Removal of Co (II), Pb (II) and Zn (II) Ions by Dialdehyde Starch Aminopyrazole Schiff Base from Aqueous Solution

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Abstract: *Dialdehyde starch aminopyrazole (DASAPyZO) was prepared by the reaction of dialdehyde starch (DAS) from periodate oxidized cassava starch with aminopyrazole. The oxidized starch (DAS) was successfully reacted with aminopyrazole in order to form dialdehyde starch aminopyrazole (DASAPyZO), which was then used to remove Co(II), Pb(II) and Zn(II) ions from aqueous solution. Starch and modified starches and polymer complexes were characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) in order to determine the structure and morphology respectively. The degree of substitution (DS) of DASAPyZO was found to be 0.84. Adsorption capacity of DASAPyZO for Co(II), Pb(II) and Zn(II) ions were 17.31mg/g, 37.07mg/g and 41.85mg/g respectively. However, the percentage removal efficiency of DASAPyZO for Co(II), Pb(II) and Zn(II) ions were 34.64%, 74.15% and 83.70% respectively. The polymer was found to be more sensitive to Pb(II) and Zn(II).*
Keywords: *Starch Polymer, Dialdehyde starch, Starch Aminopyrazole, Chelating resin,*

I.   Introduction

The occurrence of heavy metals beyond permissible limits in industrial effluents affects human health as well as natural ecosystems [1]. Heavy metals are toxic substances originating from industrial activities, such as mining, agriculture, combustion of fossil fuels, waste disposal, battery manufacture, and petroleum refining. These are non biodegradable, can accumulate in internal organs, and cannot be utilized by living organisms, thus causing various problems and disorders [2]. Heavy metal pollution is assuming a dreadful dimension throughout the world with the expansion of industrial activities. However, the concentration of these metals in the effluent must be brought down to permissible limit before discharging into water bodies [3]. There is a continuous need for new separation techniques which selectively extract metal ions from aqueous solution and industrial process streams [4]. Various methods have been suggested and investigated for the removal of heavy metal ions from aqueous solutions, including chemical precipitation, electrochemical separation, ion exchange, membrane filtration, reverse osmosis, solvent extraction, coagulation, evaporation, adsorption, etc. Adsorption is considered as more attractive in terms of its low cost, high efficiency, production of less toxic sludge, etc [5].

Dialdehyde starch (DAS) is a polymeric aldehydes obtained by the reaction of native starch with periodate, which has shown nontoxic and biodegradable macromolecule [6]. DAS has highly reactive dialdehyde groups which is obtained from the periodate oxidative cleavage of the C_2-C_3 bond of the anhydroglucose units of starch polysaccharide chains [7]. It has ability to remove heavy metals from aqueous solution [8].

Removal of Pb(II), Mn(II), Cu(II), Co(II), and Ni(II), by silica gel supported hyperbranched polyamidoamine dendrimers had been investigated [9]. It has been demonstrated by [10] carboxymethyl starch (CMS) when grafted with N-vinyl imidazole can be used as a heavy metal removal from aqueous solutions. The grafted material was used for the sorption of Mn(II), Zn(II) and Cd(II). Removal of Ni(II) ions from aqueous solution by using dialdehyde o-phenylenediamine starch (DASPDA) was reported [11]. The adsorption results revealed that the optimal pH was 5.0, the equilibrium time was about 120 min, and the adsorption capacity increased with the increase of degree of substitution DS (0.33, 0.49 and 0.90) of the DASPDA.

In this paper adsorption method was considered in order to remove some heavy metals such as Co(II), Pb(II) and Zn(II) from aqueous solution using modified starch with aminopyrazole for the purpose of making it heavy metal scavenger.

