

2, Amino-4,6-Dihydroxypyrimidine Modified Corn Starches For Uptake Of Cu (II) Ions From Aqueous Media

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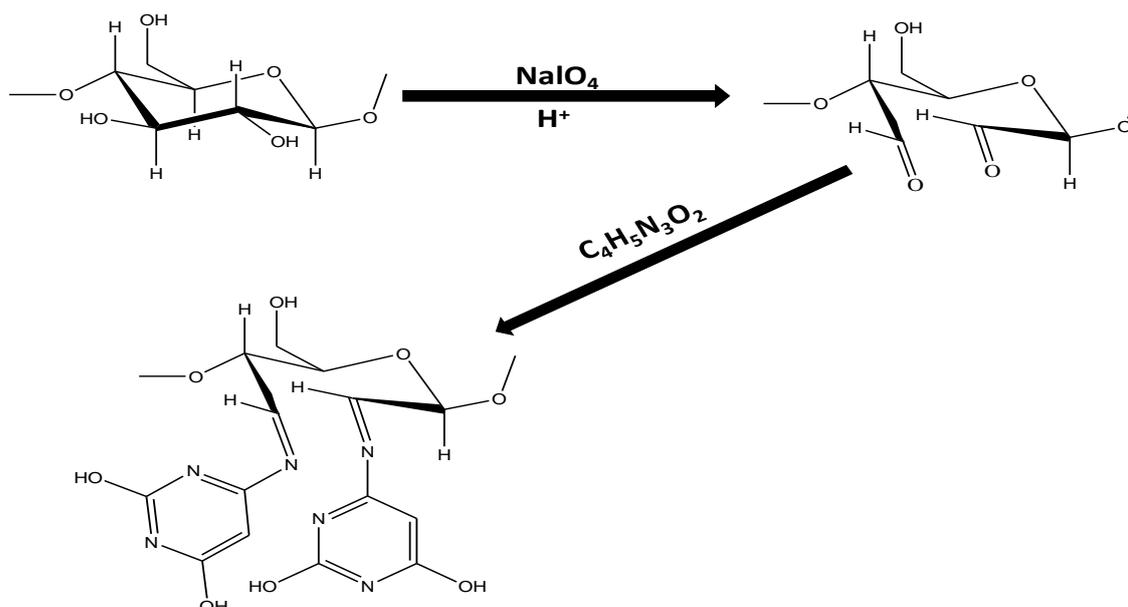
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Abstract: Schiff base type starch aldehyde 2, amino-4,6-dihydroxypyrimidine (DASAP) was synthesized by the reaction of 2, amino-4,6-dihydroxypyrimidine and dialdehyde starch (DIAS) from periodate oxidized corn starch, and was employed to adsorb Cu (II) ions from aqueous media. DASAP was characterized by Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and CHNS microanalysis. The medium pH influenced significantly the Cu²⁺ ions adsorption capacity. The adsorption capacity increased with increasing DS of the aminopyrimidine groups. ICP-OES analysis revealed that when the initial Cu²⁺ ion concentration was increased from 20 mg/L up to 100 mg/L, the adsorption capacity of DASAP1 and DASAP2 increased from 1.8 to 7.7 mg/g, and 2.1 to 8.1 mg/g, respectively. The accuracy of the method was validated by analyzing the certified reference material of water (BCR®-610) and concentration of Cu²⁺ in the CRM was found to be 47.1 µg/kg, which was significantly comparable with the certified value of 45.7 µg/kg. The DASAP presents a selective sorbent that is well suited to handling of trace metals in aqueous media.

