

# Dialdehyde starch orthoaminopyridine Schiff base Preparation, Characterization and its adsorption of Cr(II), Mn(II) and Cu(II) ions from *aqueous* solution

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**Index Terms**—About four key words or phrases in alphabetical order, separated by commas.

## I. INTRODUCTION

Native starches irrespective of their source are undesirable for many industrial applications because of their inability to withstand processing conditions such as extreme temperature (has low thermal resistance), diverse pH and high shear rate (has low shear resistance), high ability to retrograde, loss of viscosity and syneresis tendency. In order to improve on the desirable functional properties and overcome its limitations, native starches are often modified [1].

Modification of starch means: (alteration of the physical and chemical characteristics of the starch to improve structural properties) that can be used to improve inherent poor physiochemical properties of the native starch thus tailor it to specific industrial applications [1].

Starch is renewable and biodegradable polymer and many approaches have been used to utilize starch as a metal adsorbent, by introducing the activity substituents, such as carboxylate, xanthate, acrylamide, acrylonitrile, primary amine and phosphate [2]. Dialdehyde Starch (DAS) has highly reactive dialdehyde groups which are obtained from periodate oxidative cleavage of the C<sub>2</sub>-C<sub>3</sub> bond of the anhydroglucose units of starch polysaccharide chains. Derivatives of starch dialdehyde such as dihydrazone, semicarbazone, dithiosemicarbazone, and dioxime which were used to form water-insoluble complexes with heavy metal ions were used to remove heavy metals from their aqueous solution [3]. Chelating polymers, in general,

incorporate with a variety of metal-chelating ligands which contain one or more electron donor atoms (Lewis base) such as N, S, O, and P that can form coordinate bonds with most of the toxic heavy metals (Lewis acid) has been prepared in the literature [4]. It is well known that Schiff bases (-C=N) having multidentate coordination sites are easy to form complexes with transition metal ions [5]. In the other hand, the molecular structure of thiazoles contains N and S atoms, which are easily able to bridge with other molecules or metals too has been studied [3]. Many polymer matrixes containing Schiff base or thiazole ligands were investigated to adsorb Cu (II) ions [3]. Starch aldehyde 2-amino-4, 6-dihydroxypyrimidine (DASAP) was synthesized by the reaction of 2-amino-4,6-dihydroxypyrimidine and dialdehyde starch (DIAS) from periodate oxidized corn starch, and was employed to adsorb Cu (II) ions from aqueous media [6]. Starch-urea-based biodegradable coordination polymer modified by transition metals Mn(II), Co(II), Ni(II) Cu(II), and Zn(II) were prepared by polycondensation of starch and urea. The thermogravimetric analysis of the complexes revealed that all the polymeric metal complexes are more thermally stable than the parental ligand [4].

In this paper cassava starch was utilized to produce dialdehyde starch (DAS) using Sodium periodate oxidation. The DAS was utilized to prepare a dialdehyde starch aminopyridine Schiff's base ligand which was subsequently used to adsorb Cr(II), Mn(II) and Cu(II) ions from aqueous solution to produced a chelating polymer resin.

## II. MATERIALS AND METHODS

### A. Materials

Native cassava tubers were purchased from Gwarzo market in Kano, Nigeria), Distilled water, Methanol, Ethanol, Acetone, Chloroform, Dimethylsulfoxide, Hydrochloric acid (BDH), Sulphuric acid (BDH), Acetic acid (BDH), Sodium hydroxide (Sigma Aldrich), Ammonium hydroxide, Phenolphthalein (BDH), Sodium periodate (Sigma Aldrich), 2-aminopyridine (BDH), Copper(II) chloride (BDH), Chromium(II) chloride and Manganese(II) chloride (BDH). FT-IR 84003 spectrophotometer (shimadzu), Scanning Electron Microscope (SEM) Pw 100-002 microscope (phenon proxy), Magnetic susceptibility balance MSB-MK1 (sharwood scientific Cambridge UK) WRS-IB micro processed melting point apparatus, NL-420S water bath, centrifuge machine 80-2, magnetic stirrer UC 152 (stuart), Hot air oven BS-130, pH meter 3320 (Jenway), Digital titrator, Electric mettler balance AB 54 (Toledo), Innova 4000 incubated shaker (New Branswick scientific), (Jenway) conductivity meter 4010 model.

