



PREPARATION AND CHARACTERIZATION OF DIALDEHYDE STARCH UREA (DASU) AND, IT`S SORPTION POTENTIAL FOR Co(II), Pb(II) and Zn(II) IONS FROM AQUEOUS SOLUTION

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ABSTRACT

Dialdehyde starch urea (DASU) was prepared by the reaction of dialdehyde starch (DAS) from periodate oxidized cassava starch with urea, which was then used to adsorb Co(II), Pb(II) and Zn(II) ions from aqueous solution. Starch modified starches and starch complexes were characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) to determine the structure and morphology respectively. The percentages of aldehyde contents of the three kinds of DAS, designated as DAS1, DAS2 and DAS3 were 45.2%, 61.2% and 86.94% respectively. The results indicated that the higher the concentration of periodates, the higher the percentage of aldehyde content in DAS. 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. When the content of aldehyde groups increased to 86.94%, the average molecular weight of DAS3 was found to decrease to 13,182. The Degree of substitution (DS) of urea was 0.67 and DS significantly increase with the increase in percentages of nitrogen content in the polymer adsorbent. Adsorption capacity for Co(II), Pb(II) and Zn(II) ions were found to be 16.01mg/g, 21.73mg/g and 7.18mg/g respectively. Keywords: Starch Polymer, Dialdehyde starch, Dialdehyde Starch Urea, Chelating resin

INTRODUCTION

There are many adsorbents that can be used to remove heavy metals from aqueous solutions such as oxidized carbon nanotubes (Tofighy and Mohammadi, 2011), graphene oxide (Wang, *et al.*, 2013), clay (Sdiri, *et al.*, 2012), and biomass sources (Altun and Pehlivan, 2012). Activated carbon has undoubtedly been the most widely applied adsorbent in wastewater treatment due to its porous structure with a large surface area. However, the applications of activated carbon are restricted due to its high operational costs. The same applies to the other commercial adsorbents such as activated alumina and cation exchange resins (Zhao, *et al.*, 2013). Charcoals produced by chemical carbonization (by 95% sulfuric acid) and by further activation (by 65% nitric acid) were successfully applied for the removal of lead(II), nickel(II), chromium(VI) and arsenic(III) (Varga, *et al.*, 2015). An acrylic resin containing imidazole groups was used as a selective sorbent for copper with a capacity of 0.35 mmol/g over Nickel, Zinc and Cadmium by Zhu *et al.* 2013.

Generally, an efficient adsorbent material should consist of a stable matrix and suitable functional groups (Zhu, *et al.*, 2013). Nowadays, adsorption materials, such as activated carbon (Giri, *et al.*, 2012), Coir pith (Suksabye and Thiravetyan, 2012), Chitosan (Hu, *et al.*, 2011), have been used to dispose chromium. Polyaniline, a classical conducting polymer, is representative one for the treatment of heavy metal

ions including Cr(VI), since it bears interesting redox properties, powerful chelation ability and high stability at ambient conditions (Li, *et al.*, 2002). Natural polysaccharide based adsorbents have been focused on because of their low cost, availability, and biodegradability. The building blocks of biomass based polysaccharides have a substantial number of reactive hydroxyl, carboxyl, and amino groups that can be further modified for the removal of heavy metals (Chang, *et al.*, 2015). For example, a magnetic chitosan adsorbent was synthesized by surface modification of chitosan/SiO₂/Fe₃O₄ with EDTA using 3-ethyl-1-(3-dimethylaminopropyl) carbodiimide hydrochloride as the cross-linker in a buffer solution (Ren, *et al.*, 2013). Because of the low cost, biodegradability and abundant resources cellulose and its derivatives has been good candidate for the removal of heavy metal ions from aqueous solutions (Anirudhan and Shainy, 2015). Furthermore, the low cost modified starch is capable of adsorbing heavy metal ions (Li, *et al.*, 2011).

A variety of different approaches have been used to modify starch as a metal adsorbent (Awokoya and Moronkola, 2013). It was reported that Potassium butyl dithiophosphate (PBD) can be used as a new chelating agent for heavy metal removal (Xu, *et al.*, 2011). The potential of a lignocellulosic jute fibres were assessed and reported (Shukla and Pai, 2005), for adsorption of heavy metal ions like Cu(II), Ni(II) and Zn(II) from their aqueous solutions.