Keywords: Dialdehyde starch, Dialdehyde starch 2, amino-4,6-dihydroxypyrimidine, Adsorption, Cu (II),

I. Introduction

The scientific world has no widely accepted definition for 'heavy metal'. However, it is generally accepted that the term 'heavy' refers to metals having atomic weights between 63.5 and 200.6, and a specific gravity that is greater than 5.0 [1]. With the prompt development of industries such as metal mining and smelting operations, batteries industries, fertilizer, paper industries and pesticides, etc., heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries [2]. Heavy metals ions from industrial wastewater and sewage are of environmental concern due to their acute toxicity, non-biodegradable nature and build-up of high concentrations in water bodies all over the world [3]. Various technologies have been developed to remove toxic metal ions from water over the years. The most important of these technologies and processes include biological treatments, membrane processes, ion exchange, solvent extraction, advanced oxidation processes, chemical and electrochemical techniques and adsorption procedures are the most widely used for removing metal ions from industrial effluents. Among all the treatments proposed, adsorption may be considered as preferable due to its economical advantages, high efficiency and applicability [4,5]. However, conventional chemical precipitation method does not always provide better satisfactory removal effect to meet the demands of the pollution control. Ion exchange is considered a better alternative technique for such purpose but it is not economically appealing because of high operational cost [6]. In addition, the processes often result in secondary environmental pollution, and many efforts have been made to search for cheaper method of pollution control in order to solve the problems mentioned above [7-10]. In recent years, 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 [11]. Biocompatible polysaccharide polymers, such as, chitosan, have also been found to be capable of chemically or physically entrapping various metal ions due to high concentration of amino and hydroxyl groups in the polyaminoglucosan chain [12]. In the present work, Schiff base type starch dialdehyde 2, amino-4,6-dihydroxypyrimidine (DASAP) was synthesized by the reaction of 2, amino-4,6-dihydroxypyrimidine and dialdehyde starch (DIAS) from oxidation of corn starch by periodate. Therefore, the objective of this study was to prepare DASAP with different degree of substitution (DS) and to determine the ability of these adsorbents in removing Cu (II) ion from aqueous medium.



Scheme 1. Preparation process of the dialdehyde 2, amino-4,6-dihydroxypyrimidine starch.

II. Materials And Methods

2.1. Materials

Corn starch (food grade) was dried at 105 °C before it was used. NaIO₄, Cu (Ac)₂, NaOH and 2, amino-4,6-dihydroxypyrimidine were purchased from Sigma Aldrich (Johannesburg, South Africa) and used as obtained. All the chemicals used were of analytical grade. Standard solutions were freshly prepared using ultrapure water generated from milliQ system (Massachusetts, USA).

2.2. Preparation Of Dialdehyde Starch

The method of *Yin et al* [13] was used. Corn starch (dry base) (20 g) suspended in 50 mL water was mixed with 100 mL various concentrations of sodium periodate solutions (0.5, and 0.9 molL⁻¹). The pH of the suspension was adjusted to 3.5 by adding 0.2 molL⁻¹ H₂SO₄. The mixture was stirred gently at 20 °C in the dark for 6 h. The reaction mixture was filtered and washed three times with distilled water (3x 100 mL), and dried at 50 °C to a constant weight.

2.3. Determination of aldehyde content

Two kinds of DIAS, designated as DIAS1 and DIAS2 were prepared to obtain two different DS. The aldehyde group content was determined using the rapid quantitative alkali consumption method [14] and the results were 66% and 88% for DIAS1, DIAS2, respectively. The percentage of dialdehyde units was given by the eqn 1;

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

where V₁, V₂ and W represent the total volumes (L) of H₂SO₄, NaOH and the dry weight (g) of the oxidized starch, respectively. C₁, C₂ (molL⁻¹) represent the concentration of H₂SO₄ and NaOH. 161 is the average weight of the repeat unit in dialdehyde starch.

2.4. Preparation of starch dialdehyde 2, amino-4,6-dihydroxypyrimidine

8.2 g of DIAS was slurried in 50 mL milliQ water in a two necked flask, which was equipped with an electromagnetic stirrer and thermostart oil bath. Then, 50 mL of 2, amino-4,6-dihydroxypyrimidine 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 h at 55 °C on an oil bath. The slurry was filtered and extensively rinsed with milliQ water and with ethanol for one time, the product was then dried at 50 °C in vacuum.

