a rotating ceramic plate in the domestic microwave oven (Model WMO20L-MGSB, Skyrun, Nigeria). The reaction vessel was then exposed to microwave radiation at 900W 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 polymer was precipitated by adding excess acetone. The grafted sample thus obtained was dried in hot air oven at 50°C. The product was washed with DMF solvent to remove acrylonitrile homopolymer using Soxhlet extractor. The percentage grafting was determined using equation (1).

$$(\%)\ \text{Grafting} = \frac{W_2 - W_1}{W_1} \times 100 \qquad \text{Eq. '(1)'}$$

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 (Salisu *et al.,* 2016).

Characterization Techniques

Fourier Transform Infrared analysis was conducted using FTIR VERTEX 70/70v spectrophotometer (Agilent Technologies, USA). 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) operated at 40 kV and 30 mA.

Batch Equilibrium Experiment

The adsorption experiments were performed by the batch equilibrium method. The experiments were carried out in 250mL conical flasks by mixing 0.2g of the grafted fiber with 50mL of each metal ion solution of concentrations, 30, 60, 90, 120, 150, and 180mg/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 (Shimdzu, 6800, Japan, 210) to determine the equilibrium metal ion concentrations. All the experiments were conducted in duplicate and averages of duplicate readings were presented using (mean ± SD). 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 (2) and (3) respectively:

$$(\%\ R) = \frac{C_O - C_e}{C_O} \times 100 \qquad \text{Eq. '(2)'}$$

$$q_e\ (mg/g) = \left(\frac{C_o - C_e}{M}\right) \times V \qquad \text{Eq. '(3)'}$$

where c_o 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 isotherm model (Langmuir, 1918) and Freundlich isotherm model (Frendlich, 1906) as shown in equations (4) and (5), respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m Q_L} + \frac{C_e}{q_m} \qquad \text{Eq. '(4)'}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad \text{Eq. '(5)'}$$

In order to determine the rate of adsorption and the possible adsorption mechanisms the pseudo-first-order (Gurgel and Gil, 2009) pseudo-second-order models (Ho and McKay, 1999) were used.

Pseudo-first-order model

Pseudo-first-order kinetic model was expressed in equation (6)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad \text{Eq. '(6)'}$$

Where q_e and q_t(mg/g) are the amount of (metal ions) adsorbed at equilibrium and at time t respectively, and k_1(min^{-1}) is the rate constant for pseudo-first-order equation.

Pseudo-second-order model

Pseudo-second-order kinetic model is expressed by using equation (7).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad \text{Eq. '(7)'}$$

Where q_e and q_t(mg/g) are the amount of the uptake of adsorbate at equilibrium and at time *t* respectively, and k_2(g/mg/min) is the equilibrium rate constant for pseudo-second order equation.

Results

The synthesis details of the graft copolymers were shown in Table 1. It was observed that the percentage grafting was optimum at an acrylonitrile concentration of 5g, and KPS concentration of 0.3g and 180 seconds irradiation exposure time.

Table 1. optimization of various reaction parameters.

S/N	wt of fiber (g)	wt of acrylonitrile (g)	wt of KPS (g)	Time (S)	% grafting
1	0.5	5	0.1	180	26
2	0.5	5	0.2	180	32
3	0.5	5	0.3	180	56
4	0.5	5	0.4	180	47
5	0.5	2.5	0.4	240	11
6	0.5	7.5	0.4	60	28
7	0.5	5	0.5	180	19

Table 2. Adsorption Parameters and Correlation Coefficients for Adsorption of Pb^{+2} and Cu^{+2} onto Cell-g-PAN.

	Langmuir model				Freundlich model		
Metal ion	q_{max} (mg/g)	R_L	Q_L (L/mg)	R^2	K_F (mg/g)	*n*	R^2
Pb^{+2}	84	0.455	0.082	0.996	23.42	0.34	0.815
Cu^{+2}	63	0.245	0.065	0.999	42.15	0.63	0.824

Table 3. Kinetic Rate Constants and Correlation Coefficients for Adsorption of Pb^{+2} and Cu^{+2} onto Cell-g-PAN.