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### III. METHODOLOGY

#### A. Extraction of Cassava Starch and Preparation of Dialdehyde Starch (DAS)

Cassava starch was prepared following the method described by [1]. Cassava roots were peeled washed with water and crushed using mortar and pestle, the resulting cassava mesh was reground and mixed with water in the ratio 1:5 (w/v%). The mesh was filtered through the double layer of nylon cloth to obtain starch solution. The starch was separated from the water by sedimentation and decantation. The starch was set in an oven at 48°C to dry until constant weight. The dialdehyde starch (DAS) was prepared by following the modified method for dialdehyde tapioca starch described by [7]. The dried cassava starch (20.0g) was suspended in 80 ml distilled water in a suitable reaction vessel. Then various quantities of sodium periodate [13.2g (0.7714M), 19.8g (1.1571M) and 26.4g (1.5428M)] were added into the suspension and the pH value was adjusted to 3.0 by adding 2% (w/v) hydrochloric acid. The mixture was vigorously stirred and incubated in a water bath at 35°C for 4 hours. The reaction mixture was filtered and washed five (5) times with 200ml distilled water. The product was washed with 50ml acetone and then dried in convection oven at 48°C until constant weight. The dried material was milled and sieved to get the dialdehyde cassava starch. The dialdehyde starches were labeled as DAS1, DAS2 and DAS3 respectively.

#### B. Determination of Carbonyl Content

The dialdehyde group content was determined using the quantitative alkali consumption method [3]. Dried dialdehyde starch (DAS) 0.2g was weighted into a 250ml Erlenmeyer flask and 10ml of standardized 0.2M sodium hydroxide was added. The flask was swirled in a water bath at 70°C for 2mins, and then cooled immediately under running tap water with rapid swirling for 1min. 10ml of standardized 0.2M sulphuric acid, 50ml of water and 1ml of neutral 0.2% phenolphthalein was added in turn. Titration of the acid solution was carried out using 0.2M sodium hydroxide.

#### C. Preparation of Dialdehyde Starch Aminopyridine (DASPy)

The dialdehyde starch (DAS) slurry was prepared from 4.3g dried DAS and 50ml distilled water in a 500ml three-necked flask, which was equipped with a mechanical stirrer and thermostat water bath. A solution of ortho-aminopyridine (100ml) with respect to stoichiometric amount was slowly dropped into the flask under nitrogen. The pH of the reaction was adjusted to 5.0 by adding sodium acetate. The reaction was carried out at 48°C for 4 hours duration. The resulting solid was separated from the solution by filtration and washed three times with distilled water (3x 100ml), then dried at 48°C to a constant weight, according to the method reported by [3].

#### D. Adsorption Experiment

The adsorption experiment was carried out in the series of 100ml Erlenmeyer flask containing the desired dose of DASAPy and 50ml of CrCl<sub>2</sub>, MnCl<sub>2</sub> and CuCl<sub>2</sub> solutions at desired concentration in a shaking bath. The initial pH was adjusted with acetic acid before adding the adsorbent. After shaking for a certain time, the mixture was centrifuge and filtered. The resulting solid materials were dried in an oven at 48°C until constant weight [6].

#### E. Magnetic Susceptibility/Moment Measurement

The magnetic susceptibility test was carried out using MSB-MK1 machine to measure the susceptibility value of the polymer metal complexes by running the capillary tube + sample in the machine.

#### F. Fourier Transform Infrared Spectroscopy (FT-IR)

The FTIR spectra in the 4500-300cm<sup>-1</sup> wavenumber range were recorded with an FTIR 8400S (Shimadzu) using potassium bromide (KBr) discs prepared from powdered samples mixed with dry (KBr). Samples were prepared by grinding about 1.2mg of native starch and its derivative samples with 150mg (KBr) and pressing the mixture into very thin disc.

