INDIAN JOURNAL OF SCIENCE AND TECHNOLOGY

RESEARCH ARTICLE

Effects of Controlled Oxidation on the Functional Properties of Potato, Yam, Cassava and Corn Starches

Ouattara Taniky Sy Hamed[1], Yacouba Zoungranan[1,2]*, Ekou Lynda[1], Ekou Tchirioua[1]

1 Department of Chemistry, University NANGUI ABROGOUA, Abidjan, Côte d'Ivoire
2 Department of Mathematics, Physics and Chemistry, University Peleforo GON COULIBALY, Korhogo, Côte d'Ivoire

OPEN ACCESS

Received: 20-11-2024
Accepted: 01-02-2025
Published: 24-02-2025

Citation: Hamed OTS, Zoungranan Y, Lynda E, Tchirioua E (2025) Effects of Controlled Oxidation on the Functional Properties of Potato, Yam, Cassava and Corn Starches. Indian Journal of Science and Technology 18(6): 452-463. https://doi.org/10.17485/IJST/v18i6.3736

* **Corresponding author**.

zoungranan@gmail.com

Funding: None

Competing Interests: None

Published By Indian Society for Education and Environment (iSee)

ISSN
Print: 0974-6846
Electronic: 0974-5645

Abstract

Objectives: To investigate the effect of hydrogen peroxide oxidation on the functional properties of four native starches extracted from Cor, Cas, potato and Yam. **Method:** Native starches from Cor, Cas, potato and Yam were oxidized using concentrations of H_2O_2 ranging from 0.1 M to 1 M. Structural changes were analyzed by FT-IR and polarized light microscopy, while functional properties such as solubility index, specific surface area, water absorption and moisture content were determined. **Findings:** The study demonstrated that oxidation of H_2O_2 improves the functional properties of starches. The oxidation rate was found to depend on the H_2O_2 concentration, with the highest oxidation rates being 1.00% for Cor starch (0, 6 M H_2O_2), 0.73% for Pot starch (0.2 M H_2O_2), 0.60% for Yam (1 M H_2O_2) and 0.55% for Cas starch (0.2 M H_2O_2). These results highlight that H_2O_2 oxidation significantly improves the functional properties of native starches, making them suitable for industrial or scientific use. The results concur with previous studies while providing new insights into the optimal conditions for starch modification. **Novelty:** The study proposes innovative approaches by revealing the optimal levels of H_2O_2 required to modify the functional characteristics of naturally occurring starches. It also highlights the environmental and economic benefits of H_2O_2 as an oxidizing agent, compared with traditional oxidants, while opening up prospects for applications in industry.

Keywords: Oxidized starch; Hydrogen peroxide; Extraction; Oxidation rate; Functional properties

1 Introduction

Starch is a polysaccharide of vital importance to various industries due to its abundance, availability and low cost[(1)]. A natural polymer mainly derived from plants; it is used in applications ranging from food to the manufacture of materials. The native form of starch has several drawbacks that limit its use in specific industrial applications. These include its low water solubility, high gel viscosity and tendency to retrograde, resulting

in the formation of undesirable gels over time [2]. To overcome these limitations, several chemical methods have been developed to improve the functional properties of starch. Among these methods, oxidation is that by which hydroxyl groups (-OH) are transformed into carbonyl (-CO) and carboxyl (-COOH) groups [3]. Oxidation takes place under strictly controlled conditions, particularly with regard to time, temperature and pH, thus modifying the molecular structure of the starch. Many conventional oxidizing agents, such as sodium hypochlorite, potassium permanganate and potassium periodate, have significant limitations, including the production of toxic by-products that are difficult to treat, making them unsuitable for certain industrial applications. [4] In addition to these oxidizing agents, hydrogen peroxide is also used for starch oxidation and is the subject of much research. It offers specific advantages over other oxidizing agents, mainly thanks to its biodegradability and low environmental impact, making it a more sustainable and eco-responsible choice. [5] These changes influence viscosity, clarity, as well as starch's tendency to retrograde, making oxidized starch more suitable for specific applications in sectors such as paper, textiles and other industries requiring enhanced properties. Despite these advantages, current research shows a lack of in-depth studies on the optimal conditions for H_2O_2 oxidation, particularly with regard to the effect of different optimal concentrations on the functional properties of starches. This study fills this gap by analyzing the effects of optimal H_2O_2 concentrations on the functional properties of starches, thus providing essential information for improving oxidation conditions for each type of modified starch.

