

## Adsorption of Cd (II), Cu (II) and Ni (II) Ions by Dialdehyde Starch Aminopyrazine Schiff Base from Aqueous Solution

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**Abstract:** Removal of Cadmium (II), Copper (II) and Nickel (II) ions from aqueous solution by using dialdehyde starch aminopyrazine (DASN<sub>2</sub>PYZ) was investigated. Dialdehyde starch (DAS) was obtained from periodate oxidative cleavage of C<sub>2</sub>-C<sub>3</sub> bond of anhydroglucose units of the cassava starch. The DASN<sub>2</sub>PYZ was prepared from a reaction between dialdehyde starch (DAS) and aminopyrazine, and characterized by elemental analysis, Solubility Test, Scanning Electron Microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FT-IR). The FT-IR, results confirmed that DASN<sub>2</sub>PYZ has different functional groups compared with DAS and these functional groups are able to react with metal ions in aqueous solution. Batch adsorption experiment was conducted and the study showed that parameters such as pH and the initial metal ions concentrations play an important role in the adsorption capacity and removal efficiency. Solubility test revealed that the Schiff base is soluble in dimethylsulfoxide (DMSO) and dimethylformamide (DMF).

**Keywords:** Starch Polymer, Dialdehyde starch, Starch Aminopyrazine, Chelating resin,

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### I. Introduction

Removal of heavy metal ions from wastewater and contaminated soil is a matter of great importance because of their toxic effects on the human health and on the natural environment in general [1]. These toxic heavy metals are introduced into the environment from a number of industrial activities like mining, plating, dyeing, automobile manufacturing and metal processing. The presence of heavy metals in the environment has caused various environmental issues. In order to meet the water and food quality standards, the monitoring of heavy metals in waste water is necessary [2]. Most of these metal ions have been discharged into the environment and human body through the food chain from diverse manufacturing, mining and casting industries. Some metal ions like Copper ions are an essential elements in living organisms and play an important role in body functions, but an excess intake of Cu (II) ion is adversely affected and associated with a number of diseases such as hepatitis, liver cirrhosis, kidney disease, anemia, bone disorders and Parkinson's diseases. Removal of heavy metal ions is of great significance to keep control of water quality and human health [3]. Techniques such as adsorption, ion exchange, dialysis, precipitation and extraction have been widely used to purify water containing excessive amounts of heavy metal ions. Adsorption technique has received much attention because it allows the use of many materials that are environmental friendly and have low production cost [1]. Several works have been carried out using different adsorbent, developed from various industrial waste materials, for the removal of toxic heavy metals and organic waste pollutants [4], [5], [6], [7], [8], [9], [10]. But all these adsorbents have their own inherent limitation, since they often involve high capital and operational costs and may also be associated with the generation of secondary wastes which present treatment problems [11] and [13].

As a natural polysaccharide, adsorbents based on starch have become a focus of study owing to starch's renewable and biodegradable properties. A variety of different approaches have been used to modify starch as a metal absorbent [13]. The effective method is the chemical modification which include esterification, etherization or oxidation (periodate oxidation). Dialdehyde starch (DAS) was obtained from the periodate oxidative cleavage of the C(2)-C(3) bond of the anhydroglucose units of starch polysaccharide chains. Since aldehyde groups form hemiacetals and acetals, their good cross-linking ability has rendered DAS great industrial application potentials especially in the formation of Schiff base that will give very good room for the metal ion complexation [14]. The ability of a material to chelates with metals is controlled in part by the number of available functional groups used for metal ion chelation.

Recently, it was shown that dialdehyde starch 2, Amino-4,6-Dihydroxypyrimidine [15], o-phenylenediamine [14] and 8-aminoquinoline [16] formed stable complexes with heavy metals. Complex formation from dialdehyde aminothiazole starch and Cu(II) ions and its adsorption properties in aqueous solution has also been reported [17]. The chelate formed from polymeric ligands was characterized by reactive functional groups containing O, N, donor atoms and its capability of coordinating to different metal ions was extensively studied. Schiff bases with N and O as donor atoms are well known to form strong complexes with transition metal ions. Many Schiff bases were reported to form strong complexes with a specific ion due to

geometric factors [14]. Recently, Adsorption of Cd(II), Cu(II) and Ni(II) ions from aqueous solution by cross-linked magnetic chitosan- 2-aminopyridine glyoxal Schiff base resin (CSAP) was studied in a batch adsorption system [18], and was found to be more effective.