	Pseudo-first-order model				Pseudo-second-order model		
Metal ion	$q_{max\ exp}$ (mg/g)	$q_{max\ cal.}$ (mg/g)	k_1 (1/min)	R^2	$q_{max\ cal.}$ (mg/g)	k_2 (g/mg /min)	R^2
Pb^{+2}	36.76	64.22	0.0022	0.806	35.14	0.0043	0.999
Cu^{+2}	25.23	48.33	0.0013	0.835	26.11	0.0012	0.999

Fourier transforms infrared spectroscopy

FTIR spectra of the mercerized fiber and grafted sample were shown in supplementary (Fig. 6 and 7). In the FTIR spectrum of raw *Hyphaene thebaica* fiber (Fig. 6), absorption peak at 3335cm⁻¹ was due to the stretching vibration of O-H functional group. The peak observed at 1026cm⁻¹ was assigned to C–O stretching vibrations. In case of the grafted fiber (Fig. 7), additional absorption peaks which appeared at 2921cm⁻¹ and 2247cm⁻¹were due to of C-H stretching and nitrile group (-CN) respectively in the grafted chains. The appearance of these peaks confirmed the grafting chemical modification of *Hyphaene thebaica* cellulosic fiber with acrylonitrile.

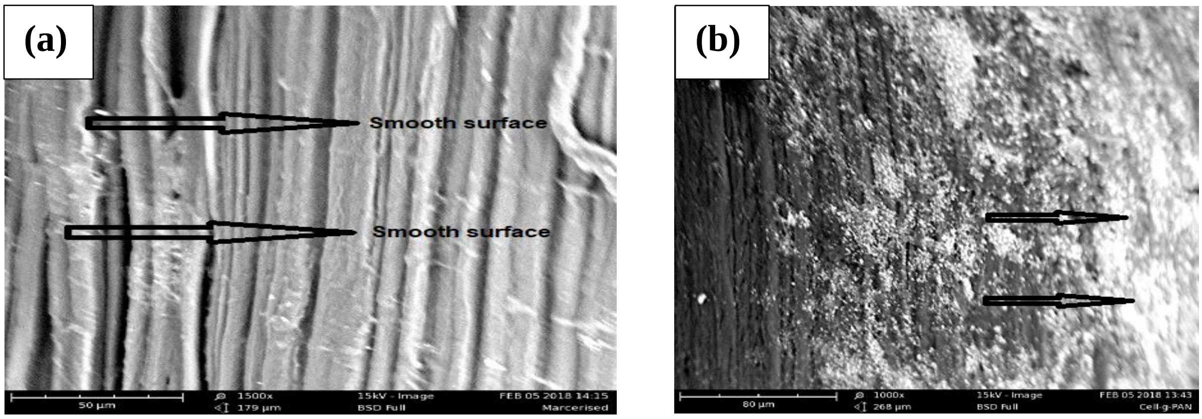

Fig. 1. SEM Images of (a) mercerized fiber and grafted fiber Cell-g-PAN.

Scanning electron microscopy (SEM)

SEM images of mercerized fiber and grafted sample were shown in Fig. 1. It was observed that substantial amount of polyacrylonitrile polymer was deposited onto the fiber backbone upon grafting as evidence in Fig. 1b as indicated by arrows. This result confirmed the grafting of the acrylonitrile on the fiber.

X-ray Diffraction Study (XRD)

The XRD diffractogram of mercerized and grafted Hyphaene thebaica fiber was shown in Fig. 2. The characteristic peaks of mercerized fiber were observed at 22.13 and 14.3 (2θ angles) with relative intensities of 1400 and 906 respectively. The peaks of grafted sample were found at 21.33 and 17.83 (2θ angles) with relative intensities of 955.5 and 754.2 respectively. This showed that grafting has resulted in the decrease in the peak intensity of grafted fiber that indicated the decreased in the crystallinity of the fiber.

Effect of pH of Solution

The effect of solution pH on the adsorption of Pb^{2+} and Cu^{2+} was investigated and the results were shown in Fig. 3. The highest percentage removal was observed at pH of 6 with 87% and 79% for Pb^{2+} and Cu^{2+}, respectively. However, at lower pH, the percentage removal was decreased. This could be due to increase in protons which caused protonation of hydroxyl group and consequently repelled the metal ions.