2 Methodology

2.1 Biomass harvesting

Yam (*Dioscorea alata* L), Pot (*Ipomea batatas*), Cas (*Manihot Esculenta* Crantz) and Corn (*Zea mays* saccharata) tubers were harvested in Abengourou , a town in eastern Côte d'Ivoire, 210 km from the economic capital Abidjan. After harvesting, the tubers (Yam, Pot, Cas) and Corn kernels (Cor) were placed separately in plant fiber bags and immediately transported to the laboratory for further study.

2.2 Extraction of native starches

Fig 1. Native starches of the study

The extraction and purification of starch from Yam, Pot and Cas biomasses were carried out using the method described by Weligama [6] with some modifications. Fresh tubers were peeled and cut into small pieces, then washed with distilled water. For Cor biomass, the method was applied with a few modifications. The grains were first soaked in water for 10 hours. Then, Cor grains and tubers were ground separately with distilled water in a 1:1 ratio, using a laboratory grinder (Silver Crest 5500, France). The resulting grindings were transferred to a 1 L beaker, then pressed through a 100 μm sieve (Saulas, Paris, France)

to obtain a starch milk. The milk obtained was decanted for 2 hours to separate the pellet (crude starch) from the supernatant liquid phase. The resulting pellet was successively washed with a 4% NaCl solution and a 0.1 M ethanol solution in a 1:1 ratio, using an immersion-sedimentation process. The aim of this wash is to remove the proteins and lipids contained in the pellet, respectively. The pellet is then washed with distilled water, using the immersion-sedimentation process, to obtain a purified starch pellet. The moist pellet is dried in a universal oven (Memmert Un55-53l, France) with air circulation at 60°C for 24 hours.

2.3 Extraction efficiency

It is obtained by calculating the ratio between the mass of dry starch obtained and the mass of fresh biomass used during grinding (tuber or grain). The yield, expressed as a percentage, is calculated using the following formula:

$$R = \frac{m'}{m} \times 100$$

- R: Yield of starch obtained
- m': mass of starch extracted
- m: mass of ground material

2.4 Starch oxidation

For the preparation of oxidised starches, the methods of Barbosa[7] and Muflihati[8] were adapted with some modifications. Six (06) solutions of hydrogen peroxide (H_2O_2) contained in six 250 ml Erlenmeyer flasks, with respective concentrations of 0.1, 0.2, 0.4, 0.6, 0.8 and 1 M, were obtained by dissolving 50% (H_2O_2). To each Erlenmeyer flask, a quantity of starch in a ratio of 1:5 (m/v) was added, then the flask was covered with aluminum foil and placed on a magnetic stirrer (Bioblock Scientific N° 0189A, USA) at 750 rpm for 24 hours. Preparation was carried out at a temperature of 25°C and pH adjusted to around 4.5 to promote the oxidation reaction. After stirring, the supernatant was removed and the solid residue, representing the oxidized starch, was oven-dried at 50°C for 72 hours. The oxidized starches obtained were labelled according to the codes in Table 1.

Table 1. Codes for the various starches in the study

C H_2O_2 (mol/L)	Cassava Starch	Potato Starch	Yam Starch	Corn Starch
0	Cas	Pot	Yam	Con
0,1	Oxcas1	Oxpot1	Oxyam1	Oxcor1
0,2	Oxcas2	Oxpot2	Oxyam2	Oxcor2
0,4	Oxcas3	Oxpot3	Oxyam3	Oxcor3
0,6	Oxcas4	Oxpot4	Oxyam4	Oxcor4
0,8	Oxcas5	Oxpot5	Oxyam5	Oxcor5
1	Oxcas6	Oxpot6	Oxyam6	Oxcor6

2.4.1 Determination of carboxyl content

The methods described by Pham[9] and Zhang[10], with some modifications, were used to determine the carboxyl content of oxidized starch. 1g oxidized starch dissolved in 50 ml distilled water was heated for 30 min with stirring until gelatinization began. After cooling, the solution was titrated with 0.1 M NaOH to the phenolphthalein point. Native starch was used as a control. The carboxyl content of oxidized starch is given by the following formula:

$$COOH\ (\%) = 0.045 \times M \times \frac{V_{ox} - V_{nat}}{m} \times 100 \quad (2)$$

With:

