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EFFECTS OF IONIC COMPOUNDS ON OPTIMIZATION OF PHYSICOCHEMICAL PROPERTIES OF BIOPOLYMER ISOLATED FROM PAKISTANI WATER CHESTNUTS

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ABSTRACT

The purpose of this study was to examine the physicochemical properties of biopolymer extracted from water chestnut in the presence of different ionic compounds (KCl, Na_2HPO_4, $CaCl_2$) at fixed starch (5%) and salts (1%) concentration. Experimental results showed that the presence of $CaCl_2$ had a significant impact on swelling and thermal properties of water chestnut starch. The onset temperature of starch was found to be increased in the presence of KCl and $CaCl_2$, whereas a reverse trend was observed in case of Na_2HPO_4. Furthermore, the addition of salts drastically reduced the swelling power and water absorption of water chestnut starch. The increase in peak viscosity and retrogradation was noticed after the addition of Na_2HPO_4 and $CaCl_2$, respectively.

Key-words: Biopolymer, Viscoamylograph, Differential Sensory Calorimeter, Swelling Power

INTRODUCTION

Recently, the use of biodegradable polymers have been increasing in many applications such as in agriculture, biomedical, forestry, medicines, wild life conservation and waste management. Starch due to naturally occurring and readily available obtained from different sources such as wheat, rice, tapioca etc, is used extensively in food as well as non-food applications.

Water chestnut starch is underutilized by the food industry because of limited understanding of its modifications and uses. It is cheap and has sufficient starch content which is promising in itself. The edible region of water chestnut is rich in starch and composed of thin walled storage parenchyma quite similar to potato starch in appearance and has vascular strands in between. It maintains a crunchy and firm texture after cooking and long heat treatment which was commendable and was unlike what is seen in case of conventional starches such as potato and rice (Singh *et al.*, 2011). Water chestnut is a good contender for utilization in food and related industries owing to its large starch reserves.

Salt is a common additive in starch based products for improving organoleptic properties of the product. The most common salt additives are sodium chloride and calcium chloride (Albarracín *et al.*, 2011). Addition of sodium chloride has shown increase in gelatinization temperature of tapioca starch and retrogradation time of the starch gel upon cooling (Chuang *et al.*, 2017). Various salts have been tried and their effects on potato starch have been documented (Wang *et al.*, 2016).

It was imperative that due attention was given to characterization of water chestnut starch. This would allow for its utilization in the industry and also customize its properties through physical and chemical modifications to suit specific requirements and applications. Eventually it will raise the economic status of people as well (Lutfi *et al.*, 2017b). Water chestnut starch has not been subject to much study especially in the area of interaction with various salts. If the said study is conducted it could open new avenues for tailoring the water chestnut starch to suit myriad of applications. It is an exploitable source thus making it a good study candidate. Therefore, the main purpose of this experiment was to observe the effects on physicochemical, swelling and thermal properties of biopolymer (starch) extracted from Pakistani water chestnuts in the presence of Ions.

MATERIALS AND METHODS

Materials

The water chestnuts were obtained in dried form from the local market of Karachi, Pakistan. The extraction of starch was done according to the method reported previously by our group (Lutfi *et al*., 2017a). Analytical grade calcium chloride ($CaCl_2$), potassium chloride (KCl) and sodium dihydrogen phosphate (Na_2HPO_4) were provided by Sigma-Aldrich Co. (St. Louis, MO). The moisture, protein, fat, ash and total amylose content of extracted starch was found to be 8.5, 0.1, 0.19, 0.17 and 28.5%, respectively (Lutfi *et al.*, 2017b).

Methods

Swelling Capacity and Solubility

The evaluation of swelling power and solubility were performed according to the method of (Waliszewski *et al.*, 2003) with slight modifications. The water chestnut starch (1% w/w) was dispersed in solution containing salts (1% w/w). The samples were poured into the screw cap graduated centrifuge tubes. These tubes were then placed in shaking water bath for 30 mins, while maintaining the temperature of 90 °C. Then, the tubes were immediately put in chilled water and allowed to cool to room temperature. After cooling, the samples were centrifuged at 3000 x g for 15 mins and then the supernatant were dried at 130 °C for 24 h. Swelling capacity was calculated as

$$\text{Swelling capacity (g/g)} = \frac{\text{Wet precipitated paste}}{\text{Dry weight}}$$

$$\text{Solubility (\%)} = \frac{\text{Dry precipitated paste}}{\text{Dry weight}} \times 100$$

Transparency

The aqueous suspensions of WCS (1% w/w) with different salts in were kept in water bath maintained at 100°C for 30 min with constant stirring to avoid any lump formation followed by rapid cooling at 35°C. The transmittance (%) of suspensions was measured at 650 nm against water as a blank with spectrophotometer (Beckman DU-650, CA (USA).