#### G. Scanning Electron Microscopy (SEM)

The morphological features of native starch and modified starches were observed with scanning electron microscope (phenom proxy, model no, Pw 100-002). The dried samples were mounted on the machine and the images were taken at an accelerating voltage of 5-15Kv, micrographs were recorded at different magnifications.

#### H. Solubility Test

Polymer-Metal-Chelates were tested for their solubilities in water, methanol, ethanol and dimethylsulfoxide by dissolving 0.1g of the samples in 10ml of each individual solvent at room temperature.

#### I. Determination of Melting Point/Decomposition Temperature

The determination of melting point/decomposition temperature of the starch and its derivative was carried out using WRS-IB microprocessor melting point apparatus by inserting the capillary tube + samples in the machines.

#### J. Elemental Analysis

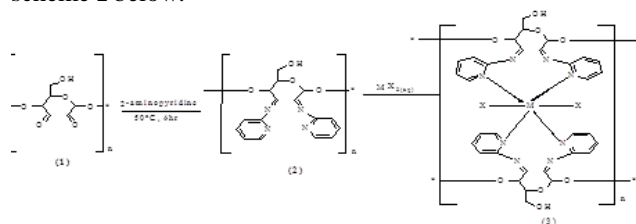
The elemental analysis for the determination of the composition of C, H and N in the polymer was carried out using SEM (phenom proxy Pw 100-002 machine).

#### K. Molar Conductivity Measurement

The molar conductivity test was carried out using Jenway conductivity meter 4010 for all the polymer-metal-chelates in dimethylsulfoxide (DMSO) at concentration of (10<sup>-3</sup> mol/L) at room temperature.

### IV. RESULTS AND DISCUSSION

The synthetic reaction routes for the intermediate and final compounds are presented in scheme I, native cassava starch was treated with sodium periodate (NaIO<sub>4</sub>) to give dialdehyde starch DAS **1**, and the dialdehyde starch DAS was treated with ortho-aminopyridine to get dialdehyde starch ortho-aminopyridine Schiff base DASAPy **2**. The dialdehyde starch ortho-aminopyridine Schiff base was further reacted with metal chlorides to yield dialdehyde starch ortho-aminopyridine Schiff's base metal chelates **3** as shown in scheme I below.



**Scheme I:** The reaction routes to the chelating resins polymeric complexes

The dialdehyde starch (DAS) were designated as DAS1, DAS2 and DAS3, of which the degree of oxidation could be controlled by the addition of sodium periodate [(13.2g (0.7714M), 19.8g (1.1571M) and 26.4g (1.5428M)] respectively. Their percentages of aldehyde units were determined using the rapid quantitative alkali consumption method and was 55.65%, 70.16% and 87.30% respectively. The percentage of dialdehyde unit (Da) was calculated using the equation (1) below.

$$Da\% = \frac{V_1 C_1 - 2 V_2 C_2 \times 100\%}{W/161} \dots \dots \dots (1)$$

Where,  $V_1$ ,  $V_2$  and  $W$  represent the volumes (L) of total  $H_2SO_4$ , total NaOH and dry weight (g) of oxidized starch respectively.  $C_1$ ,  $C_2$  (mol/L) represent the concentrations of  $H_2SO_4$  and NaOH respectively. 161 is the averages molecular weight of the repeat unit in the dialdehyde starch (DAS) [6] (Awokoya *et al.*, 2013). The content of the aldehyde groups of DAS increased with higher amount of sodium periodate to cassava starch. Similar observation was reported by [1] and [6]. Elemental analysis of the Schiff base for the determination of the composition of (N, C, and H), degree of substitution, colours, and reaction yields of the condensation products are presented in Table 2.