- V_{ox} (mL): the volume of NaOH required to achieve the turn with oxidized starch.
- V_{nat} (mL): is the volume of NaOH required to achieve conversion with native starch.
- m (g): is the mass of starch
- M (mol/L): is the concentration of NaOH

2.4.2 Determining carbonyl content and oxidation rate

The methods described by Pham[9] and Zhang[10], with some modifications, were used to determine the carboxyl content of oxidized starch. A quantity of 0.5 g dry starch was dissolved in 50 ml distilled water and heated to 80°C in a water bath for 30 minutes with stirring until gelatinization began. After cooling, the pH was adjusted to 3.8 with 0.1 M HCl. A 15 ml volume of hydroxylamine chloride solution was then added. The hydroxylamine solution was prepared in a volumetric flask by dissolving 7g of hydroxylamine chloride in water, then adding 100 ml of 0.5 M NaOH solution. The mixture is then made up to 500 ml with distilled water. After adding the hydroxylamine chloride solution, the beaker is covered with plastic film and left to stand for 2 h. The mixture is then rapidly titrated with 0.1 M HCl to pH 3.8. The carbonyl content of the oxidized starch is given by:

$$CO(\%) = 0.028 \times M \times \frac{V_{ox} - V_{nat}}{m} \times 100 \quad (3)$$

Oxidation rate

For each type of oxidized biomass, the total oxidation rate was defined according to the following formula:

$$Total\ oxidation\ rate\ \ (\%) = COOH(\%) + CO(\%) \quad (4)$$

2.5 Physico-chemical characterization of starches

Characterization of oxidized starches is carried out by selecting the optimum oxidation rates for each type of biomass.

Water absorption capacity and solubility index:

in a centrifuge tube of mass m_o, a quantity m1 of dry starch is mixed with distilled water in a 1:50 (m/v) ratio. The whole mixture is left to stand for 24 h, then centrifuged at 3000 rpm for 30 min, using a centrifuge (Centrifuge Sigma 1-15 PK, Germany). After centrifugation, the tube is weighed and the mass (m_2) of saturated starch is deduced by subtracting the mass m_0 of the centrifuge tube. The whole tube is placed in an oven at 105°C for 24 h. After cooling, the tube is re-weighed with its contents and the mass m_3 of dry starch obtained by subtracting the mass m_0 of the tube. The water absorption capacity (WAC) was calculated as follows:

$$WAC(\%) = \frac{m_2 - m_3}{m_3} \times 100 \quad (5)$$

The solubility index was calculated using the following equation:

$$IS\ (\%) = \frac{m_3 - m_1}{m_1} \times 100 \quad (6)$$

Moisture content:

For each biomass, the water content was determined. In a ceramic crucible of mass m_0, a quantity of native starch is introduced and the mass m_1 of the whole is taken at room temperature. The assembly is oven-dried at 105°C for 24 h, then weighed after cooling to obtain mass m_2. The moisture content (H) is calculated using the following formula:

$$H(\%) = \frac{m_1 - m_0}{m_2 - m_0} \times 100 \quad (7)$$

Specific surface area:

For each type of starch, the specific surface area was determined. In 06 Erlenmeyer flasks, each containing a mass m = 1 g of starch, a volume V_o = 50 mL of acetic acid solution (CH_3COOH) was added, with initial concentrations (C_i) of 0.015, 0.030, 0.045, 0.060, 0.090 and 0.15 mol.L^{-1}. The whole mixture is stirred at 200 rpm on a magnetic stirrer (Bioblock Scientific N° 0189A, USA) for 120 min, this time corresponding to the equilibrium time, then decanted for 30 min before collecting the supernatant. A 10 mL volume of the supernatant is titrated with a 0.1 mol. L^{-1}. The quantity of acetic acid adsorbed per gram of starch is determined by the following relationship**:**

$$Q_e = \frac{(C_e - C_i)\ V_o}{m} \quad (8)$$

Q_e: quantity of acetic acid adsorbed at equilibrium (mol. g^{-1})

C_e: equilibrium concentration of acetic acid
C_i: initial concentration of acetic acid
m: mass of starch

To determine the specific surface area S_L, we determine the maximum adsorption capacity Qm from the Langmuir equation in its linear form.

$$\frac{Ce}{Q_e} = \frac{Ce}{Q_m} + \frac{1}{K_L Q_m} \tag{9}$$

K_L: Langmuir constant linked to temperature and the adsorbent-adsorbate system.