The reaction process of dialdehyde 2, amino-4,6-dihydroxypyrimidine starch is shown in Scheme 1. The degree of substitution of 2, amino-4,6-dihydroxypyrimidine for DASAP was theoretically calculated from the nitrogen content using the eqn 2;

$$DS = \frac{161 \times N\%}{2800 - 109.1 \times N\%} \times 100\% \quad 2$$

2.5. FT-IR Spectroscopy and CHNS Microanalysis

The Fourier transform infrared (FT-IR) spectra of DIAS and DASAP starches were obtained using a PerkinElmer Spectrum 100 FT-IR spectrometer with an AutoIMAGE System. Elemental analysis was performed directly with Vario Elementar Microtube ELIII (Hanau, Germany) after carefully drying of the samples.

2.6. Scanning Electron Microscopy (SEM) And Effect Of Temperature On Swelling Power & Solubility

To determine the surface morphology of the DASAP1 and DASAP2 starches, the starches were taken and dusted onto a carbon sticker, then coated with gold using a sputter coater (Balzers Union, FL-9496) for 30 min. Images were recorded using INCA PentaFETx3 (Vega Tescan) SEM fitted with an Oxford ISIS EDS. Swelling power and solubility was determined as described by Waliszewski *et al* [15]

2.7 Adsorption Experiments

The adsorption of copper (II) ions on DASAP was studied by batch technique. It was performed at room temperature by adding an optimal quantity of DASAP starch (0.15 g) into 50 mL of a Cu(Ac)₂ aqueous solution with initial concentrations ranging from 20 to 80 mg/L. The initial pH was adjusted with 0.1 M HNO₃ or 0.1 M NaOH before adding the adsorbent. After shaking for 90 min to ensure full equilibration, the mixture was centrifuged at 12 000 rpm for 5 min, and the final concentration of copper(II) was determined by ICP-OES. The adsorption quantity (Q_e, mg/g) was calculated before and after the adsorption according to the eqn 3;

$$Q_e = \frac{V(C_0 - C_e)}{M} \quad 3$$

where C₀ is the initial copper (II) ions concentration (mg/L), C_e is the copper(II) ions concentration at adsorption equilibrium (mg/L), V is the volume of copper(II) ions solution (L), and M is the weight of the adsorbent (g). where C_t (mg/L) is the concentration of Cu (II) ions in the desorption solution at time t (min), V is the volume of the desorption, and M₀ (g) is the amount of Cu (II) ions adsorbed.

III. Results And Discussion

3.1. Characterization of the prepared DASAP

3.1.1. The FT-IR spectra of DIAS and DASAP

The infrared spectra of DIAS and DASAP are presented in Fig. 1. In the DIAS spectrum, the characteristic band at 1730 cm⁻¹ corresponded to the stretching vibrations of the C=O groups. Compare with DIAS, the spectrum for DASAP showed new bands at 1625, 1200 and 2928 cm⁻¹. The band at 1625 cm⁻¹ can be assigned to the C=N stretching vibrations of the imine group, confirming the formation of Schiff bases between 2, amino-4,6-dihydroxypyrimidine and dialdehyde starch. The bands at 1200 and 2928 cm⁻¹ were due to the stretching vibrations of the C-N bonds and C-H bonds.