In the present work, Schiff base type dialdehyde aminopyrazine starch (DASN<sub>2</sub>PYR) was synthesized by the reaction of aminopyrazine and dialdehyde starch (DAS) from the oxidation of cassava starch by periodate. The aim is to prepare starch DASN<sub>2</sub>PYR and determine the ability of this adsorbent in removal of Cd(II), Cu(II) and Ni(II) ions from aqueous media. Batch adsorption experiments were carried out to investigate the adsorption capacity and removal efficiency of the adsorbent.

## **II. Materials and Methods**

### **2.1.0 Materials**

Cassava tubers were purchased from Janguza market Kano, Nigeria, starch was extracted and oven dried to a constant weight, Potassium periodate (Xilong chemical co., ltd), Aminopyrazine 99+%, Sodium hydroxide, phenolphthalein, Dimethyl sulfoxide (DMSO), Dimethylformamide (DMF), ethanol, hexane, chloroform, acetone and were obtained from Sigma-Aldrich chemical co., ltd. All the other commercial chemicals were of analytic reagent grade and used without further purification. An infrared spectrum was characterized by mid infrared spectrophotometer (Agilent technologies 4000-650 cm<sup>-1</sup>). The elemental analysis (C, H and N) and morphology of the samples was identified by Phenom ProX Scanning electron microscopy (SEM) and Energy dispersive x-ray spectroscopy (EDX) 80-130,000x magnifications, Agilent technologies Atomic absorption spectrophotometer was used to determined final concentration of the metal ions.

### **2.2.0 Methods**

#### **2.2.1 Preparation of Dialdehyde Starch (DAS)**

Dialdehyde starches were prepared according to [17]. Potassium periodate solutions (0.25 mol/l, 0.50 mol/l, and 0.75 mol/l) were adjusted to pH 3.5 with dilute sulfuric acid. Exactly 20g of native cassava starch was added to each beaker containing the potassium periodate mentioned above under vigorous mechanical stirring. The reaction was kept at 30°C for 8hrs, the slurry was filtered and the product was washed three times with distilled water. After anhydrous ethanol was used to remove water, the powder was dried at 40°C to a constant weight.

#### **2.2.2 Determination of Content of the Aldehyde Groups**

The aldehyde group content was determined using the rapid quantitative alkali consumption method [19]. Dried DAS (0.4g) was suspended in 20ml of standardized 0.25 mol/l sodium hydroxide in a 250ml conical flask. The flask was swirled in a water bath at 70 °C for 2min, and then cooled immediately under running tap water with rapid swirling for 1min. After that 20ml of standardized 0.2mol/l sulfuric acid, 100ml of distilled water and 1ml of neutral 0.2% phenolphthalein was added in turn. Titration of the acid solution was carried out using 0.25 mol/l sodium hydroxide.

#### **2.2.3 Determination of Average Molecular Weight of Dialdehyde Starch**

The determination of average molecular weight (M<sub>w</sub>) of dialdehyde starch was based on the measurement of intrinsic viscosity [η], the measurements were carried out in triplicate at 25.0±0.2 with an Ubbelohde viscometer (capillary tube with 0.58mm in diameter). The samples were dissolved in DMSO, and several concentrations of 0.12M, 0.14M, 0.16M, 0.18M and 0.20M of dialdehyde starch were prepared from 0.025L of Dimethyl sulfoxide (DMSO).

#### **2.2.4 Preparation Of The Schiff Base**

The Schiff base was prepared according to the method described by [16]. 8g aminopyrazine and 4g of DAS-A was slurried from 100 ml ethanol in a 250 ml three-necked flask which was equipped with magnetic stirrer and thermostat water bath under nitrogen protection. The pH value of the mixture was adjusted to 5.0 with sodium acetate. The reaction was carried out at 50°C and 4 hours duration. The resulting solid was separated from solution by filtration and washed three times with distilled water (3x100 ml), then dried at 50°C to a constant weight.