The specific surface area is given using the following equation:

$$S_L = N_A \times S \times Q_m \tag{10}$$

With:

N_A: Avogadro number
S: theoretical surface area occupied by the acetic acid molecule (21 ´^{2}).

2.6 Morphological and structural characterization of starches

The morphology of oxidized and native starch granules was observed using a binocular polarizing microscope (Optika B-150p-Brpl, Italy). Observations were made at microscopic scale (40x). Starch surface functional groups were determined by Fourier transform infrared spectrophotometry using a spectrophotometer (Agilent Cary 630 FTIR, Santa Clara, California, USA.), equipped with the ART module. Analysis was carried out with the ART module, in a wavenumber range from 4000 to 500 cm^{-1}.

2.7 Data treatment

All calculations and graphs were performed with Microsoft office Excel 2016 Professional and Originpro 2018. Mean values and standard deviation were determined from three individual measurements.

3 Results and Discussion

3.1 Starch extraction yields

The extraction yields of Yam, Cas, Pot and Cor starches were evaluated in this study. Analysis revealed that extraction yields ranged from 7.303% to 23.453%, reflecting variability in starch richness. The highest yield was obtained with Cas starch (R=23.453%), which may reflect a high carbohydrate content, mainly in the form of starch. These observed results are similar to those reported by [11,12], who also noted a yield in excess of 20% in tubers, illustrating their potential as a source of starch for various industrial applications. The lowest yield was obtained with yam (R=7.303%), which could be due to the presence of fibers, in agreement with observations [13,14], it has been shown that fibers have an unfavorable impact on the efficiency of starch extraction techniques. With Cor (corn) biomass (R=10.459%), extraction efficiency is of the same order as that of Zhang et al., (2023) [15], which was 11% in similar situations. This demonstrates the consistency of this biomass as a reliable source of starch. According to the work of Rashwan et al., (2024) [16], the rather low yield (7.858%) of potato could be due to a lower starch concentration or a higher amount of plant fiber. The results of this study indicate that the protocol applied resulted in a higher yield of cassava starch than that published by [17,18]. (21.5% vs 23.453%), testifying to the effectiveness of the proposed method.

3.2 Effect of oxidizing agent on oxidation rate

Yam, Cas, Pot and Cor starches were oxidised with hydrogen peroxide at different concentrations in order to assess the effect of the oxidising agent on the total oxidation rate of the target starch. Oxidised starches OxYam, OxCas, OxPot and OxCor showed a more or less white colour depending on the H_2O_2 concentration. This suggests a partial degradation of the granular structure of the starch during the oxidation process. Phi Hung et al., (2016) [19] who oxidised Corn starch by varying the concentration of sodium hypochlorite between 0 and 3%, also noted this change in color. This discoloration could be the result of the alteration of glycosidic bonds, affecting the functional properties of native starches. Carbonyl and carboxyl contents were calculated, and

the results are presented in Table 2. For example, for OxCor, carbonyls (%CO) and carboxyls (%COOH) reached 0.94 ± 0.017 %CO and 0.274 ± 0.012 %COOH respectively. These values are higher than those observed for the other starches (OxYam, OxCas and OxPot), suggesting that maize starch undergoes more pronounced oxidation under the effect of hydrogen peroxide. These results are comparable to those of Dao et al., (2017) [20] who reported carbonyl levels of up to 0.80%CO and carboxyl levels of up to 0.60% COOH for maize starch treated with 3% sodium hypochlorite. The levels obtained in this study are similar, but slightly higher for (OxCor), which could indicate a better oxidation efficiency with hydrogen peroxide under similar conditions. Thus, the results presented in this study confirm the efficiency of hydrogen peroxide in starch oxidation, producing high rates of oxidised functional groups, reinforcing the interest of this method to modulate the functional properties of starches for industrial applications. Carbonyl and carboxyl contents were calculated and the results are presented in Table 2.