The degree of substitution (DS) of aminopyridine for DASAPy was theoretically calculated from the nitrogen content with the following equation:

$$DS = \frac{161 \times N\%}{(2800 - 76.114 \times N\%)} \dots \dots \dots (2)$$

Where; 161 = molecular weight of DAS, 76.114 = molecular weight of 2-aminopyridine – 18,  $N\%$  = % of nitrogen content and 2800 = (molecular weight of nitrogen X 2) X 100. While, the percentage yields for DASAPy 1, 2 and 3 was calculated using equation (3):

$$\% \text{ Yield} = \frac{\text{experimental weight}}{\text{theoretical weight}} \times 10 \dots \dots \dots (3)$$

Where, experimental weight = experimental mass of the samples, theoretical weight = calculated mass of the samples. The products were in good yield and gave dark green and dark brown colours for DASAPy1, DASAPy2 and DASAPy3 respectively. Moreover, it can be seen that the nitrogen content, the percentage yield and degree of substitution in DASAPys increased from DASAPy1 to DASAPy3, these could be due to the increase in the amount of the oxidizing agent (i.e sodium periodate) concentration.

Table 1: Percentage of aldehyde unit

Compounds	DAS1	DAS 2	DAS3
Aldehyde Content (%)	55.65	70.16	87.30

Table 2: Degree of Substitution, % Yield, Elemental Analysis and Physical Property for DASAPy1, 2 and 3.

Products	React ant	Colour	Yield (%)	Elemental analysis			DS
				N (%)	C (%)	H (%)	
DASAPy1	DAS1	Dark Green	69.16	9.1	40.99	6.14	0.7
DASAPy2	DAS2	Dark Brown	73.33	12.4	44.2	5.7	1.1
DASAPy3	DAS3	Dark Brown	78.66	13.2	48.73	6.9	1.2

#### A. FT-IR Spectra of NS, DAS, DASAPy and DASAPy-Metal-Chelate

The FT-IR spectrum of native cassava starch (NS) (Fig. 1a) shows a broad band at  $3395\text{cm}^{-1}$  which is assigned to O-H stretching vibration. Peak at  $2924\text{cm}^{-1}$  is assigned C-H alkane stretching vibration, C-H alkane bending vibration at  $1365\text{cm}^{-1}$  and O-H bending of the retain waters in the starch at  $1643\text{cm}^{-1}$ , Stretching vibration at  $1148\text{cm}^{-1}$  is assigned to cyclic ether group C-O-C of glucose molecule and peak appears at  $1021\text{cm}^{-1}$  is attributed to C-O bond [7]

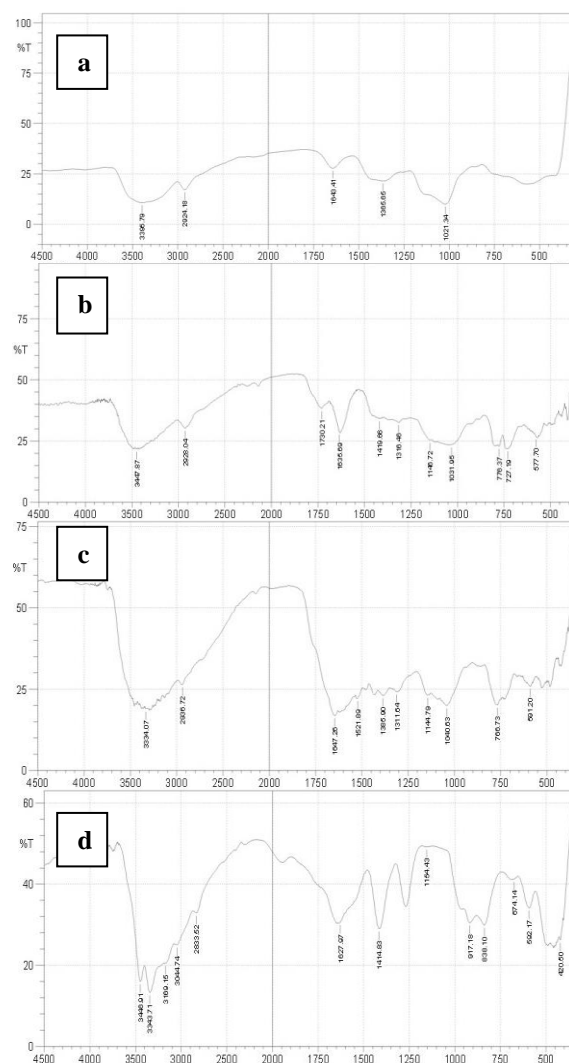


Fig 1: FT-IR Spectra of (a) Native starch (b) DAS (c) DASAPy (d) DASAPy-M-Chelate