The fibre was also used as adsorbent after chemically modifying it by two different techniques viz; loading of a dye with specific structure, C.I. Reactive Orange 13, and oxidizing with hydrogen peroxide. Both the modified jute fibres gave higher metal ion adsorption. The current use of the naturally occurring material cellulose, its modified forms and their efficacy as adsorbents for the removal of heavy metals from waste streams has been reported (Zhu, *et al.*, 2013). Graft copolymers of cassava starch and acrylonitrile were reported (Ekebafe, *et al.*, 2012), in aqueous solution using ceric ammonium ion as the initiator. The grafted copolymer and the hydrolyzed graft copolymer (hydrogel) were used as sorbent for the uptake of heavy metals from the aqueous media. Fiedorwicz and Para, (2006) reported the preparation of dialdehyde starch (DAS) of degree of oxidation (DO) of 1.5% (DAS1-5), 5% (DAS5), 15% (DAS15) and 25% (DAS25) from potato starch in the periodate oxidation reaction with electrochemical recovery of the oxidant. Awokoya and Moronkola, (2012), reported the reaction of corn starch with succinic anhydride. The synthesized sorbent (SCSs) with different degree of substitution DS (0.19, 0.28 and 0.47) were used as an adsorbent for the removal of Pb(II) ions from aqueous media.

However, in this paper a report for the preparation of dialdehyde starch (DAS) urea was prepared and characterized. The prepared DAS was successfully reacted with urea and applied as a sorbent for Co(II), Pb(II) and Zn(II) ions from aqueous solution.

Materials and Methods

Materials

Cassava tubers were purchased from Dawanau Market, Kano, Nigeria. Sodium periodate (NaIO₄), zinc nitrate [Zn(NO₃)₂] and lead nitrate [Pb(NO₃)₂] were obtained from Xilong Chemical Co. Ltd. Urea, cobalt chloride (CoCl₂), sodium hydroxide (NaOH), hydrochloric acid (HCl), Methanol, Ethanol, Chloroform, Hexane, Diethylether and Dimethyl sulphoxide (DMSO) were obtained from Sigma Aldrich. Infrared spectra were obtained from FT-IR Spectrophotometer Cary630 (FTIR Agilent Technologies). Viscosity was determined by 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-ray mode (SEM-EDX). Initial and final concentrations of the metal ions were determined using Atomic Absorption Spectrophotometer (Buck scientific 210VGP).

MATERIALS AND METHODS

Extraction of starch and Preparation of dialdehyde starch (DAS)

Starch was extracted according to modified method of pestle and mortar reported by Yin *et al.*, (2008). Dry base of Cassava starch (20g) was mixed with sodium periodate (100cm³) 0.4, 0.6 and 0.8mol/L (Zhang, *et al.*, 2008). The pH of the suspension was adjusted to 3.5 by adding 0.2mol/L Sulfuric acid. The mixture was stirred gently at 30°C in the dark for 4 hours. The reaction mixture was filtered and washed three times with distilled water (3 X 150ml), and then dried at 40°C to a constant weight.

Determination of percentage of aldehyde content

The aldehyde group content was determined using the rapid quantitative alkali consumption method (Hofreiter, *et al.*, 1995). Dried 0.2g DAS was weighed into 250cm³ conical flask and 20cm³ of standardized 0.2mol/L sodium hydroxide was added. The flask was swirled in a water bath at 70°C for 5mins, and then cooled immediately under running tap water with rapid swirling for 3mins. 20ml of standardized 0.2mol/L sulfuric acid, 100cm³ of water and 2cm³ of neutral Phenolphthalein were added in turn. Titration of the acid solution was carried out using 0.2mol/L sodium hydroxide solution. The percentages of dialdehyde content were obtained from eqn1

$$Da = \frac{C_1V_1 - 2C_2V_2}{W} \times 100\% \quad \text{-----1}$$

Where: V₁, V₂ and W are the volumes (L) of total H₂SO₄, total NaOH and the dry weight (g) of the oxidized starch, respectively. C₁ and C₂ (Mol/L) represents the concentrations of H₂SO₄ and NaOH, respectively; 161 is the average molecular weight of the repeat unit in dialdehyde starch.