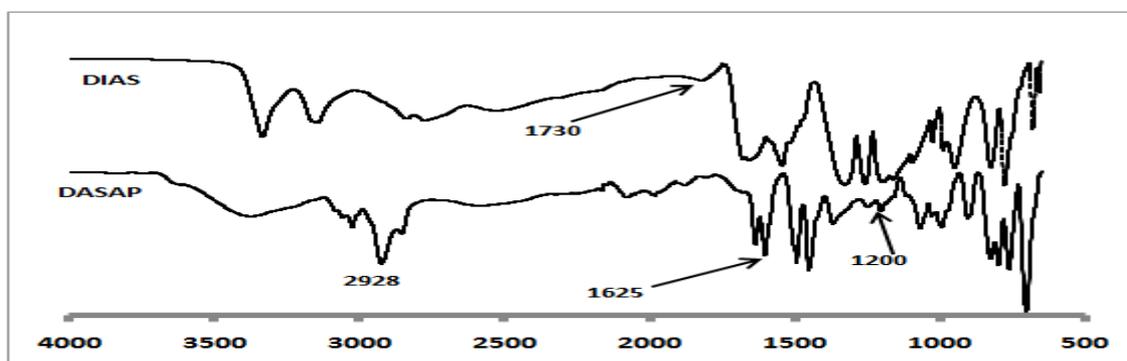


Fig. 1 FT-IR spectra DIAS and DASAP

3.1.2 Surface morphology of DASAP

Fig. 2 shows the scanning electron micrographs of the DASAP1 and DASAP2 dialdehyde 2, amino-4,6-dihydroxypyrimidine starches. The surface morphology of the low DS starch (DASAP1) was composed of granules with irregular shapes and various sizes. The morphology of DASAP2 displayed granular fragmentation, and some granules had deep holes. Granules with deep holes were also reported [16]. The cause of the deep holes might be resulted from the swelling of starch granules during oxidation process.

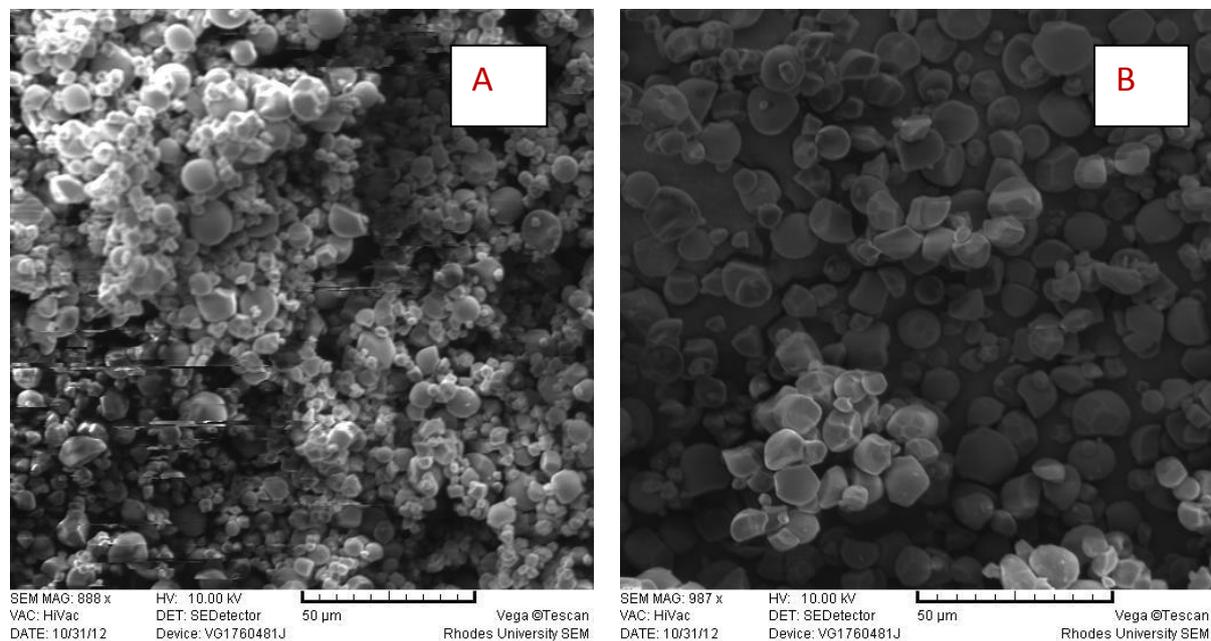


Fig. 2 (A) The scanning electron micrographs of DASAP2, and (B) DASAP1

3.1.3 CHNS Microanalysis

The results of the CHNS microanalysis are listed in Table 1. It was evident that the nitrogen content in DASAP increased notably with the increase of dialdehyde percentage in DIAS. The DS of 2, amino-4,6-dihydroxypyrimidine which represented the average molecular number of the repeat unit in DASAPs is 0.49 and 0.90 for DASAP1 and DASAP2, respectively.