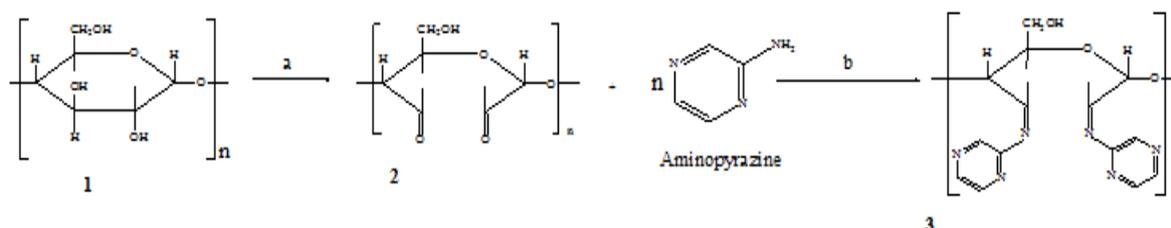
#### **2.2.5 Adsorption Experiments**

The adsorption experiment was carried out at room temperature according to [17]. 100mg/l of metal ions concentrations was prepared from the stock solution, 0.5g of the adsorbent was added to the beakers containing different metal solutions. Initial pH of the solutions was adjusted to 6.0 by adding 0.1M NaOH before adding the adsorbent and the solution was shaken for 90mins to ensure full equilibration, the mixture was

centrifuged at 4000 r/m for 20 min and filtered. The final concentration of Cd(II), Cu(II) and Ni(II) ions was measured by atomic adsorption spectrophotometer (AAS).

### III. Results and Discussion

The synthetic reaction routes for the intermediate and final compounds are presented in scheme I, native cassava starch **1** was treated with sodium periodate (NaIO<sub>4</sub>) to give dialdehyde starch DAS **2**, and the dialdehyde starch DAS was subsequently treated with 2, 3-diaminopyridine to produced dialdehyde starch 2, 3-diaminopyridine (DAS2,3-DNH<sub>2</sub>PYR) cross linked polymer material **3**. The dialdehyde starch 2, 3-diaminopyridine Schiff's base as ligand was further reacted with metal chlorides to yield dialdehyde starch 2, 3-diaminopyridine Schiff's base metal chelates **3** as shown in scheme I below.



**Scheme 1:** Reagents and conditions: (a) KIO<sub>4</sub> (b) ethanol

#### 3.1.0 Content of the Aldehyde Groups of DAS

Dialdehyde starch was prepared by periodate oxidation using potassium periodate as an oxidant. The content of an aldehyde was found to increase with increasing concentration of potassium.

The Percentage of dialdehyde units was given by equation (1);

$$Da\% = \frac{(C_1V_1 - 2C_2V_2)}{w/161} 100\% \quad (1)$$

Where: V<sub>1</sub>, V<sub>2</sub> and W represent the total volumes (L) of H<sub>2</sub>SO<sub>4</sub>, NaOH and the dry weight (g) of the oxidized starch, respectively. C<sub>1</sub> and C<sub>2</sub> (mol/l) represent the concentrations of H<sub>2</sub>SO<sub>4</sub> and NaOH. 161 is the average molecular weight of the repeated unit in dialdehyde starch.

The content of the aldehyde groups was 37.38% for DAS-A, 50.72% for DAS-B, and 67.62% for DAS-C.

Table 1. Titration Result for Aldehyde Content Determination

DAS	1 <sup>st</sup> Reading (cm <sup>3</sup> )	2 <sup>nd</sup> Reading (cm <sup>3</sup> )	3 <sup>rd</sup> Reading (cm <sup>3</sup> )	Volume of acid
DAS-A	24.60	24.80	24.70	24.60+24.80+24.70/3=24.70
DAS-B	26.30	26.20	26.40	26.30+26.20+26.40/3=26.30
DAS-C	28.50	28.40	28.30	28.50+28.40+28.30/3=28.40

The increased in aldehyde content could be due to the fact that, when the molar ratio of potassium periodate to cassava starch increased, the superfluous oxidant degraded the starch and caused some of the DAS to dissolve in the water, resulting in a reduced DAS yield [20]. Total volume of the acid used was obtained from the titration result given in Table 1.

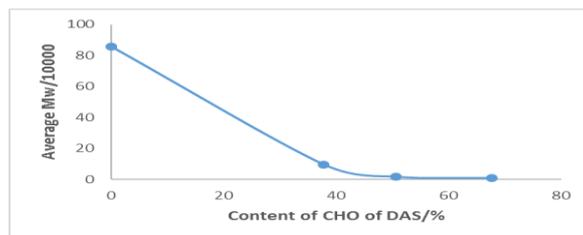
#### 3.2.0 Average Molecular Weight of DAS

The average molecular weight of the polymers was obtained according to Mark-Houwink equation given in equation (2) below.

$$[\eta] = KM^\alpha \quad (2)$$

Where  $[\eta]$  = Intrinsic Viscosity, K and  $\alpha$  are constants given as  $8.5 \times 10^{-3}$ , ml/g and 0.76, respectively and M is the molecular weight, [21].