II.   Materials And Methods

2.1.0 Materials

Cassava tubers were purchased from Dawanau Market, Kano, Nigeria, Sodium periodate ($NaIO_4$), Zinc nitrate [$Zn(NO_3)_2$] and Lead nitrate [$Pb(NO_3)_2$] were obtained from Xilong Chemical Co. Ltd. Aminopyrazole, Cobolt chloride ($CoCl_2$), Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Methanol, Ethanol, Chloroform, Hexane, Diethylether and Dimethylsulfuroxide (DMSO) were obtained from Sigma Aldrich. Infrared spectra were obtained by Fourier infrared spectroscopy FT-IR (Cary630 FTIR Agilent Technologies). Viscosity was

determined by an Ubbelohde Capillary Viscometer. Morphology was obtained by scanning electron microscopy (SEM, Phenom ProX). The elemental analysis of C, H and N were obtained from SEM machine in elemental dispersive X-rays (SEM-EDX). Initial and final concentrations of the metal ions were determined using Atomic Absorption Spectrophotometer (Buck scientific 210VGP).

2.2   Methodology
2.2.1 Extraction of Starch and Preparation of Dialdehyde Starch (DAS)
The tubers were peeled and put into a Mortar. $200cm^3$ of distilled water was added. The cassava was grinded carefully and the liquid was poured off through a strainer into the beaker leaving the cassava behind in the mortar. $200cm^3$ of distilled water was also added, grinded and strained twice more. The mixture was left for 20mins in the beaker to settle. The water was then decanted from the beaker leaving behind the white starch settled in the bottom of the beaker. $500cm^3$ of distilled water was also added to the starch and stirred gently, the suspension was also allowed to settle and the water was decanted leaving the starch behind. The starch was air dried to a constant weight.

DAS was prepared by modified method of [12]. 20g of starch was suspended in distilled water to produced starch slurry. The slurry was heated in a water bath to boil until it completely dissolved, the required amount of sodium periodate was added while stirring with a magnetic stirrer. The sodium periodate/starch molar ratio was 0.4, 0.6 and 0.8mol/L respectively. The reaction was carried out at 35^oC and pH of 3.5 in dark for 4 hours. The oxidized product was precipitated with ethanol, washed with distilled water several times [13].

2.2.2 Determination of Percentage of Aldehyde Content
The aldehyde group content was determined using the rapid quantitative alkali consumption method [14]. Dried 0.2g DAS was weighed into 250ml conical flask and 20ml of standardized 0.2mol/L Sodium hydroxide was added. The flask was swirled in a water bath at 70^0C for 5mins, and then cooled immediately under running tap water with rapid swirling for 3mins. 20ml of standardized 0.2mol/L Sulfuric acid, 100ml of water and 2ml of neutral Phenolphthalein were added in turn. Titration of the acid solution was carried out using 0.2mol/L Sodium hydroxide.

2.2.3 Fourier Transform Infrared (Ft-Ir) Spectroscopy
FT-IR spectra of the native starch, oxidized starches (DAS), modified starches and complexes were recorded on a Fourier transform infrared spectrometer (Cary630 Agilent Technologies) in a range of wave number from 4000 to $650cm^{-1}$.

2.2.4 Determination of Average Molecular Weight of Starch and Dialdehyde Starch
The average molecular weight (M_w) of starch and dialdehyde starch were determined based on the measurement of intrinsic Viscosity [15]. The measurements were carried out in triplicate at 25.0 ± 0.1^oC with an Ubbelohde Viscometer in a water bath.

2.2.5 Preparation of Starch Dialdehyde Aminopyrazole
Exactly 6g of DAS was suspended in 50ml distilled water in a three necked flask, which was equipped with an electromagnetic stirrer and thermostat water bath. Then, 50ml of aminopyrazole solution with a molar ratio of 2:1 to dialdehyde was slowly added into the flask under nitrogen protection. The pH value of the mixture was adjusted to 5.0 with acetic acid. The mixture was stirred for 4 hours at 55^oC on a water bath. The slurry was filtered and rinsed with distilled water and ethanol one time, the product was then dried at 50^oC to a constant weight [16]

2.2.6 Adsorption Experiments
Adsorption experiments were carried out by batch method [17], at room temperature. 0.1g of DAS-ligand was added into a 100ml conical flask with 50ml of metal solution. The initial pH was adjusted with 0.1M HNO_3 or 0.1M NaOH before adding the adsorbent. After shaking for 120 min to ensure full equilibration, the mixture was centrifuged at 12000 rpm for 5 min, and the final concentration of metal ion was determined using atomic absorption spectrophotometer.