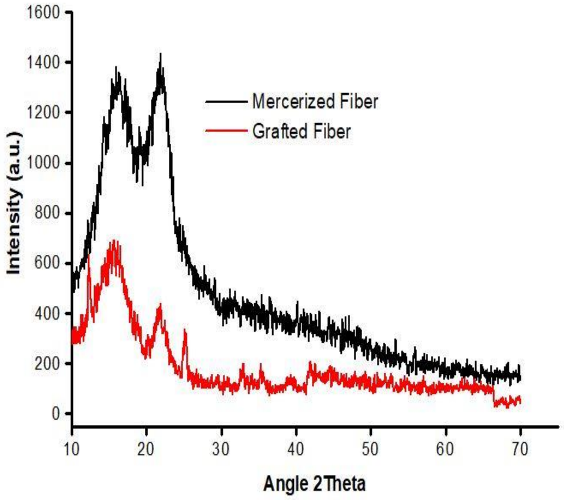

Fig. 2. X-ray diffraction pattern of mercerized fiber and grafted fiber (Cell-g-PAN).

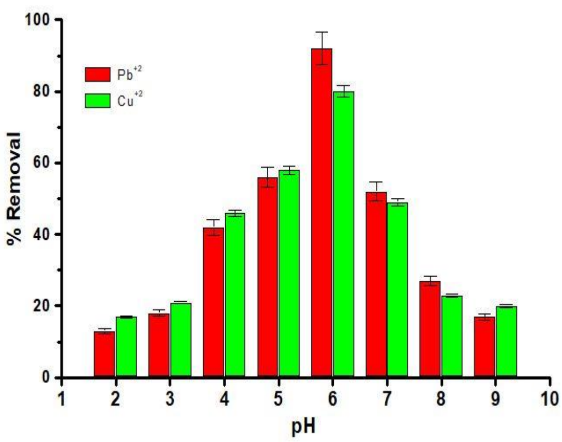

Fig. 3. Effect of pH on the adsorption of metal ions by Cell-g-PAN (initial conc. of Pb^{+2} and Cu^{+2} = 100mg/L, contact time = 60 mins, adsorbent dose = 0.1g).

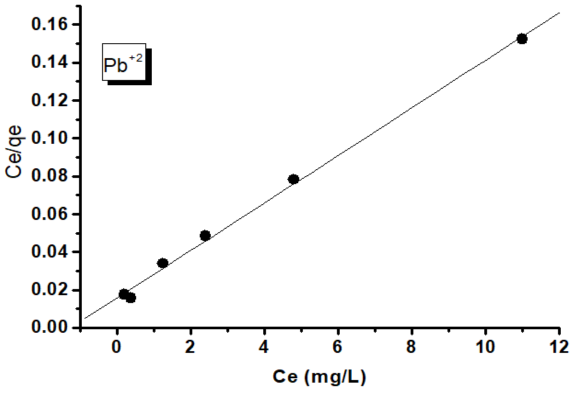

Fig. 4. Langmuir isotherm for adsorption of Pb^{+2} onto Cell-g-PAN.

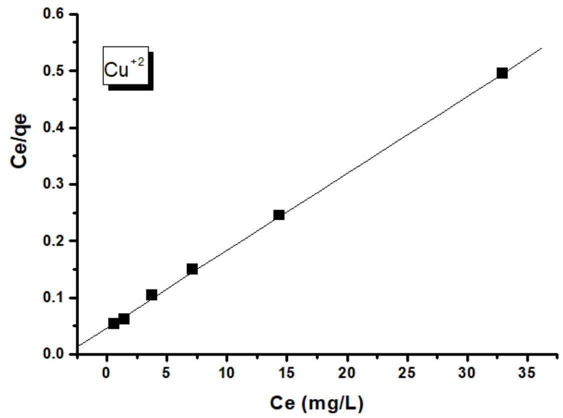

Fig. 5. Langmuir isotherm for adsorption of Cu^{+2} onto Cell-g-PAN.

Supplementary figs

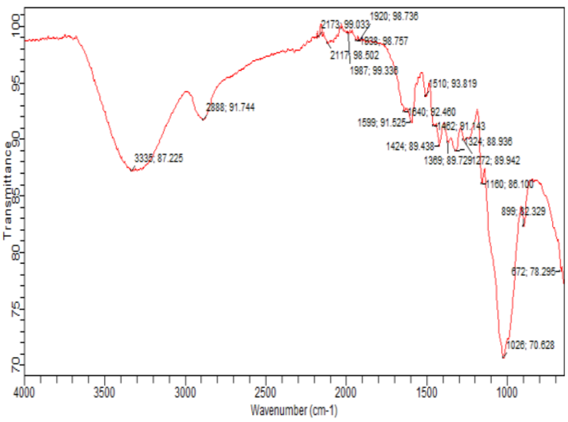

Fig. 6. FTIR spectrum of mercerized fiber.