The molecular weight of DAS decreases drastically when dialdehyde starch was prepared by using potassium periodate under acidic condition. Native cassava starch was found to have average molecular weight of about 861, 800, and for the DAS-C, DAS-B and DAS-A was 97,016, 17, 044, and 9, 820 respectively. The molecular weight of DAS as a function of carbonyl content is shown in Fig. 1.

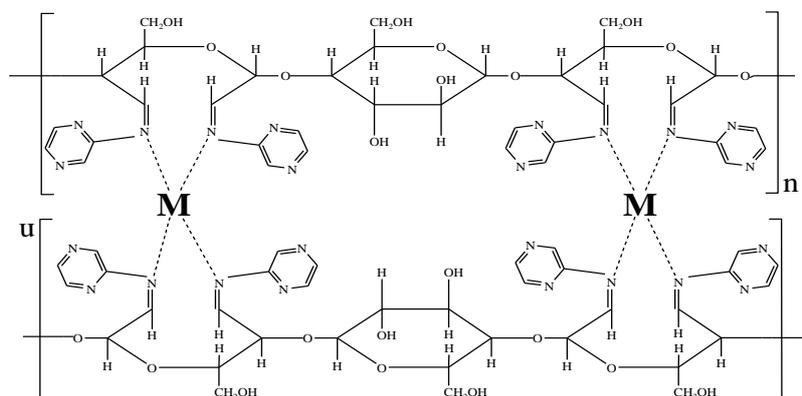


**Fig1:** Relationship between Average Mw of DAS and Content of the Aldehyde Groups

The reason for this decreased in average molecular weight with increasing aldehyde content could be that, when potassium periodate cleaved the C2–C3 bonds of the glucose units of cassava starch, the oxidation also led to disruption of  $\alpha$ -D-(1–4) and  $\alpha$ -D-(1–6) glycosidic bonds which causes the average molecular weight of dialdehyde starch to declined drastically [20]. According to [21], the molecular weight of DAS decreased even under mild oxidizing conditions during the preparation of dialdehyde starch, and the degree of degradation depends on the degree of oxidation (at pH value of 7.0).

### 3.2.0 Adsorption Capacity and Removal Efficiency

Polymeric complexes were obtained after adsorption experiments and the proposed general molecular structures of the  $\text{DASNH}_2\text{PYZ}$  complex is given in scheme 2 below.



**Scheme 2:** Proposed General Molecular Structure of  $\text{DASNH}_2\text{PYR}$  Complex

The degree of substitution of aminopyrazine for  $\text{DASNH}_2\text{PYZ}$  was theoretically calculated from the nitrogen content using the equation (3).

$$DS = \frac{161 \times N\%}{(28)100 - 95.1026 \times N\%} \quad (3)$$

Where, N% was obtained from the elemental analysis, 28 is the molecular mass of  $\text{N}_2$ , 95.1026 g/mol is the molecular weight of aminopyrazine.

The metal concentration (mg/g) retained on the adsorbent phase ( $q_e$ ) and the removal efficiency (%) of the adsorbent preparations were calculated using the following equations (4) and (5) respectively [22].

$$q_e = \frac{(C_o - C_e)V}{m} \quad (4)$$

$$\text{Removal efficiency (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (5)$$

Where,  $C_o$  is initial concentration of the metal,  $C_e$  is the final concentration of the metal,  $v$  = volumes of the adsorption solution (L) and  $m$  = dose of the adsorbent (g). The degree of substitution (DS), adsorption capacity, removal efficiency and elemental analysis was given in Table 2;

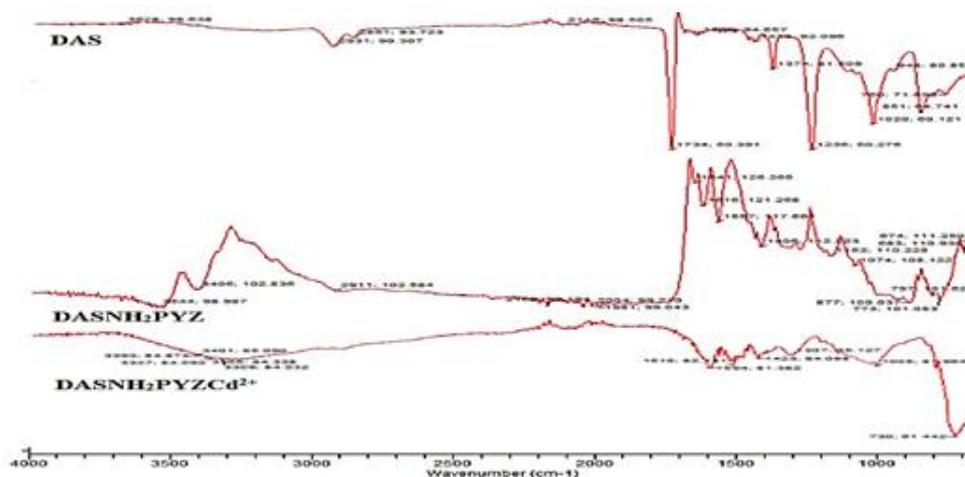
Table2. Degree of Substitution for  $\text{DASNH}_2\text{PYZ}$