For DAS1, Average volume of acid used

$$(Va) = \frac{22.80 + 22.80 + 22.90}{3} = 22.80\text{cm}^3$$

$$Da = \frac{C_1V_1 - 2C_2V_2}{W} \times 100\% = 45.2\%$$

Fourier Transform Infrared (FT-IRT) Spectroscopy

FTIR spectra of the native starch, oxidized starches (DAS), ligands and complexes were recorded on FT-IR Machine (Cary630 Agilent Technologies) with a range of wave number from 4000 to 650cm⁻¹.

Determination of average molecular weight of starch and dialdehyde starch

The average molecular weight (M_w) of the starch and dialdehyde starch were determined based on the measurement of intrinsic viscosity (Zhang, *et al.*, 2011). The measurements were carried out in triplicate at 25.0±0.1°C with an Ubbelohde Viscometer in a water bath. The samples were dissolved in DMSO and efflux time of polymer and solvent were recorded. The average molecular weight of starch and DAS were obtained based on intrinsic viscosity measurements. Intrinsic viscosity was determined using Mark-Houwink eqn 2

$$[\eta] = KM^a \quad \text{-----2}$$

Where: [η] is intrinsic viscosity. Defined as [η] = η_{sp}/C, K and a were given as constant as 8.5×10⁻³mL/g and 0.76, respectively. M is the average molecular weight.

Preparation of starch dialdehyde urea

Exactly 6g of DAS was suspended in 50cm³ distilled water in a three necked round bottomed flask which was equipped with an electromagnetic stirrer in a thermostated water bath and then 50cm³ of urea solution with a molar ratio of 2:1 to dialdehyde was slowly added into the flask under nitrogen gas protection to form slurry. The mixture was stirred for 4 hours at 55°C on a water bath.

The slurry was filtered and extensively rinsed with distilled water and ethanol three more time and the product was then dried at 50°C to a constant weight (Li, *et al.*, 2010).

Adsorption experiments

Adsorption experiments were carried out by batch method (Li, *et al.*, 2011), at room temperature. 0.1g of DAS-urea was added into a 100cm³ conical flask with 50cm³ of metal solution. The initial pH was adjusted with 0.1M HNO₃ 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 concentrations of metal ions were determined using Atomic Absorption Spectrophotometer. The Degree of substitution (DS) for DAS-ligand was theoretically calculated from the nitrogen content from the eqn 3

$$DS = \frac{(161 \times N\%)}{2800 - 83 \times N\%} \text{-----3}$$

Where N% is the percentage of nitrogen in the Polymer adsorbent And the adsorption capacity was calculated from equation 4

$$Q = \frac{(C_0 - C_t)V}{m} \text{-----4}$$

Where: Q is the adsorption capacity of the adsorbent (mg/g), C₀ 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. The Percentage removal efficiency was also calculated from equation 5

$$R.E = \frac{(C_0 - C_t)}{C_0} \times 100\% \text{-----5}$$

Where: R.E is the percentage removal efficiency; C₀ and C_t (mg/L) are the initial and final concentration of the metal ions in the adsorption solution.

Scanning Electron Microscopy (SEM)

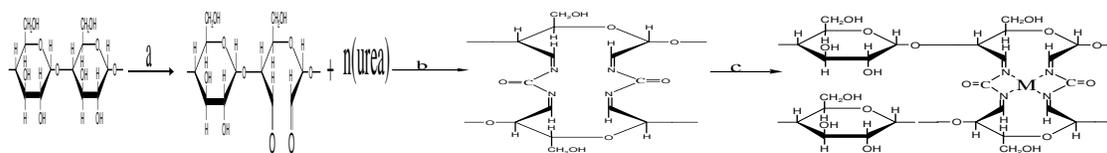
The surface morphology of the Native starch, DAS, DAS-ligand and DAS-ligand-metal complexes were determined using scanning electron microscopy (SEM). The elemental analysis of C, H and N were obtained from SEM machine in elemental dispersive X-rays (SEM-EDX, Phenom Pro X).

Solubility test

DAS-ligand-metal complexes were tested for the solubility in some common solvents by introducing the sample in the solvent at room temperature (Salisu, *et al.*, 2013).