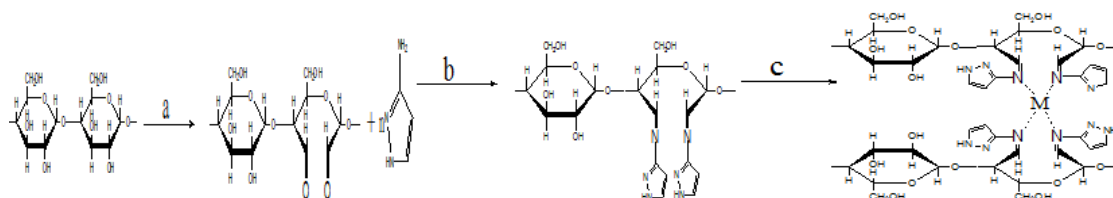### 2.2.7 Scanning Electron Microscopy (Sem)
The surface morphology of the Native starch, DAS, DAS-ligand and DAS-ligand-metal complexes were determined using scanning electron microscopy (SEM), with different sizes. The elemental analysis of C, H and N were obtained from SEM machine in elemental dispersive X-rays (SEM-EDX, Phenom Pro X).

2.2.8 Solubility Test

The DAS-ligand-metal complexes were tested for the solubility in some common solvents by dissolving the sample in the solvent at room temperature [8].

III.   Results and Discussion

The dialdehyde starch was prepared by periodate oxidation using Sodium periodate as an oxidant, the oxidation leads to the cleavage of C_2–C_3 bonds of anhydrous glucose units. Dialdehyde starch formed was further successfully reacted with aminopyrazole to formed dialdehyde starch aminopyrazole (DASAPyZO). Then, the metal ion formed co-ordinate bonds with dialdehyde starch aminopyrazole which gives polymer complexes as illustrated in scheme 1 below:

Scheme 1: Synthesis of dialdehyde starch aminopyrazole complex from starch; (a) NaIO$_4$; (b) ethanol; (c) Co(II), Pb(II) or Zn(II) salts

3.1.0 Percentages of Aldehyde Content

Cassava starch was oxidized by sodium periodate to formed DAS. The content of the aldehyde groups, which reflect the degree of oxidation, were expressed as the number of carbonyl groups per 100 glucose units. The percentages of dialdehyde content were obtained from equation (1) below:

$$Da = \frac{C_1V_1 - 2C_2V_2}{W/161} \; X \; 100\% \qquad\qquad (1)$$

Where: V_1, V_2 and W are the volumes (L) of total H_2SO_4, total NaOH and the dry weight (g) of the oxidized starch, respectively. C_1 and C_2 (Mol/L) represents the concentrations of H_2SO_4 and NaOH, respectively: 161 is the average molecular weight of the repeat unit in dialdehyde starch.

Table 1: Average Titre Values and Percentages of Aldehyde Content of DAS1, DAS2 and DAS3

Samples	Average titre Value (cm³)	Aldehyde content(%)
DAS1	22.80	45.20
DAS2	23.80	61.20
DAS3	25.40	86.94

The percentages of aldehyde content of the three kinds of DAS, designated as DAS1, DAS2 and DAS3 were 45.2%, 61.2% and 86.94% respectively. The higher the concentration of periodate, the higher the percentage of aldehyde content in DAS. Similar observation had been reported by [15].

3.2.0 Estimation of Average Molecular Weight

The average molecular weight of dialdehyde starch (DAS) decreases drastically with the increase of concentration of sodium periodates. Native starch had an average molecular weight of 838,503. DAS1 with the content of the aldehyde groups of 45.2% had an average molecular weight of 85,853, while the average molecular weight of DAS2 with the content of the aldehyde groups of 61.2% was 15,466.