Schiff base	DS	Adsorption Capacity $q_e = \frac{(C_o - C_e)V}{m}$			Removal Efficiency $R. E. = \frac{C_o - C_e}{C_o} 100\%$			Elemental Analysis		
		Cd	Cu	Ni	Cd	Cu	Ni	N%	C%	H%
$\text{DASNH}_2\text{PYZ}$	0.59	26.7mg/g	24.0 mg/g	26.67 mg/g	66.7%	60%	66.7%	7.6	49.2	6.2

Acidity of the metal ion solutions is one of the important factor affecting adsorption capacity, this is because  $H^+$  ions compete with the metal cations for the binding sites on the Schiff base. Starch dialdehyde aminopyrazine having DS of 0.59 was found to have adsorption capacity for Cd(II), Cu(II) and Ni(II) ions as 26.67mg/g, 24mg/g and 26.67mg/g and removal efficiencies as 66.7%, 60% and 66.7% respectively.

### 3.3.0 FT-IR Spectra

The FT-IR spectrum of the native cassava starch shows a broad band at  $3291\text{cm}^{-1}$  and is assigned to O–H stretching which is due to hydrogen bonding involving the hydroxyl groups on starch molecules. The band at  $2931\text{cm}^{-1}$  is assigned to  $\text{CH}_2$  symmetrical stretching vibrations. Fig 2 Show the effect of content of the aldehyde

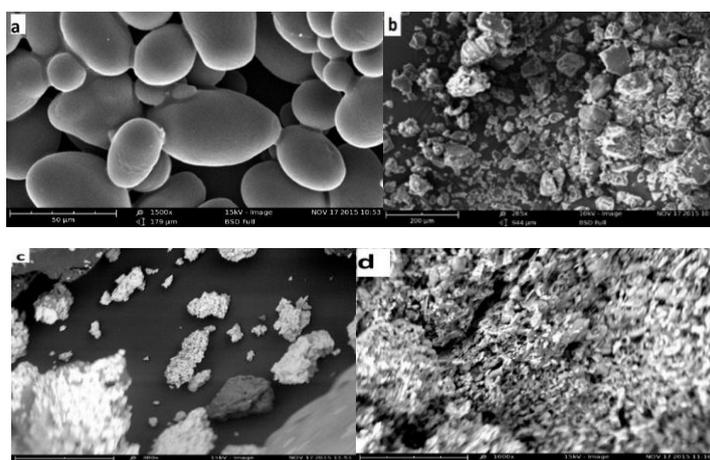


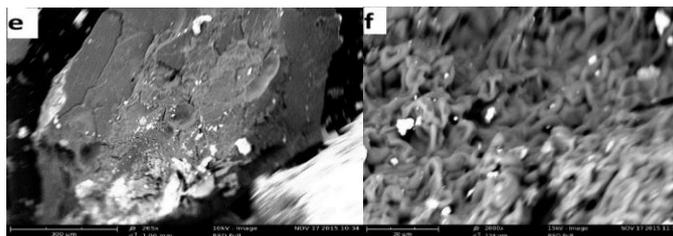
**Fig 2:** FT-IR spectra of DAS, DASNH<sub>2</sub>PYZ and DASNH<sub>2</sub>PYZCd<sup>2+</sup>

groups on spectra of DAS. The DAS of high content of the aldehyde groups (DAS-A) show a very sharp peak at  $1734\text{cm}^{-1}$ , which is the most characteristic band of C=O vibrations in aldehyde groups. There was a new strong absorption peak at  $1641\text{cm}^{-1}$  in the spectrum of the Schiff base, this bands can be assigned to the C=N stretching vibrations of the imine group which indicated the new generation of carbon–nitrogen double bond, confirming the formation of Schiff bases between aminopyrazine and dialdehyde starch. An intense band at  $1423\text{cm}^{-1}$  corresponding to the C=N stretching of the aminopyrazine ring. After adsorption, new bands appeared at  $730\text{cm}^{-1}$ ,  $681\text{cm}^{-1}$ , and  $732\text{cm}^{-1}$  in DASNH<sub>2</sub>PYZCd<sup>2+</sup>, DASNH<sub>2</sub>PYZCu<sup>2+</sup>, DASNH<sub>2</sub>PYZNi<sup>2+</sup> respectively, these bands were assigned to M-N bond and confirming the formation of the polymeric complexes.