Microviscoamylography

Pasting behavior of 5% (w/w) WCS alone and WCS/salts blends were measured using a Brabender microviscoamylograph (Model 803201, Germany). The samples were heated from 30 to 95 °C with a constant heating rate of 1.5 °C/min and then held at 95 °C for 30 min. The paste was cooled to 50 °C with constant rate and held at this temperature for 10 min.

Thermal properties

Thermal properties of water chestnut alone and water chestnut/salts blends were measured by differential scanning calorimeter (DSC Q10, TA Instruments, USA). In 20 mL aluminum pan, starch and deionized water was added with the help of syringe in the ratio of 1:2. Hermetically sealed aluminum pan is equilibrated for 1 hr and then passed through gelatinization thermal scan at the rate of 10 °C/ min at the temperature range of 30 °C to 120 °C and empty aluminum pan is used as reference.

Universal Analysis software is used for the calculation of onset temperature (To), peak gelatinization temperature (Tp), conclusion temperature (Tc), and enthalpy change (ΔT).

Statistical analysis

Statistical analysis was performed by using SPSS (Version 17.0. Inc, Chicago, USA). The data was evaluated by ANNOVA followed by LSD at $p=0.05$.

RESULTS AND DISCUSSION

Swelling capacity and Solubility

Swelling capacity is defined as the quantity of water absorbed by the starch granules at elevated temperature. Table 1 shows the results of swelling capacity of water chestnut starch in presence of different salts.

The presence of salts significantly changed the swelling capacity and solubility of water chestnut starch (WCS). In precise words, salts reduced the swelling power of WCS substantially. Equipollent results were obtained with cassava starch when its swelling capacity was tested with and without the addition of salts as reported by Jyothi *et* *al.*,(2005). The reason for reduction of swelling power of starch in presence of salts can be explained by citing two reasons. 1) There is an attractive and repulsive interaction between starch and salt ions (Oosten, 1982; Oosten, 1983; Oosten, 1990) and 2). Salts and starch compete for available water. This result in reduction of swelling of starch granules and consequently decreased leaching of amylose.

All salts increased the solubility of water chestnut starch. Solubility of NaH_2PO_4> $CaCl_2$ >KCl was recorded at a temperature of 90 °C. In the report by Zhou *et al.*,(2014), similar results were mentioned and he went on to explain that the monoatomic Cl^- ion which has a large diameter and greater degree of polarization tends to disrupt the hydrogen bonds between starch-starch and starch-water thus leading more water molecules access which further increased the solubility as opposed to native starch. Therefore, such solutes can increase water solubility of native WCS.

Transparency

Transparency of starch paste can be determined by passing the light through it. Many factors affected the transparency such as swelling capacities, amylose and amylopectin ratio, and size of the granules (Singh and Singh, 2003; Sitohy *et al.*, 2000). Table 2 showed the transparency of water chestnut starch pastes in the presence of salts during storage at room temperature. Starch showed significant change in transparency after the treatment with salts.

Sodium dihydrogen phosphate was found to increase the transparency of water chestnut starch. The results were similar to the results from Li *et al.* (2011). On the other hand, no change was observed in the presence of calcium chloride and potassium chloride on the transparency of water chestnut starch.

Table 1. Swelling capacity (g/g) and solubility (%) of Water chestnut starch with different salts.

Sample	**Temperatures (°C)**	
	Swelling power	**Solubility**
Control	12.23 ± 0.61	5.7 ± 0.37
KCl	5.67 ± 0.2	16.7 ± 0.35
$CaCl_2$	5.83 ± 0.31	31.7 ± 0.26
NaH_2PO_4	5.54 ± 0.42	31.7 ± 0.21
LSD $_{0.05}$	0.15	0.12

Table 2. Transparency of water chestnut starch with different salts.

Samples	**Transparency (%)**
Control	3.5 ± 1.11
KCl	3.5 ± 1.21
$CaCl_2$	3.4 ± 2.31
NaH_2PO_4	4.3 ± 1.22
LSD $_{0.05}$	0.11

Pasting Properties

The effect of salts on the pasting properties of water chestnut starch was determined by Viscoamylograph and is illustrated in the Table 3. The peak viscosity of water chestnut starch was significantly increased after the addition of salts from 72.3 BU to 76 BU and 88 BU for potassium chloride and sodium di hydrogen phosphate respectively. An increase in peak viscosity of water chestnut starch could be due to the influence of interaction between salts (potassium chloride and sodium di hydrogen phosphate) to the proteins and lipids components present in starch. Our results were similar to previous studies conducted by Samutsri and Suphantharika, (2012). In another observation the viscosity of starch was dramatically reduced in presence of calcium chloride at similar concentrations due to the higher ionic strength of calcium chloride as opposed to the other salts tested. Comparable results were reported by Yu *et al.* (2016) for sweet potato starch.

The gelatinization temperature of water chestnut starch was found to be marginally increased in the presence of salts. This result could be confirmed by the observation that the swelling power of water chestnut starch decreased drastically after the addition of salts. Similar results have been observed for potato starch (Chen *et al.*, 2014), rice starch (Samutsri and Suphantharika, 2012), and sago starch (Ahmad *et al.*, 1999a). The theory of limited swelling and gelatinization of starch granules in the presence of salts has been well explained by Oosten (1982). Correspondingly, the altered structure of water and decrement in "free" water for absorption by starch granules have been established as causative factors for suppression of swelling and gelatinization.