Table 2. Relative carbonyl and carboxyl content of oxidized starches

Serial Numbers	Oxcas serial		Oxpot serial		Oxyam serial		Oxcor serial	
	%CO	%COOH	%CO	%COOH	%CO	%COOH	%CO	%COOH
1	0.1±0.01	0.27±0.008	0.098±0.008	0.045±0.003	0.093±0.012	0.045±0.017	0.094±0.015	0.225±0.011
2	0.504±0.012	0.135±0.003	0.554±0.018	0.18±0.027	0.102±0.010	0.09±0.006	0.12±0.031	0.270±0.014
3	0.113±0.006	0.126±0.004	0.108±0.005	0.135±0.010	0.131±0.007	0.18±0.011	0.101±0.021	0.274±0.012
4	0.108±0.004	0.09±0.012	0.115±0.005	0.123±0.008	0.145±0.006	0.18±0.019	0.94±0.017	0.090±0.009
5	0.095±0.005	0.045±0.014	0.056±0.002	0.09±0.004	0.168±0.010	0.09±0.027	0.308±0.023	0.063±0.008
6	0.088±0.008	0.036±0.009	0.012±0.004	0.045±0.006	0.56±0.014	0.04±0.003	0.132±0.019	0.045±0.007

The results concerning the impact of the oxidizing agent on the overall oxidation rate are summarized in Figure 2.

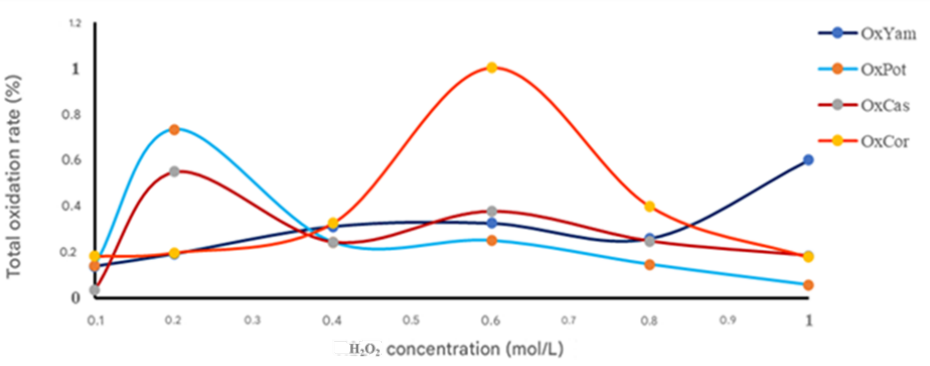

Fig 2. Overall oxidation rate of oxidized starches as a function of oxidizing agent (H_2O_2)

Analysis of Table 2 shows that CO content varies from 0.012% to 0.94%, and COOH content from 0.036% to 0.274%. The relatively low levels can be explained by the highly complex reaction mechanism of the oxidation reaction with hydrogen peroxide. Indeed, Valerio et al., (2019) [21] reported that it is a radical chain reaction, initiated by the hydroxyl radical (OH•). This radical originates from the homolytic decomposition of hydrogen peroxide, which reacts with starch so rapidly that most of the reagent is initially consumed to give a large amount of carbonyl group. It is therefore possible that in this study, less oxidant was available for the oxidation of carboxyl groups, which explains the low concentrations observed for the latter. Table 2 also reveals that for a given H_2O_2 concentration, the oxidized starches obtained contain higher amounts of carbonyl than carboxyl. This result is in line with previous work by Sumardiono et al., (2020) [22], who indicated that oxidation by hydrogen peroxide favored the formation of carbonyl groups. This represents a point of innovation in this study, as the dynamics of this modification reaction have not been explored in depth in the previous literature, particularly with regard to the weak formation of carboxyl groups. The variation in hydrogen peroxide concentration during the modification process had a significant influence on the type and quantity of functional groups formed in oxidized starches. However, the work of [23] on the oxidation of starch by NaOCl revealed that only a small amount of carbonyl was formed. Other studies have also found an increase in carbonyl groups in potato, Cor and rice starches, but with NaOCl as the oxidizing agent, which differs from the use of H_2O_2 in this study. This difference may be explained by the fundamental differences in oxidation mechanisms between hydrogen peroxide

and sodium hypochlorite, highlighting the interest of this study, which specifically explores the effect of H_2O_2 on starch. The overall oxidation rate analysis in Figure 2 shows that Cas and Pot starches oxidize best for $[H_2O_2] < 0.4$ M. These two starches have an optimum oxidation rate for $[H_2O_2] = 0.2$ M. Yam and Cor starches oxidize to give optimal Oxyam and Oxcor at concentrations of $[H_2O_2] = 1$ M and $[H_2O_2] = 0.6$ M respectively. This study was able to identify optimal H_2O_2 concentrations that maximize oxidation for each starch type, thus providing optimized conditions for selective starch oxidation.