RESULTS AND DISCUSSION

The oxidation of starch by periodates leads to the oxidative cleavage of C₂, C₃ bonds of anhydrous glucose unit of starch molecule (Li, *et al.*, 2010). Dialdehyde starch having the degree of oxidation which was formed by periodate oxidation of cassava starch was successfully reacted with urea to formed dialdehyde starch urea schiff base (DASU). Then, the metal ion formed co-ordinate bonds with the schiff base, which gives polymer complexes as illustrated in scheme 1



Scheme 1: Synthesis of dialdehyde starch urea complex from starch; (a) NaIO₄; (b) ethanol; (c) Co(II), Pb(II) or Zn(II) salts

Percentages of aldehyde content

The content of the aldehyde groups, which reflected the degree of oxidation, were expressed as the number of carbonyl groups per 100 glucose units. The

percentages of aldehyde content of the three different DAS, designated as DAS1, DAS2 and DAS3 were 45.2%, 61.2% and 86.94% respectively.

Table 1: Average titre values and percentages of aldehyde content of DAS1, DAS2 and DAS3.

Samples	Average Titre value (cm ³)	Aldehyde content (%)
DAS1	22.80	45.20
DAS2	23.80	61.20
DAS3	25.40	86.94

The higher the concentration of periodate, the higher the percentage of aldehyde content in DAS. Similar observation had been reported by (Zhang, *et al.*, 2011).

Estimation of average molecular weight

The average molecular weight of Dialdehyde starch (DAS) decreases drastically with the increased in concentration of sodium periodate. Native starch had an average molecular weight of 838,503 (Zhang, *et al.*, 2011). 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. 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 (Zhang, *et al.*, 2011; Zhang, *et al.*, 2010). The reasons for this could be that, when NaIO₄ cleaved the C₂-C₃ bonds of the glucose units of cassava starch, the oxidation led to disruption of both α- d-(1-4) and α-d-(1-6) glycosidic bonds of the starch which caused the average molecular weight of dialdehyde starch to declined drastically, and also as the NaIO₄ cleaved the C₂-C₃ bonds of the glucose units of cassava starch, there would be loss of hydrogen atoms which also leads to decrease in average molecular weight.

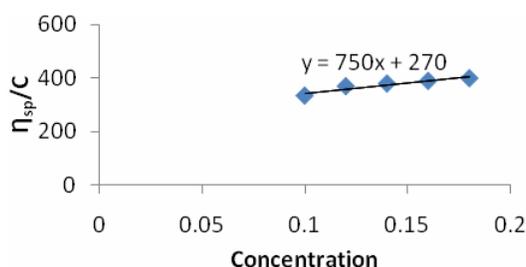


Fig.1: Graph of η_{sp}/C against concentration for Native starch

For Native starch, graph of η_{sp}/C against concentration (C) was plotted in Fig. 1 and the intercept was found to be 270, which was the intrinsic viscosity $[\eta]$. However, average molecular weight was determined using Mark-Houwink equation, $[\eta] = KM^a$. Hence,

$$M = \text{Antilog of } \frac{(\log[\eta] - \log K)}{\alpha} = 838,503.$$

For DAS1 (45.2% of CHO), graph of η_{sp}/C against concentration (C) was also plotted in fig. 2 and the intercept was found to be 47.77, which was the intrinsic viscosity $[\eta]$, and the average molecular weight of DAS1 was found to be 85,853.

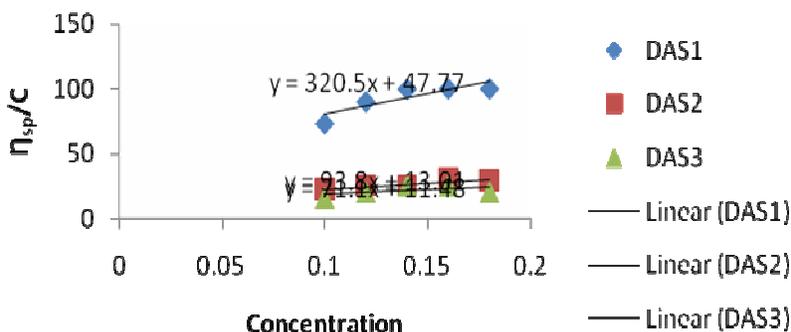


Fig. 2: Graph of η_{sp}/C against concentration for DAS1, DAS2 and DAS3

For DAS2 (61.2% of CHO), it was shown in Fig. 2 that the graph of η_{sp}/C against concentration (C) was plotted and the intercept was found to be 13.012, which was the intrinsic viscosity $[\eta]$, and the average molecular weight of the DAS2 was obtained as 15,466. However, For DAS3 the intrinsic viscosity $[\eta]$ which is the intercept was found to be 11.484 and the average molecular weight of DAS3 was 13,182. The reason for this could be that, when KIO₄ cleaved the C₂-C₃ bonds of the glucose units of cassava starch, the oxidation also led to disruption of both α- D-(1-4) and α-D-(1-6) glucosidic bonds which causes the average molecular weight of dialdehyde starch to decline drastically (Fiedorowicz and Para, 2006).