Table 1 Degree of substitution for DASAP

Product	Reactant	Colour	CHNS Microanalysis			DS
			N (%)	C (%)	H (%)	
DASAP1	DIAS1	Yellow	6.29	48.20	5.99	0.49
DASAP2	DIAS2	Yellow	9.67	52.73	6.83	0.90

3.2 Swelling power and solubility

The swelling power of both DASAP1 and DASAP2 were measured from 40 to 80 °C at 10°C intervals (Fig. 3) shows an increased swelling power of all the starches as the temperature increased, in the following order: DASAP2 > DASAP1. The solubility power of the DASAPs starch at different temperature (Fig. 4) shows that there was an increase in the solubility of the starches as the temperature increased, with the DASAP2 starches having highest solubility at all the temperature studied. This is probably due to the weakening of the starch granules during periodate oxidation leading to improved solubility [17].

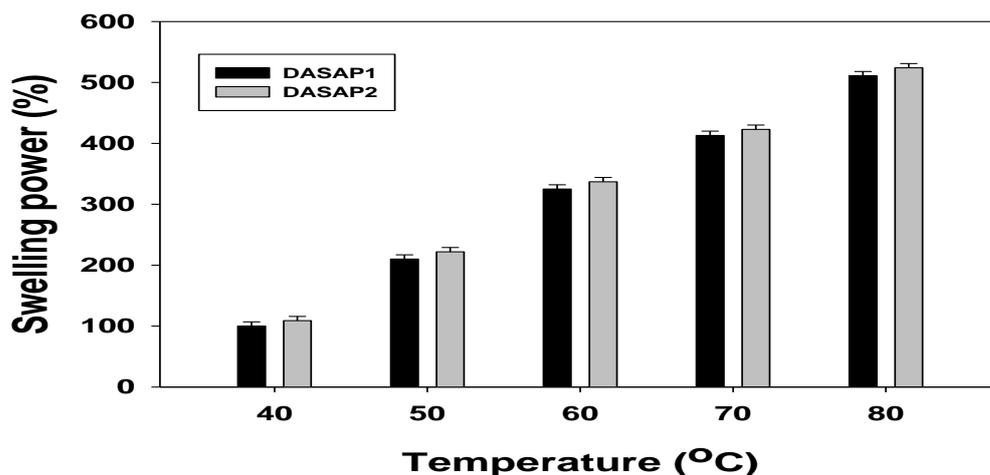


Fig. 3 Swelling power of DASAP1 and DASAP2 starch (on dry basis)

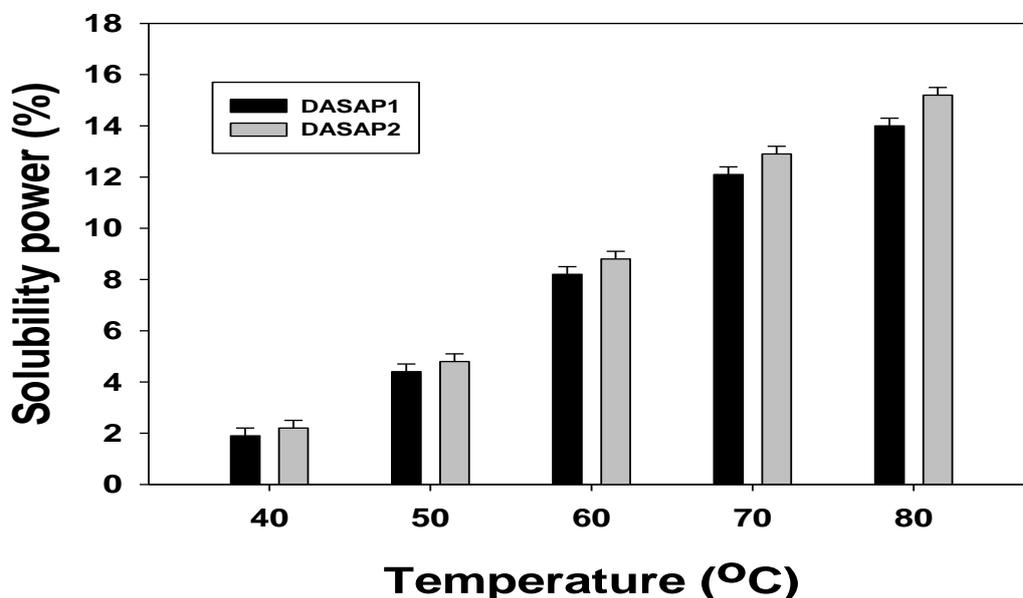


Fig. 4 Solubility power of DASAP1 and DASAP2 starch (on dry basis)