Discussion

The results of this study indicated that microwave radiation and KPS initiator could lead to the formation of the graft copolymer. The details of the synthesis of the graft copolymer were presented in Table 1. The approach of the synthesis was optimization with respect to KPS, keeping the acrylonitrile concentration constant (i.e. S/N 1, 2, 3, & 4); followed by optimization with respect to acrylonitrile, keeping the KPS concentration as optimized previously (i.e. S/N 5 & 6). The highest grafting percentage was obtained at 5g of acrylonitrile and 0.3g of the initiator (KPS). This was because more radicals were generated on the cellulose backbone and interacted with enough acrylonitrile monomer in the solution that subsequently formed the graft copolymer. Similar observations were reported in many research works on the dependency of initiator and monomer concentration in grafting yield (Bhattacharya and Misra, 2004; Misra *et al.,* 1984). Fig. 3 showed the effect of pH on percentage removal of the metal ions. Lower percentage removal at pH 2-3 could be due to the electrostatic repulsion between the metal cation and the protonated hydroxyl group. The metal adsorption percentage decreased since most of the OH groups of cellulose were in the protonated form (H^+), a similar observation was reported previously (Harish and Tharanathan, 2003). Fig. 2, showed the FTIR spectrum of modified Hyphaene thebaica fiber. The appearance of absorption band at 2247cm^{-1} confirmed the grafting of polyacrylonitrile on its backbone (Boufi and Alila, 2011). The morphological changes that were induced by chemical modification were examined by SEM. The appearance of polymer deposits was observed when the fiber was grafted with polyacrylonitrile was shown in Fig. 1b. Regarding the XRD analysis, Fig. 2 revealed the decreased in the crystallinity of the fiber after modification that could possibly be due to disruption of some linkages between hemicellulose and lignin during the alkaline pre-treatment (Agu *et al.,* 2015; Zhu *et al.,* 2006). The effect has also been reported by other authors on grafting vinyl monomers onto cellulosic fibers (Sharma *et al.,* 2013). The Langmuir and Freundlich isotherms were used to fit the experimental equilibrium data. From the data shown in Table 2, it was concluded that the experimental values fitted well into the Langmuir isotherm model with good linearity as indicated in Fig. 4 and 5 for Pb^{+2} and Cu^{+2} ions, respectively, thus indicating the monolayer adsorption on the adsorbent surface (Mishra *et al.,* 2011). The maximum adsorption capacity (q_{max}) was 84mg/g and 63mg/g for Pb^{+2} and Cu^{+2} respectively. Furthermore, separation factors (R_L) calculated was less than unity in all cases which indicated favourable adsorption. A similar work was reported on cellulosic materials containing various amounts of grafted polyacrylonitrile and poly(acrylic acid) molecules were used to remove Cd^{+2} and Cu^{+2} ions from aqueous solution. The equilibrium adsorption data fitted the Langmuir isotherm equation and it was found, that grafting enhanced the metal ion binding capacity of the cellulosic material (Okiemen *et al.,* 2015). Kinetic studies revealed good agreement between experimental data and calculated values with the pseudo second-order kinetic model as can be seen in Table 3. The results are in agreement with the work reported by Okareh and Adeolu (2015), who showed that adsorption of Pb^{+2} ions by plantain waste, fitted a second-order model better than a first-order model. Chand *et al.,* (2014) compared a pseudo-first-order Lagergren model and a second-order model; similarly found that the second order model was superior for the binding of divalent cations by the chemically modified apple pomace. They concluded that the adsorption reaction was the rate-limiting step. In general, the results of this study showed that *Hyphaene thebaica* fiber was successfully grafted with polyacrylonitrile and the material displayed good potential as an adsorbent for removal of metal ions from aqueous solution. Although, the grafting percentage was not significantly higher, but it could be improved if the reaction is conducted in homogeneous phase.

Conclusions

From this study, it can be concluded that, grafting of polyacrylonitrile onto *Hyphaene thebaica* fiber showed high sequestration performance toward Pb^{+2}

and Cu^{+2} from aqueous solution. Moreover, a comparison of two isotherm models revealed that the equilibrium data perfectly fitted the Langmuir isotherms model with correlation coefficients $R^2 > 0.99$ for all the studied metal ions. The kinetic studies indicated that the experimental data followed the second-order kinetic model. This work also showed that modified Hyphaene thebaica fiber could be used to treat wastewaters containing Pb^{+2} and Cu^{+2} ions.

Acknowledgement

Financial support from the TETFund through the institutional-based research grant is gratefully acknowledged.

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