FT-IR Spectral Analysis

The FTIR spectrum of native starch is shown in Fig. 3. The broad band at 3291cm⁻¹ was assigned to the O-H stretching and it was associated with hydrogen bonding of the hydroxyl groups on starch molecules. The band at 2931cm⁻¹ was assigned to C-H stretching vibrations. However, in the fingerprint region, characteristic peak appeared at 1078cm⁻¹ was attributed to C-O bond stretching of the starch. In Fig. 4, IR spectrum of DAS is presented. Compared with spectrum of native starch, a new peak was observed at 1737cm⁻¹ which corresponds to the stretching vibrations of the C=O groups.

While, Fig. 5 represents the IR spectrum of DAS-Urea where a new peak was observed at 1657cm^{-1} which was attributed to stretching vibration of C=N. DAS-Urea complexes IR spectrum (Fig. 6) exhibited a band at 713cm^{-1} which is attributed to metal nitrogen bond.

The characteristics IR bands are in conformity with the findings in the literature (Awokoya and Moronkola, 2012, 2013; Ekebafé, *et al.*, 2012; Rahman, *et al.*, 2014; Salisu, *et al.*, 2013; Yang, *et al.*, 2008).

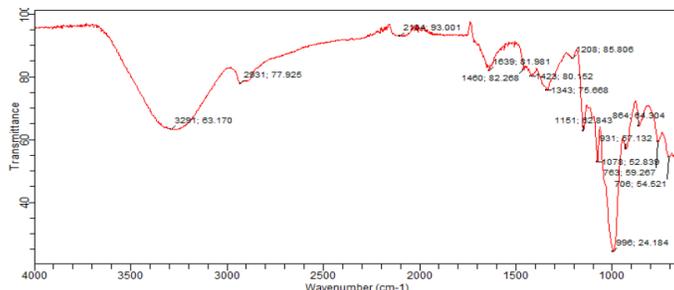


Fig. 3: FTIR spectrum of native cassava starch

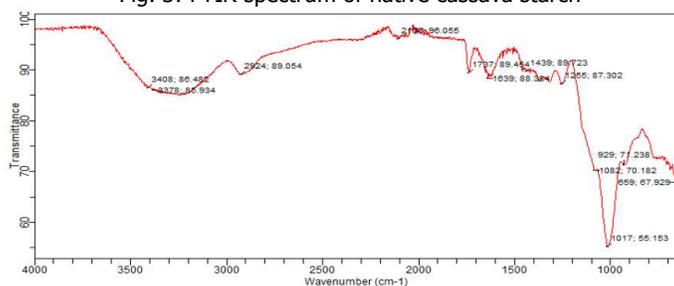


Fig. 4: FTIR spectrum of dialdehyde starch (DAS)

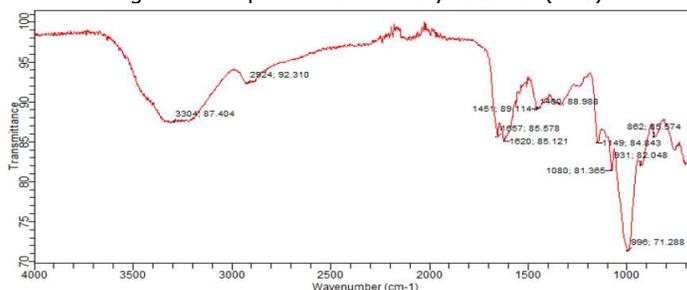


Fig. 5: FTIR spectrum of DAS-Urea

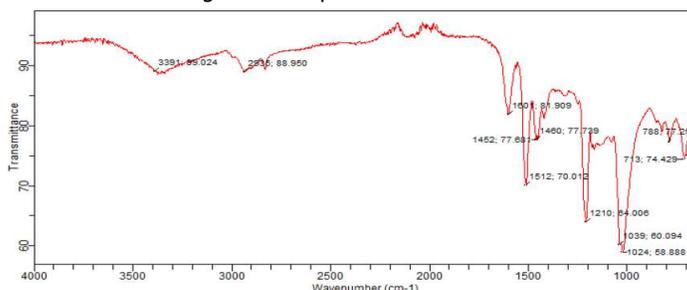


Fig. 6: FTIR spectrum of DAS-Urea Complex

Elemental analysis and degree of substitution

The degree of substitution (DS) of urea was found to be 0.67. DS increased with the increase of

percentages of nitrogen content in the polymer adsorbent. Similar results were reported by (Awokoya and Moronkola, 2013; Zhang, *et al.*, 2008)