3.2.1 Physico-chemical characterization of native and modified starches

The physico-chemical characteristics of native and maximally oxidized starches are summarized in Table 3.

Table 3. Native and oxidised starches physico-chemical properties

	Native starches				Oxidized starch			
	Yam	**Pot**	**Cas**	**Cor**	**Oxyam 6**	**Oxpot 2**	**Oxcas 2**	**OxCor 4**
Solubility (%)	54.03±1.0	19.1±0.5	37.2±1.0	26.4±0.7	81.13±2.0	34.6±1.0	31.27±0.9	51.2±1.5
Specific surface (m^2/g)	1017.71±1.5	1087.32±2.3	874.21±1.2	672.37±1.1	1091.36±3.0	1337.65±2.2	988.92±1.8	1403.73±1.0
Water absorption capacity (%)	95.65±2.0	60.49±1.5	90.48±1.8	79.19±1.7	93±2.0	48.5±1.4	75.25±1.1	60.56±1.2
Humidity (%)	17.12±0.5	7.46±0.3	13.22±0.4	7.96±0.3	7.55±0.2	8.23±0.7	7.96±0.6	92.82±2.5

Analysis of Table 3 reveals that, whatever the native starch considered, the solubility of Oxcas 2 decreases by reducing water absorption capacity. An increase in specific surface area is also observed during the oxidation process. This means that oxidation of starches modifies their physico-chemical properties by altering their molecular structure. The increase in solubility index is due to the breaking of glycosidic bonds in the polysaccharide chains, and to the increase in water affinity favored by the introduction of carbonyl (C=O) and carboxyl (-COOH) groups into the starch structure. The increase in specific surface area when switching from native to oxidized starch could be explained by the disorganization of the granules' crystalline structure, creating pores and microcracks. Lovera et al., (2020)[24] also demonstrated an increase in specific surface area in their study of oxidized sorghum starches. This disorganization increases the proportion of amorphous regions, favoring interaction with water and increasing starch reactivity. Water absorption capacity, although decreasing slightly for some oxidized starches (e.g. Yam from 95.65% to Oxyam from 93%) remains high, suggesting that the new functional groups create hydrogen bridges with water stabilizing the oxidized starch structure. The increase in water content in Cor (Cor 7.96% to Cor 92.82%) could be attributed to advanced hydrolysis of polysaccharide chains during the oxidation process. Indeed, advanced hydrolysis produces smaller, hygroscopic molecular fragments capable of absorbing large quantities of water. In short, oxidation induces structural modifications that increase the solubility and specific surface area of starches, while influencing their water absorption capacity and water content. The results obtained in this study are in line with observations made in the literature. For example, previous studies[25] on corn and potato starches revealed similar increases in solubility and specific surface after oxidation. However, this study stands out for its broader approach, including a variety of starches from Yam, sweet potato, cassava and maize. This diversity of biomasses studied provides a better understanding of the impact of oxidation on the physico-chemical properties of these starches. chemical properties of these starches. In addition, the focus on water uptake and changes in the hydrophilic properties of oxidized starches represents a significant contribution to our understanding of these materials. This study thus presents an innovative approach in terms of raw material diversity and in-depth analysis of the hydrophilic properties of oxidized starches.

3.2.2 FTIR analysis

The spectra of native starches and those of starches oxidized at optimum oxidation rates are shown in Figure 3. The spectra of native and oxidized starches are similar. For Oxyam. Oxcas. Oxcor and Oxpot starches, there is absorption at peaks 3244.4 cm^{-1}, 3258.3 cm^{-1}. 3,256.94 cm^{-1} and 3265.2 cm^{-1} which represent O-H stretching vibrations. Absorption peaks 2922.2 cm^{-1}, 2927.7 cm^{-1}, 2923.6 cm^{-1} and 2913.8 cm^{-1} represent CH2- elongations of the glucose unit. Oxyam and Oxcas starches also show a slight increase in absorption intensity at these wavelengths, reflecting a reduction in the number of functional groups.