For the DAS (Fig 1b) the peak at  $1730\text{cm}^{-1}$  is a characteristic band of carbonyl group and this did not appear as shown in the spectrum of DASAPy. In comparison with DAS, the IR spectrum of DASAPy (Fig. 1c) a new band appeared at  $1647\text{cm}^{-1}$  which confirm the presence of 2-aminopyridine group bound to the DAS which is assigned to imine group ( $C=N$ ). In the FTIR spectrum of DASAPy-metal-chelate (Fig. 1d), appearance of peak at  $420.50\text{cm}^{-1}$  is an indication of metal nitrogen bond formation (M-N) [8], [9] and [10].

#### A. Scanning Electron Microscopy

The Scanning Electron Microscopy was used to study the granule morphology before and after modification at 2250X,



1700X, 1450X and 390X magnifications respectively. Fig. 2a-d, illustrates SEM of native cassava starch (NS), DAS, DASAPy and DASAPy adsorbed metal ions respectively. The original native starch particles (Fig. 2a) present a spherical or elliptical and regular shape with smooth surface due to the nature of the structure of the starch molecules. This observation is consistent with previous reports on shapes of starches by [7] and [11]. But after oxidation with sodium periodate, the particles (Fig. 2b) appeared obviously diverse.

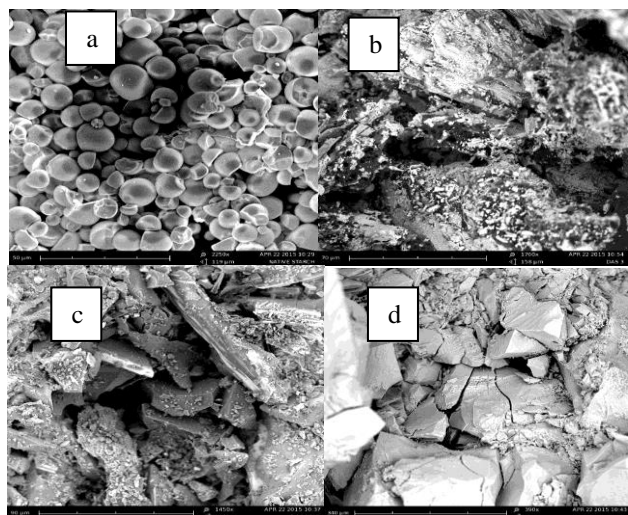


Fig. 2: SEM Photomicrograph of (a) Native Starch X 2250 (b) DAS X 1700 (c) DASAPy (d) DASAPy-M-Chelate

Clearly the cleavage of glucoside rings as revealed by FT-IR spectra leads to an altered and uneven surface, creating pores on the particles, also notable was that the particles were conglomerated closely, and the granules became much bigger in contrast to the native starch. The DASAPy (Fig. 2c) after reacting with 2-aminopyridine showed particle fragments and irregular structure due to probably cross linking disappearance as supported by FT-IR results and some granules had deep holes, the cause of the deep holes might be resulted from the swelling of starch granules during oxidation process. Similar observation has been reported by [6]. The DASAPy (Fig. 2d) shows micrograph after adsorption of Cr(II) ions, which presents that the granules are in block and more compatible in nature than DASAPy which may be attributed due to the metal-ligand coordinate bond existing in the complex compound. Similar results were observed for Cr (II) and Mn (II) ions.

#### A. Solubility Test

The polymer-metal-chelates were tested for their solubilities in water, methanol, ethanol and DMSO at room temperature (Table 3). DASAPy-M-Chelates were insoluble in water, slightly soluble in methanol, ethanol, and readily soluble in dimethylsulfoxide (DMSO) this may be attributed to the presence of hydrophilic substituents that allow the retention of solvent molecules and their tendency to form of hydrogen bond between the polar solvent and the complex whereas, it is insoluble in water due to the presence of hydrophobic groups on to the starch.

Table 3: Solubility test for Polymer-Metal-Chelates

Compounds/S	Water	Methanol	Ethanol	DMSO
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solvents				
DASAPy-M-C helates	IS	SS	SS	S

IS = Insoluble, SS = Slightly Soluble, S = Soluble.