Table 2: Average Molecular Weight of Starch, DAS1, DAS2 and DAS3

Sample	Average molecular weigth
STARCH	838,503
DAS1	85,853
DAS2	15,466
DAS3	13,182

When the content of aldehyde groups increased to 86.94% the average molecular weight of DAS3 also decreased to 13,182. Similar observations had been reported by [15]. The reasons for this is that, when NaIO$_4$ cleaved the C_2–C_3 bonds of the glucose units of cassava starch, the oxidation led to disruption both α- d-(1–4) and α-d-(1–6) glycosidic bonds of the starch which causes the average molecular weight of dialdehyde starch to declined drastically, and also as the NaIO$_4$ cleaved the C_2–C_3 bonds of the glucose units of cassava starch, there would be loss of hydrogen atoms which also leads to decrease in average molecular weight. Average molecular

weight of starch and DAS were obtained based on intrinsic viscosity measurements. Intrinsic Viscosity was determined using equation (2) below;

$$[\Pi] = KM^{\alpha} \qquad\qquad (2)$$

Where: $[\Pi]$ is intrinsic viscosity. Defined as $[\Pi] = \Pi_{sp}/C$, K and α were given as constant as 8.5×10^{-3}mL/g and 0.76, respectively. M is the average molecular weight.

3.3.0 Ft-Ir Spectral Analysis

Fig. 1, represent spectrum of native starch. The broad band at 3291cm^{-1} was assigned to O–H stretching and it was due to hydrogen bonding involving the hydroxyl groups on starch molecules. The band at 2931cm^{-1} was assigned to C–H stretching vibrations. However, in the finger print region, characteristic peak appeared at 1078cm^{-1} which was attributed to C–O bond stretching of the starch. Fig. 2, represent spectrum of DAS. Compared with spectrum of native starch, a new peak appeared at 1721cm^{-1} which was correspond to stretching vibrations of the C=O groups. The band for C–H was observed at 2929cm^{-1}. In the finger print region, band at 1013cm^{-1} was assigned to stretching vibration of C–O. In fig. 3, a new band appeared at 1655cm^{-1} which was as a result of C=N stretching vibration after introducing the aminopyrazole. Fig. 6, represent spectrum of DAS-Aminopyrazole Complex.
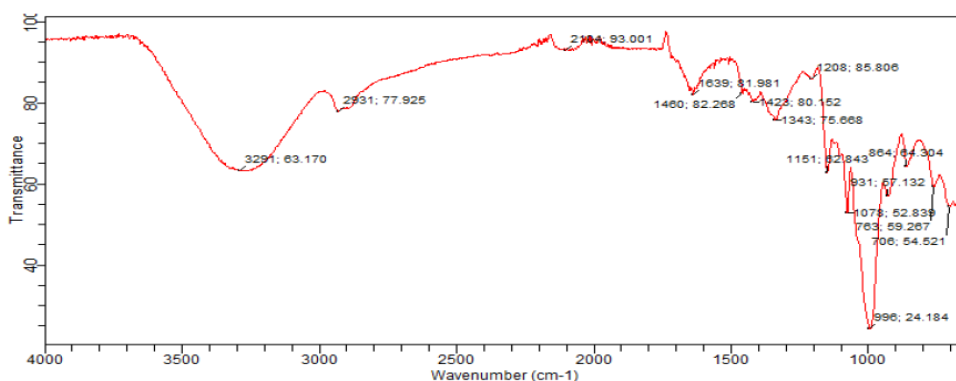

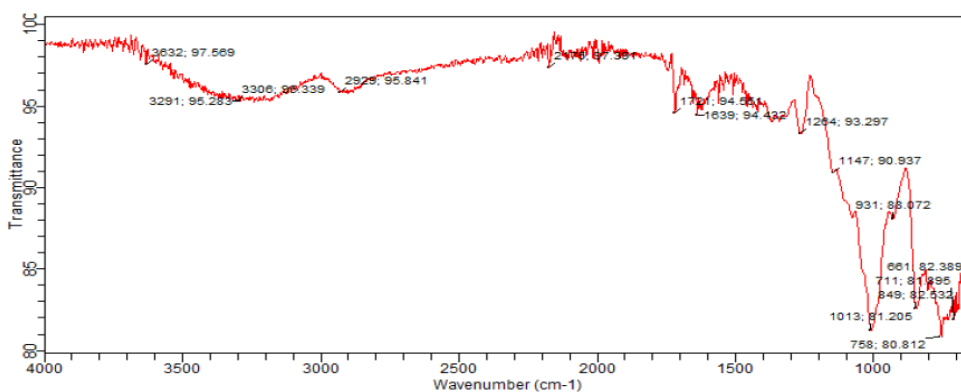**Fig. 1:** FTIR Spectrum Of Native Cassava Starch