Oxpot and Oxcor starches also show invariability of absorption intensity at these wavelengths, reflecting the stability of their chemical structures. Absorption in the spectral regions 1637.5 cm^{-1}, 1637.5 cm^{-1}, 1645.8 cm^{-1} and 1641.6 cm^{-1} respectively for Oxyam, Oxcas, Oxpot and Oxcor starches are typical bands residing in the spectra of starch and its derivatives, corresponding to the H_2O bending vibrations leading to the absorption of water in the starch molecule. This absorption is characteristic of starch and its derivatives. Whatever the starch, between 990.6 cm^{-1} and 801.3 cm^{-1} there is an intensification of absorption peaks corresponding to the C-H plane deformation vibration of the starch glycosidic structure. This intensification is due to structural modifications of the starch during the oxidation process. In addition, for Oxyam. Oxcas. Oxcor and Oxpot starches respectively, an absorption in the spectral regions 1744.4 cm^{-1}, 1720.4 cm^{-1} and 1730.1 cm^{-1} and 1733.3 cm^{-1} which are attributed to the vibrations of free C=O groups typical of carboxylic acids, formed after starch oxidation. The results indicate that the native starches in the study were successfully oxidized by hydrogen peroxide and that the hydroxyl groups were modified to carbonyl and/or carboxyl.

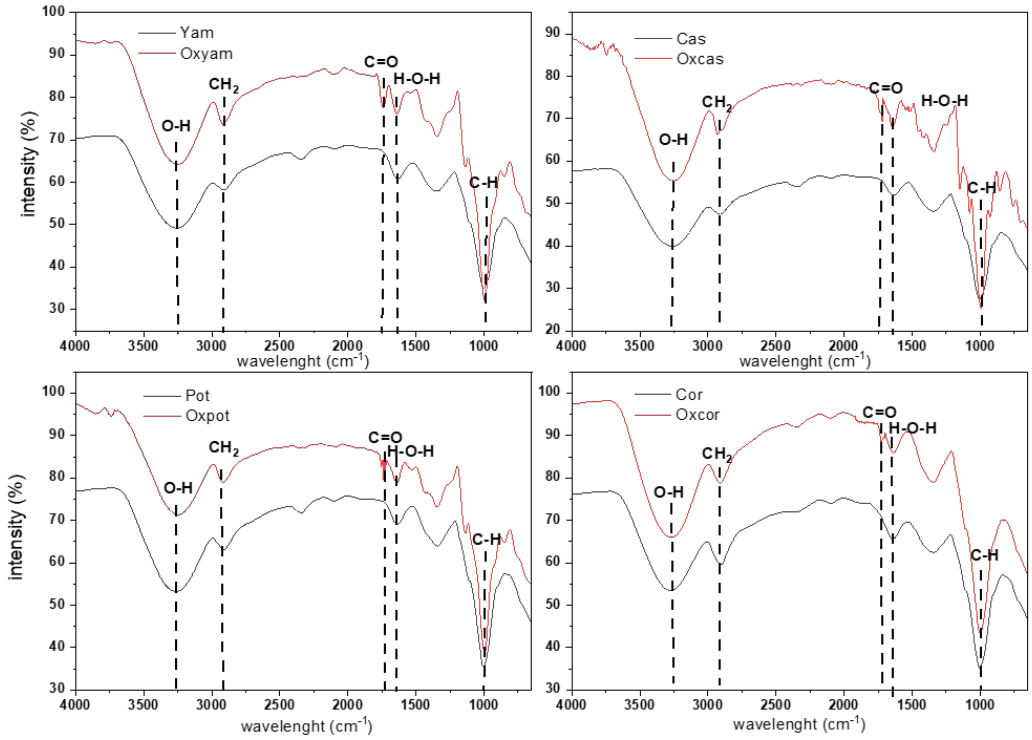

Fig 3. Comparative spectra of native and oxidized starches

3.2.3 Starch granule morphologies

The results of polarized light micrographs on native and optimally oxidized starches are shown in Figure 5. The results show that oxidation leads to significant changes in granule size and geometric shape. The main change is a decrease in granule size (from Yam to Oxyam). Oval-shaped oxidized granules (from Cas to Oxcas) and (Pot to Oxpot), and polyhedral granules transformed into spherical granules (from Cor to Oxcor). These results show that the oxidation process led to partial integration of the granules. This disintegration could be explained by the breaking of intramolecular hydrogen bonds during the oxidation process. The change in the geometric shape of the granules suggests surface erosion affecting the outer layers of the glycosidic structure. For Yam starch initially characterized by large, well-defined granules, a decrease in size is observed after oxidation. Accompanied by partial dissolution. In fact, an increase in concentration revealed a partial disintegration of the granules. These results confirm work Fonseca et al., (2022) [26], which observed a less smooth surface of oxidized starches compared to native starches. The morphological change observed suggests that the oxidation process influences the specific surface of the resulting oxidized starches. Furthermore, the observation of the transformation of polyhedral granules (Cor) into spherical granules (Oxcor) constitutes an important novelty, which has not been reported in previous studies.