It is readily soluble in DMSO because its dipolar solvent. Hence their solubilities depend on the polarity of the solvents. Similar results have been reported by [2], [4] and [12].

#### A. Melting Point/Decomposition Temperature

Table 4, showed that the melting points of native starch was at 188°C, DAS at 149°C, DASAPy at 247°C and the decomposition temperature of DASAPy-metal-chelate was at 298°C. It was found that the DASs have poor thermal stability as compared to native starch, the higher the content of dialdehyde groups, the lower the melting point.

Table 4 Melting point/decomposition temperature for native starch and its derivatives

Compounds	Melting Points (°C)	Decomposition Temperature (°C)
NS	188	
DAS	149	
DASAPy	247	
DASAPy-M-Chelate		298

This observation also corroborates with previous investigation on DAS prepared from corn starch and pea starch and could be attributed to the decreasing average molecular weight of DAS and, poor thermal stability of the aldehyde group [7]. Starch derivatives with higher thermal stabilities shows favourable thermoplastic processing properties, especially in terms of preventing thermal decomposition, which is responsible for degrading mechanical properties [12].

#### A. Magnetic Susceptibility/Moment Measurement

Based on the results of the magnetic moment, DASAPy-Cr-chelate was found to be 3.23BM, DASAPy-Mn-chelate is 6.03BM, and DASAPy-Cu-chelate is 1.88BM. Therefore, DASAPy-Cr-chelate was found to be diamagnetic, while DASAPy-Mn-chelate and DASAPy-Cu-chelate are paramagnetic respectively.

Table 5: Magnetic susceptibility/moment measurements for the polymer-metal-chelates.

Samples	DASAPy -Cr-Chelate	DASAPy -Mn-Chelate	DASAPy-Cu-Chelate
Susceptibility value (Xg) per gram of sample	8.98x 10 <sup>-6</sup>	3.12 x10 <sup>-5</sup>	2.99 x 10 <sup>-6</sup>
Magnetic moment (μ <sub>eff</sub> ) in Bohr Magneton(BM)	3.23	6.03	1.88

The susceptibility (Xg) per gram of sample was calculated using the expression (4) below:

$$X_g = \frac{CXL(R-R_0)}{10^9 M} \dots\dots\dots (4)$$

Where: C = 1, a constant, L = sample length in the tube in cm, R = Reading obtained of sample + tube, R<sub>0</sub> reading obtained of pre-weighed empty tube, M = Mass of the sample in the tube in gram. Hence, the magnetic moment was calculated using the equation (5) below:

$$\mu_{\text{eff}} = 2.828\sqrt{X_m T} \dots\dots\dots (5)$$

Where, T = temperature in Kelvin, X<sub>m</sub> = molar susceptibility. The results of the magnetic moment and/or magnetic susceptibility measurement indicated very strongly an octahedral geometry around the central metal ion in all the metal complexes. It accounts for the occupation of two coordinating sites by chlorine out of six in making the octahedral environment. This is in accordance with result reported by [4] and [13].

#### A. Molar Conductivity Measurement

The Molar conductance was calculated using the following equation (6) and the result are presented in Table 6.

$$Mc = \frac{\alpha}{C} \dots\dots\dots (6)$$

Where Mc = Molar conductance, α = specific conductivity and C = concentration of solution

Table 6 Conductivity test of the polymer-metal-chelates

Compounds	Concentration ion (dm <sup>3</sup> mol <sup>-1</sup> )	Specific Conductivity (ohm <sup>-1</sup> cm <sup>-1</sup> )	Molar Conductivity (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
DASAPy-Cr-chelate	1 x 10 <sup>-3</sup>	21.30x10 <sup>-6</sup>	21.3
DASAPy-Mn-chelate	1 x 10 <sup>-3</sup>	15.15x10 <sup>-6</sup>	15.15
DASAPy-Cu-chelate	1 x 10 <sup>-3</sup>	12.55x10 <sup>-6</sup>	12.55

The molar conductance measurement of the polymer-metal-chelates in 10<sup>-3</sup>M dimethylsulfoxide (DMSO) at room temperature was determined and the values obtained are presented in Table 6 which indicates low values for the complexes which suggested that they are non electrolytic in nature. This is in consistence with result reported by [5] and [10].