In the presence of calcium chloride and sodium dihydrogen phosphate the limited increase in breakdown was observed but it remained unaffected in the presence of potassium chloride. The granules of water chestnut starch become more tightened in the presence of potassium chloride.

Setback viscosity being the measure of reassociative tendency of starch granules. Addition of calcium chloride significantly increased the setback (i.e. amylose retrogradation) of water chestnut starch due to a higher solubility of water chestnut starch (Table 1) that resulted in higher exudation of amylose chains. Similar results were reported for sweet potato starch (Yu *et al.*, 2016). However, negligible reducing effect was observed in the presence of potassium chloride and sodium di hydrogen phosphate.

Table 3. Pasting properties of Water chestnut starch with different salts.

Samples	**Tg °C**	**Pv (BU)**	**BD (BU)**	**SB (BU)**
Control	77.2 ± 1.1	72.3 ± 3.1	0.0 ± 0.1	25.2 ± 1.3
KCl	76.6 ± 2.1	76 ± 2.2	0 ± 0.2	25 ± 0.5
$CaCl_2$	77.8 ± 3.2	67 ± 1.3	1 ± 0.1	57 ± 1.2
NaH_2PO_4	77.4 ± 2.5	88 ± 3.1	2 ± 0.2	22 ± 1.5
$LSD_{0.05}$	0.42	0.23	0.15	0.24

Table 4. Thermal properties of water chestnut starch with different salts.

Samples	**T_o (°C)**	**T_p(°C)**	**T_c (°C)**	**ΔT (T_c - T_o)**
Control	63.2 ± 1.1	66.3 ± 3.1	70.1 ± 0.1	6.9 ± 1.2
KCl	66.2 ± 2.3	70.1 ± 4.3	74.2 ± 0.2	8.0 ± 2.4
$CaCl_2$	68.8 ± 2.5	72.5 ± 2.3	76.3 ± 0.1	7.5 ± 2.6
NaH_2PO_4	64.4 ± 1.3	68.2 ± 1.2	72.3 ± 0.1	7.9 ± 1.4
$LSD_{0.05}$	0.18	0.21	0.15	0.18

onset temperature (To), peak gelatinization temperature (Tp), conclusion temperature (Tc), and enthalpy change (ΔT).

Thermal Properties

The thermal properties which include onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c) gelatinization temperatures, and the gelatinization range (ΔT) of water chestnut starch alone and water chestnut starch with salts were evaluated by DSC, were depicted in Table 4.

The increase in magnitude of T_o, T_p, and T_c and decreased ΔT values of water chestnut starch were observed in the presence of salts at 1 % concentration. It has been reported that the changing pattern of gelatinization and enthalpy of starches in the presence of salts is mainly dependent on the type of salt and their concentration used (Singh and Singh, 2003;Oosten, 1983; Oosten, 1990; Jane, 1993; Ahmad *et al.*, 1999). Previous studies showed that, at low concentration of $CaCl_2$, the T_o of corn starch, T_p of sago, wheat, corn, rice were slightly increased (Ahmad *et al.,* 1999; Maaruf *et al.,* 2001; Jane, 1993; Chinachoti *et al.,* 1991) but, these gelatinization temperatures were found to decrease on increasing the concentration of salts up to 1 M. However, some other studies reported that the ΔT of corn starch was continuously increased above 1M for $CaCl_2$ and when the concentration reached up to 6M the early gelatinization of corn starch was noticed (Samutsri and Suphantharika, 2012). However, the concentration used in this study was quite lower than those reported earlier. In the presence of salts, the mechanism of starch gelatinization was depending on different factors, especially the interaction between solvent and polymer, the structure of water, and the attractive and repulsive interactions between the ions and starch. Oosten (1982 and 1983) explained that the alcoholic groups present in the starch chain is converted into sodium and calcium alcoholate group which could be easily dissociated, resulting a increase in the difference of potential between the water phase and starch granule called Donnan potential.

In this study it was found that the addition of $CaCl_2$ has more pronounced effect on T_o, T_p, and T_c of water chestnut starch as compared to other salts. Similar results were reported by Ahmad *et al.* (1999) for sago starch. This could be due to the presence of more Cl- ions per mole of $CaCl_2$ as compared to KCl.

Conclusion

It was concluded that the addition of different salts markedly affected the pasting and thermal properties of water chestnut starch. Overall reduction in swelling power was observed in the presence of salts. Transparency was found to be increased after the addition of NaH_2PO_4. The addition of salts in varying proportions to native starch based foods open new avenues in food processing and it modifies the rheology of the starch to give the desired finished product. More research is required in this area to fully understand the potential of this novel source of starch which is a promising new ingredient in food processing.

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