### 3.4.0 Surface Morphology

The SEM photomicrographs clearly showed the structure of different samples (native cassava starch, DAS, DASNH<sub>2</sub>PYZ, DASNH<sub>2</sub>PYZ Cd<sup>2+</sup>, DASNH<sub>2</sub>PYZ Cu<sup>2+</sup>, DASNH<sub>2</sub>PYZ Ni<sup>2+</sup>). Generally, Fig. 3a, b, c, d, e and f are taken at 1500x, 285x, 380x, 1000x, 265x and 2000x magnifications.





**Fig.3.** Surface morphologies of (a) native cassava starch, (b) DAS, (c) DASNH<sub>2</sub>PYZ, (d) DASNH<sub>2</sub>PYZCd<sup>2+</sup>, (e) DASNH<sub>2</sub>PYZCu<sup>2+</sup> (f) DASNH<sub>2</sub>PYZ Ni<sup>2+</sup>

It can be seen that the surfaces of the native cassava starch particles (Fig. 3a) is smooth, however, the cleavage of glucosidal rings for particles oxidized by periodate led to uneven surface, and created pores on the particles (Fig. 3b). Furthermore, the particles were conglomerated closely, and the granules became much bigger than the original starch, the agglomeration could be due to a strong depolymerization and oxidation of the surface, which leads to higher interactions between the granules. Similar observations has been reported for the morphology of DAS prepared from corn starch [23], [17], Potato starch [16] (Ding *et al.*, 2011), yam starch [21]. Connecting with aminopyrazine (Fig. 3c), the particles fragments and the irregular structure appeared due to reduction or loss of cross-linking. After the absorption of Cd(II), Cu(II) and Ni(II) ions, the fragments (Fig. 3e, g and i) became much smaller.

### 3.5.0 Solubility Test

Dissolving a polymer is unlike dissolving low molecular weight compounds because of the vastly different dimensions of solvent and polymer molecules. Dissolution is often a slow process. While some polymers dissolve readily in certain solvents resulting in a true solution, others may require prolonged periods of heating at temperatures near the melting point of the polymer. Solubility test result was given in table 3.

**Table3.** Results of Solubility Test

Solvent	Chloroform	DMF	DMSO	Ethanol	Hexane	Methanol	Water
Solubility	Slightly soluble	Soluble	Soluble	Slightly soluble	Insoluble	Slightly soluble	Slightly soluble

The polymeric complexes were dissolved in some common solvents. All the complexes are soluble in DMSO and DMF and, slightly soluble in water, methanol, chloroform and ethanol but insoluble in hexane. This result is in consistent with the literature [25].

## IV. Conclusions

Dialdehyde cassava starches (DASs) were prepared by periodate oxidation using potassium periodate and characterized. Compared with native cassava starch, viscosity average molecular weight of DASs decreased with increasing aldehyde content. Dialdehyde starch that contains highest percentage of aldehyde group (DAS-A) reacted with aminopyrazine to produced the Schiff base. The adsorbent, dialdehyde aminopyrazine starch (DASNH<sub>2</sub>PYZ) was characterized by Elemental analysis, Solubility test, Fourier transform infrared spectroscopy and Scanning electron microscopy. Solubility test indicates that the adsorbent is soluble in DMF and DMSO. During the experiment, we can see that the pH of the solution (6.0) and the initial concentrations of Cd(II), Cu(II) and Ni(II) ions (100mg/l) had important effect on the adsorption capacity. Adsorption capacity for Cd(II), Cu(II) and Ni(II) ions were 26.67mg/g, 24mg/g and 26.67mg/g and removal efficiencies was 66.7%, 60% and 66.7% respectively. As effective and biodegradable, DASNH<sub>2</sub>PYZ can remove the cadmium, copper and nickel ions from aqueous effectively and it was relatively cheap adsorbent as well. DASNH<sub>2</sub>PYZ therefore have great potential application in the removal of metal ions from aqueous media.

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