#### V. CONCLUSION

A novel modified starch chelating resin (dialdehyde starch ortho-aminopyridine) was prepared by reacting dialdehyde starch with ortho-aminopyridine. FTIR and SEM, shows that there is an interaction between the native starch and Sodium periodate, dialdehyde starch and ortho-aminopyridine, dialdehyde starch ortho-aminopyridine and metals ion. The adsorption experiment between Cr(II), Mn(II), Cu(II) ions and dialdehyde starch ortho-aminopyridine was carried out. The polymer-metal-chelates were soluble in DMSO, insoluble in water and slightly soluble in methanol and ethanol. The chelation of the cross-linked starch polymer with transition metals can obviously improved the thermal stability of the modified cassava starches as compared with native starch. Hence, polymer metal chelates can have enhanced mechanical properties and can exhibit greater industrial applications, for example in waste water treatment.

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#### REFERENCES

- [1] Akpa, J. G., and Dagde K. K. (2012) modification of starch for industrial uses, *Intern J. Eng. Tech* 2(6): 913-919
- [2] Ashraf M., Shadma P., Tansir A., Saad M. A., Prabal K. S., and Nahid N. (2010) coordination polymer: synthesis, spectral characterization and thermal behaviour of starch-urea based biodegradable polymer and its polymer metal complex. *Bioinorganic Chemistry and Application*, DOI 10.1155/2010/848130
- [3] Qiang-Feng Y., Ben-zhiju, Shu-Fen Z., Xin-Bo W. and Jin Z. Y. (2008) Preparation and characteristics of novel dialdehyde-aminothiazole starch and its adsorption properties for Cu(II) ions form aqueous solution. *Carbohydrate Polymer* 72, 326-333
- [4] Nahid N. and Ashraf M. (2012) Biodegradable coordination polymer: Polycondensation of glutaraldehyde and starch in complex formation with transition metals Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). *Arabian J. Chem.* 05, 002
- [5] Zainab A. A. and Abid Allah M. A. (2014) Preparation and characterization of some new mixed ligand with complexes of copper (II) *Intern J. Novel Resear & Interdisciplinary Studies* 1(2), 5-13
- [6] Awokoya K. N. and Moronkola B.A. (2013) 2-amino-4,6-dihydropyrimidine modified corn starches for uptake of Cu(II) ions from aqueous media. *Intern J. Eng and Sci*, 2(5), 49-55
- [7] Liming Z., Peng L., Yugao W., and Wenyan G. (2011) Study on physico-Chemical properties of dialdehyde Yam starch with different aldehyde contents. *Thermochimica acta* 512, 196-201
- [8] Abdussalam A. M., Faten S. A., Marei M. E. and Abdunnaser M. E. (2014) Modification on synthesis of mixed ligand chelates by using Di-and trivalent transition metal ions with Schiff base as primary ligand. *Green and Sustainable Chemistry* 4, 103-110
- [9] Aliakbar D. K., Mahsa N. and Debasis D. (2014) Co(III), Ni(II), and Cu(II) complexes of bidentate N, O-Donor Schiff base ligand derived from 4-methoxy-2-nitroaniline and salicylaldehyde. *Thermal and calorim* 115, 409-417
- [10] Fatima M. N. (2010) Synthesis, Characterization, antibacterial and antifungal studies of N, N-bis(benzylidene)-O-phenylenediiminato metal (II) complexes unpublished M.sc. Dissertation, *Bayero University, Kano, Nigeria*, 11-12
- [11] Jiugao Yu, Peter R. C., Xiaofei Ma. (2010) the preparation and properties of dialdehyde starch and thermoplastic dialdehyde starch. *Carbohydrate Polymers* 79, 296-300
- [12] Salisu A. A., Musa H., Abba H. and Kogo A.A (2013) preparation and characterization of dialdehyde starch and its cross-linking with copper (II) ion. *J. chem and pharm resear.* 5(5) 153-158