Fig. 2: FTIR Spectrum of Dialdehyde Starch (DAS)

Fig. 3: FTIR Spectrum of DAS-Aminopyrazole

Fig. 4: FTIR Spectrum of DAS-Aminopyrazole Complex

On compares with spectrum of DAS-Aminopyrazole, a new sharp peak was observed at $693cm^{-1}$, which was as a result of metal nitrogen bond. Similar results were reported by [8],[20], [21], [22], [23] [24].

3.4.0 Elemental Analysis and Degree of Substitution

The degree of substitution (DS) of aminopyrazole was 0.84. DS increased with the increase of percentages of nitrogen content in the polymer adsorbent. Similar results were reported by [23], [24].

Table 3: Elemental Analysis and Degree of Substitution (DS)

Sample	Elemental analysis			DS
	C (%)	N (%)	H (%)	
DASAPyZO	47.85	10.19	6.28	0.84

The degree of substitution (DS) for DAS-aminopyrazole was theoretically calculated from the nitrogen content from the equation (3) below;

$$DS = \frac{(161 \; X \; N\%)}{2800 - 83 \; X \; N\%} \qquad (3)$$

Where, N% is the percentage of nitrogen in the Polymer adsorbent

3.5.0 Adsorption Capacity and Removal Efficiency

Batch adsorption experiments were carried out as a function of initial concentration of metal ion, and the adsorption capacity of DASAPyZO for Co(II), Pb(II) and Zn(II) ions were 17.31mg/g, 37.07mg/g and 41.85mg/g respectively.

Table 4: Adsorption Capacity and Removal Efficiency of Dasapyzo-M

Sample	Adsorption capacity (mg/g)	Removal effeciancy (%)
DASAPyZO-Co	17.31	34.62
DASAPyZO-Pb	37.07	74.15
DASAPyZO-Zn	41.85	83.70

The percentage removal efficiency of DASAPyZO for Co(II) Pb(II) and Zn(II) ions were 34.64%, 74.15% and 83.70% respectively. Hence, DASAPyZO polymer adsorbent is more sensitive to Pb(II) and Zn(II) ions and the order of metal ion binding was Zn(II) > Pb(II) > Co(II). Adsorption capacity was calculated from equation (4) below;

$$Q = \frac{(C_o - C_t)V}{m} \qquad (4)$$

Where: Q is the adsorption capacity of the adsorbent (mg/g), C_o and C_t (mg/L) are the initial and final concentrations of the metal ions in the adsorption solution, and V (ml) and m (g) are the volumes of the adsorption solution and the dose of the adsorbent, respectively.

Percentage removal efficiency was calculated from equation (5) below;

$$R.E = \frac{(C_o - C_t)}{C_o} \times 100\% \qquad (5)$$

Where: R.E is the percentage removal efficiency; C_o and C_t (mg/L) are the initial and final concentrations of the metal ions in the adsorption solution.

3.6.0 Solubility Test

The prepared polymer complexes were tested for solubility in water and some common organic solvents. The Cross-linked polymer and complex polymer were soluble in DMSO, but, slightly soluble in Water, Methanol, Ethanol and Chloroform and, insoluble in Diethylether and Hexane. Similar result was reported by [8].

Table 5: Solubility Test of Cross Linked and Complex Polymer

Solvent	Solubility
Water	SS
Methanol	SS
Ethanol	SS
Chloroform	SS
DMSO	S
Diethylether	IS
Hexane	IS

(S): Soluble, (SS): Slightly soluble, and (IS): Insoluble

3.7.0 Scanning Electron Microscopy (Sem)

Scanning electron microscopy (SEM) was used to study the morphology of the granules. The original cassava starch particles showed smooth and dispersed with oval shaped granules.