Table 2: Elemental analysis and degree of substitution

Sample	Elemental analysis			DS
	C (%)	N (%)	H (%)	
DASU	47.09	8.66	6.01	0.67

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 DASU for Co(II), Pb(II) and

Zn(II) ions were 16.01mg/g, 21.73mg/g and 7.18mg/g respectively, which were found to increase with the increase of DS.

Table 3: Adsorption capacity and removal efficiency of DASU-M

Sample	Adsorption capacity (mg/g)	Removal efficiency (%)
DASU-Co	16.01	32.02
DASU-Pb	21.73	43.46
DASU-Zn	7.18	14.36

The percentage removal efficiency of DASU for Co(II), Pb(II) and Zn(II) ions were found to be 32.02%, 43.46% and 14.36% respectively. Hence, DASU polymer adsorbent can remove Co(II), Pb(II) and Zn(II) ions from aqueous solution and is more sensitive to Co(II) and Pb(II) ions from aqueous solution. Similar results were reported by (Shukla and Pai, 2005; Varga, *et al.*, 2015; Xu, *et al.*, 2011).

Solubility test

The prepared polymer complexes were tested for solubility using water and some 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 (Salisu, *et al.*, 2013).

Table 4: 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

Scanning Electron Microscopy (SEM)

Photomicrographs of representative areas of the samples were taken at different magnifications Fig 7. Scanning electron microscopy (SEM) was used to study the morphology of the granules. The original

cassava starch particles showed smooth and dispersed particles that are oval in shaped Fig. 7a. The DAS, DAS-ligand, and DAS-ligand-metal complexes displayed a rough structure on surface Fig 7a-f.

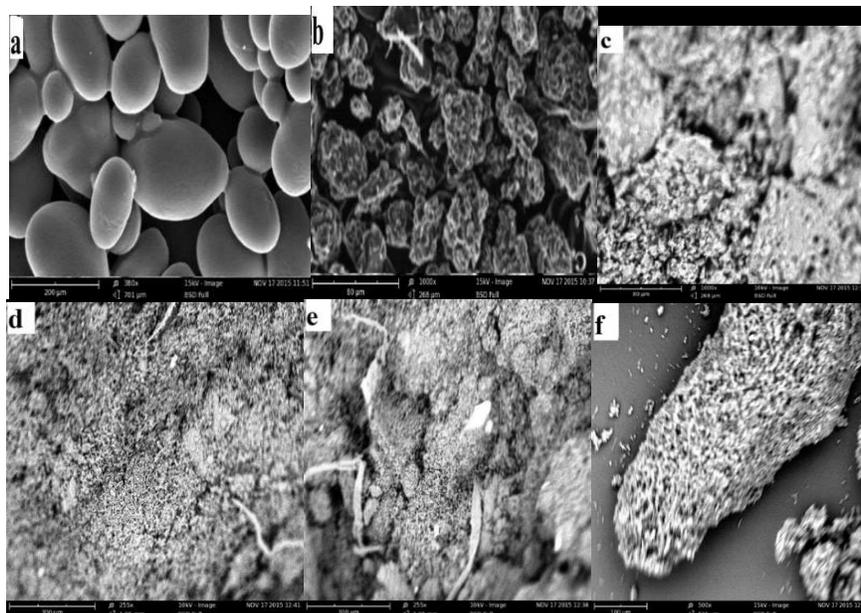


Fig. 7: Photomicrograph of (a) Starch granules X 380 (b) DAS X 1000 (c) DASU X 1000 (d) DASU-Co X 255 (e) DASU-Pb X 255 (f) DASU-Zn X 500.