3.3. Adsorption of Cu^{2+} ions

3.3.1. Effect of pH on the adsorption

One of the most important factors affecting adsorption capacity of metal ions is the acidity of solutions because H^+ ions compete with the metal cations for the binding sites on the DASAP. The concentration of H^+ ion in an acidic solution is relatively high and they tend to fill up the binding sites on the DASAP's surface. Fig.5 shows the relationship between the pH value of metal ion solution and adsorption capacity of DASAP for Cu^{2+} . A range of initial pH values of the solution from pH 2 to 8 was used, and samples were agitated for 90 mins. The adsorption of the metal ions increased rapidly with the increase in the solution pH until it reached equilibrium where no significant observed change with pH. The optimal pH for adsorption was found to be 6.0, which indicates that the maximum adsorption capacities take place in moderately and slightly acidic medium. It was also noted that the adsorption capacities increased with increase in DS. The adsorption curves and the optimal pH values obtained in the work are similar to those observed in the previous studies. For example, Onwu and Ogah found the pH of 6 as the optimal for quantitative recovery of Cd^{2+} [18].

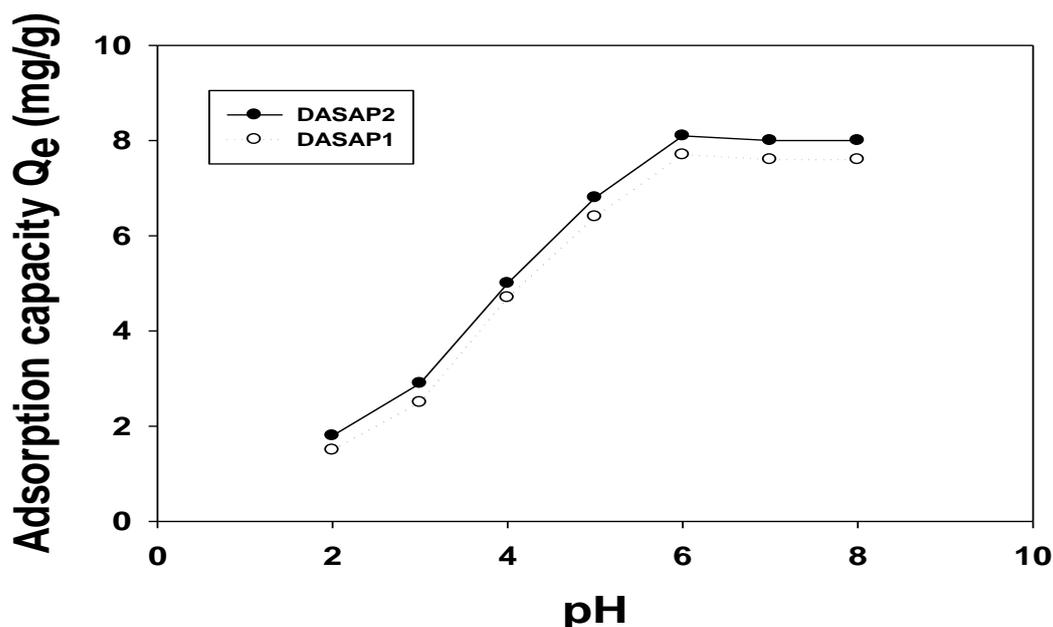


Fig.5 Effect of pH of Cu (II) ions adsorption on the DASAP adsorbents

3.3.2 Effect of the initial Cu(II) ions concentration

The effect of initial Cu^{2+} concentration on the adsorption onto different DASAPs was investigated (Fig.6), with the metal ion concentrations ranging from 20 to 100 mg/L. Adsorption increased with increase in initial Cu^{2+} concentration. The adsorption capacity of Cu^{2+} was maximum on DASAP2 (8.1 mg/g) and minimum on DASAP1 (7.7 mg/g) at 80 mg/L Cu^{2+} concentration, and remained nearly constant after the value. Moreover, the adsorption trends between the two samples were similar, which implied that the types of adsorption isotherms of them were alike.