The DAS, DAS-ligand, and DAS-ligand complexes displayed a rough structure on surface. However, after oxidation by periodate, (b), the particles were diverse, conglomerated closely, and the granules became much bigger than the original starch.
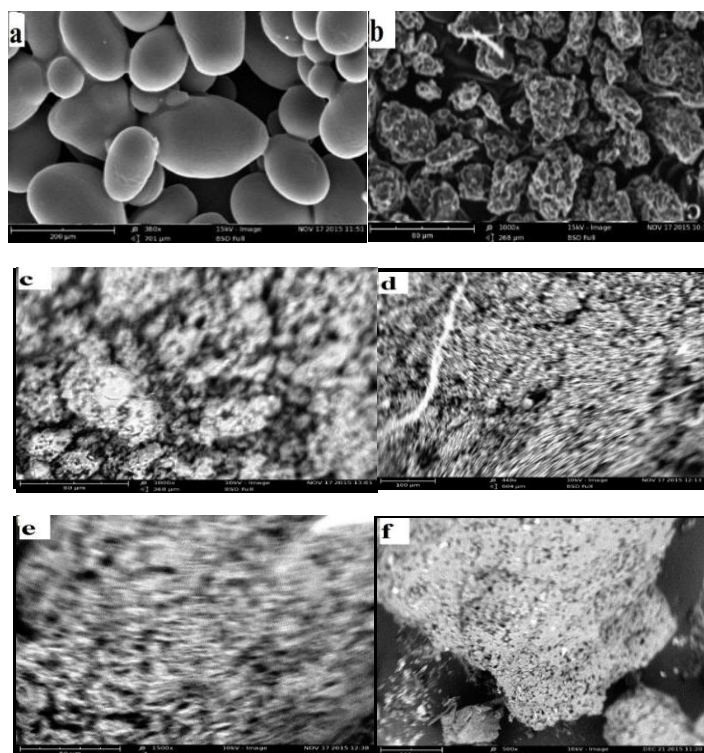

Fig.5: (a) Photomicrograph of starch granules X 380, (b) Photomicrograph of DAS X 1000, (c) Photomicrograph of DASAPyZO X 1000, (d) Photomicrograph of DASAPyZO-Co X 440, (e) Photomicrograph of DASAPyZO-Pb X 1500 and (f) Photomicrograph of DASAPyZO-Zn X 500.

These indicated clearly that the cleavage of glucoside rings as confirmed by FT-IR analysis leads to an altered uneven surface, creating pores on the particles. DASAPyZO (c) shows particle fragments and irregular structure due to reduction or loss of crosslinking. There was no clear diversification in the photomicrographs of DAS-aminopyrazole complex (d, e and f), in comparison to photomicrographs of DAS-aminopyrazole. Similar results were obtained by [25], [26].

IV.   Conclusions

Starch dialdehyde aminopyrazole (DASAPyZO) was succesfully synthesized by the reaction of aminopyrazole and dialdehyde starch (DAS) obtained from cassava starch oxidation by Sodium periodate. Adsorption capacity of DASAPyZO for Co(II), Pb(II) and Zn(II) ions were 17.31mg/g, 37.07mg/g and 41.85mg/g respectively. The adsorption behavior is dependent on the initial concentration of metal ion. The adsorption capacity increases with the increase of degree of substitution (DS) of the DASAPyZO. Percentage removal efficiency of DASAPyZO for Co(II) Pb(II) and Zn(II) ions were 34.64%, 74.15% and 83.70% respectively. Hence, DASAPyZO polymer adsorbent is more sensitive to Pb(II) and Zn(II) ions and the order of metal ion binding was Zn(II) > Pb(II) > Co(II). The results obtained in this paper indicated that the DASAPyZO is an effective low cost adsorbent for the removal of Co(II), Pb(II) and Zn(II) ions from aqueous solution.

Acknowledgements

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