However, after oxidization by periodate (7b), the particles appeared to be diverse, conglomerated closely, and the granules became much bigger than the original starch. Clearly, the cleavage of glucoside rings as confirmed by FT-IR analysis might be associated with the altered uneven surface, creating pores on the particles. The Photomicrograph of DASU (Fig. 7c) showed particle fragments and irregular structure due to reduction or loss of cross-linking, but the photomicrographs of DAS-urea-metals complexes (Fig. 7d, 7e and 7f), showed no clear diversification in the surface morphology in comparison to DAS-Urea. Similar results were obtained for Removal of Zn (II) ions by dialdehyde 8-aminoquinoline starch and thermoplastic dialdehyde starch by Li, *et al.*, 2011 and Ma, *et al.*, 2010) respectively.

CONCLUSION

Dialdehyde starch (DAS) was prepared by the oxidation of cassava starch using sodium periodate as an oxidant. Compared with Native cassava starch, DAS had lower average molecular weight. The

adsorbent dialdehyde starch urea (DASU) was synthesized by the reaction of urea and dialdehyde starch (DAS) and is relatively cheap and also can effectively remove Co(II), Pb(II) and Zn(II) ions from aqueous. However, 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. When the content of aldehyde groups increased to 86.94%, the average molecular weight of DAS3 also decreased to 13,182. Percentage removal efficiency of DASU for Co(II), Pb(II) and Zn(II) ions were found to be 32.02%, 43.46% and 14.36% respectively. Hence, DASU polymer adsorbent is more sensitive to Co(II) and Pb(II) ions from aqueous solution and the order of metal ion binding was Pb(II) > Co(II) > Zn(II). The polymer complexes formed were found to be completely soluble in DMSO and slightly soluble in water.

References

- Altun, T., and Pehlivan, E. (2012). Removal of Cr(VI) from aqueous solutions by modified walnut shells. *Journal of Food Chemistry*, 132, 693–700.
- Anirudhan, T. S., and Shainy, F. (2015). Adsorption behaviour of 2-mercaptobenzamide modified itaconic acid-grafted-magnetite nanocellulose composite for cadmium(II) from aqueous solutions. *Journal of Industrial and Engineering Chemistry*, xxx, xxx–xxx.
- Awokoya, K. N., and Moronkola, B. A. (2012). Preparation and characterization of succinylated starch as adsorbent for the removal of Pb (II) ions from aqueous media. *International Journal of Engineering and Science*, 1(2012), 18-24.
- Awokoya, K. N., and Moronkola, B. A. (2013). 2-Amino-4,6-Dihydroxypyrimidine Modified Corn Starches For Uptake Of Cu(II) Ions From Aqueous Media. *Journal of Polymer Science*, 2, 49 - 55
- Chang, P. R., Maa, X., Liu, X., and Anderson, D. P. (2015). Modification of porous starch for the adsorption of heavy metal ions from aqueous solution *Journal of Food Chemistry* 181, 133–139
- Ekebafé, L. O., Ogbefun, D. E., and Okieimen, F. E. (2012) Removal of heavy metals from aqueous media using native cassava starch hydrogel. *African Journal of Environmental Science and Technology*, 6(7), 275-282.
- Fiedorowicz, M., and Para, A. (2006) Structural and molecular properties of dialdehyde starch *Journal of carbohydrate polymers*, 63, 360-366.
- Giri, A. K., Patel, R., and Mandal, S. (2012). Removal of Cr(VI) from aqueous solution by Eichhornia crassipes root biomass-derived activated carbon. *Journal of Chemical Engineering*, 15, 71–81
- Hofreiter, B. T., Alexander, B. H., and Wolff, I. A. (1995) Rapid estimation of dialdehyde content of periodate oxystarch through quantitative alkali consumption. *Journal of Analytical Chemistry*, 27, 1930–1931.
- Hu, X., Wang, J., Liu, Y., Li, X., Zeng, G., Bao, Z., Zeng, X., Chen, A., and Long, F. (2011) Adsorption of chromium(VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: isotherms, kinetics and thermodynamics. *Journal of Hazardous Materials*, 185, 306–314.
- Li, R., Ding, W., and Zhao, P. (2011). Removal of Zn (II) ions by dialdehyde 8-aminoquinoline starch from aqueous solution. *Journal of Carbohydrate Polymers*, 83(2), 802-807.
- Li, R., Zhao, P., Jiang, J., Zhang, F., Zhao, W., and Liu, J. (2010) Review on adsorption separation of Ni(II) ions by dialdehyde o-phenylenediamine starch from aqueous solution. *Journal of Carbohydrate Polymers*, 81, 751-757
- Li, X. G., Huang, M. R., Duan, W., and Yang, Y. L. (2002). Novel multifunctional polymers from aromatic diamines by oxidative polymerizations. *Journal of Chem. Rev.*, 102, 2925–3030.
- Ma, X., Yu, J., and Chang, P. R. (2010). The preparation and properties of dialdehyde starch and thermoplastic dialdehyde starch. *Journal of Carbohydrate Polymers*, 79, 296–300.
- Rahman, M. L., Yusoff, M. M., Abd Malik, M. N., and Abu Samah, N. (2014). Synthesis of polymeric chelating ligands from sago starch for metal removal from electroplating wastewater. *Indian journal of chemical technology*, 21, 30 - 37.
- Ren, Y., Abbood, H. A., He, F. B., Peng, H., and Huang, K. X. (2013) Magnetic EDTA modified chitosan / SiO₂ / Fe₃O₄ adsorbent: Preparation, characterization, and application in heavy metal adsorption. *Journal of Chemical Engineering*, 226, 300–311