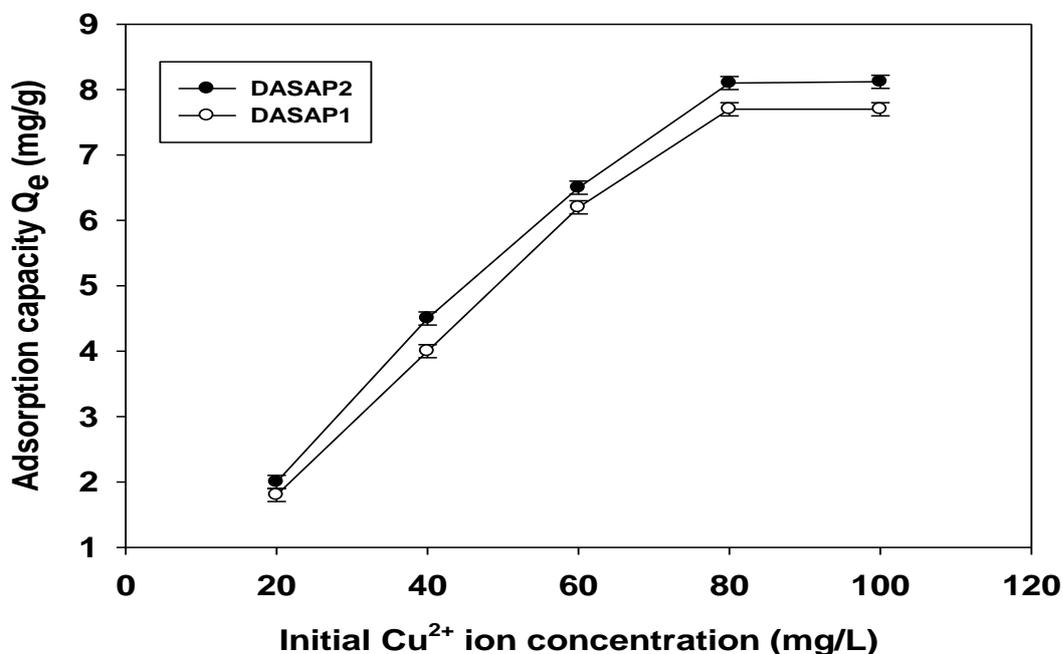


Fig.6 Effect of initial concentration of Cu (II) ions on DASAP adsorbents.

Method validation

The developed method for removal of Cu (II) ion from aqueous media was validated by analysing a custom solution of a certified reference material of water (BCR®-610), and the data is shown in Table 2. The results showed that the value obtained from the method was within the error of the standard reference material.

It may be concluded from the results presented that dialdehyde 2, amino-4,6-dihydroxypyrimidine starch could be effectively used for the specific removal of Cu (II) ion from aqueous media.

Table 2: Determination of Cu (II) ion in certified reference material

CRM	Certified concentration (µg/kg)	Concentration found (µg/kg)(n=3)	% Recovery
BCR®-610	45.7 (1.5)	47.1 (0.006)	103.06

IV. Conclusions

The study indicated the suitability of using dialdehyde 2, amino-4,6-dihydroxypyrimidine starch for the removal of Cu²⁺ ion in aqueous solution through batch adsorption studies. The obtained experimental results showed that process parameters such as pH and initial metal concentration had important effect on the adsorption ability. The optimal adsorption time and pH were 90 min and 6.0. The maximal adsorption capacities of DASAP1 and DASAP2 were 7.71 and 8.12 mg/g, respectively. The increasing adsorption capacity of DASAP was probably due to a high DS of the aminopyrimidine groups. However, it was established that both swelling power and solubility of the DASAP starch were temperature dependent. Work to verify the impact of crosslinked banana starch (*Musa paradisiacal*) on the adsorption of Cd and Ni is currently underway.

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