- 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. *Journal of Chemical and Pharmaceutical Research*, 5, 153-158.
- Sdiri, A., Higashi, T., Chaabouni, R., and Jamoussi, F. (2012). Competitive removal of heavy metals from aqueous solutions by montmorillonitic and calcareous clays. *Journal of Water, Air, and Soil Pollution*, 223 1191–1204.
- Shukla, S. R., and Pai, R. S. (2005). Adsorption of Cu(II), Ni(II) and Zn(II) on modified jute fibres. *Journal of Bioresource Technology*, 96, 1430-1438.
- Suksabye, P., and Thiravetyan (2012). Cr(VI) adsorption from electroplating plating wastewater by chemically modified coir pith. *Journal of Environmental Management*, 15, 1-8.
- Tofighy, M. A., and Mohammadi, T. (2011) Adsorption of divalent heavy metal ions from water using carbon nanotube sheets, *Journal of Hazardous Materials*, 185, 140–147.
- Varga, M., Dobor, J., Perenyi, K., and Varga, I. (2015) A new carbon diatomite earth composite adsorbent for removal of heavy metals from aqueous solutions and a novel application idea. *Journal of Microporous and Mesoporous Materials* 217, 63-70
- Wang, H., Yuan, X. Z., Wu, Y., Huang, H. J., Zeng, G. M., and Liu, Y. (2013). Adsorption characteristics and behaviors of graphene oxide for Zn(II) removal from aqueous solution. *Journal of Applied Surface Science*, 279, 432–440.
- Xu Y., Xie Z. and Xue L. (2011) Chelation of heavy metals by potassium butyl dithiophosphate. *Journal of Environmental Sciences*, 23(5), 778-783.
- Yang, D., Gao, L., and Zhao, W. (2008). Synthesis, Characterization and Catalytic Activity of Dialdehyde Starch-Schiff Base Co(II) Complex in the Oxidation of Cyclohexane. *Journal of Catal Lett*, 126, 84–88.
- Zhang, L., Liu, P., Wang, Y., and Gao, W. (2011). Study on physico-chemical properties of dialdehyde yam starch with different aldehyde group contents. *Journal of Thermochimica Acta*, 512, 196–201.
- Zhang S. D., Wang X. L., Zhang Y. R. and Yang K. K. (2010) Preparation of new dialdehyde derivative and investigation of its thermoplastics properties, *Journal of Polymer Research*, 17, 439 - 446.
- Zhang, S. F., Yin, Q. F., Ju, B. Z., Wang, X. B., and Yang, J. Z. (2008) Preparation and characteristics of novel dialdehyde aminothiazole starch and its adsorption properties for Cu (II) ions from aqueous solution. *Journal of Carbohydrate Polymers*, 72, 326–333.
- Zhao F., Repo E., Yin D., and Sillanp M. E. T. (2013) Adsorption of Cd(II) and Pb(II) by a novel EGTA-modified chitosan material: Kinetics and isotherms. *Journal of Colloid and Interface Science*, 409, 174-182.
- Zhu, C., Zhu, Q., Li, C., Dou, J., Cao, J., Li, Z., and Chen, W. (2013) A novel chelating organosilicone resin bearing long chain imidazolyl ligands: Preparation, characterization, and adsorption properties, *Journal of Organometallic Chemistry*, 727, 37-43.