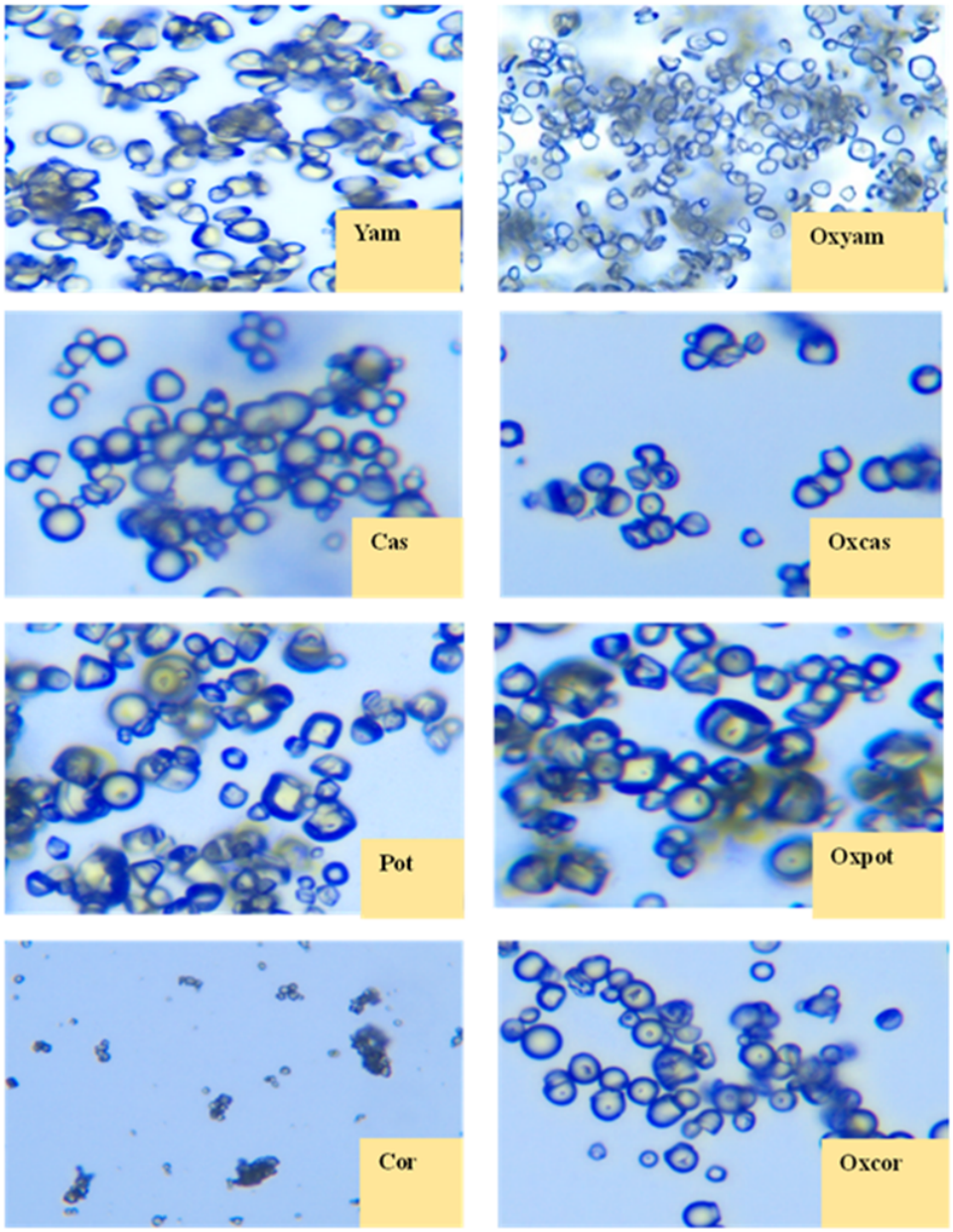

Fig 4. Morphology of native and oxidized starch granules

3.3 Effects of oxidizing agent on solubility and water retention of oxidized starches

3.3.1 Solubility index

For each element of a given oxidized starch series, the solubility was determined in order to understand the influence of the concentration of the oxidizing agent. The results of the various tests are shown in Figure 5. The histograms in Figure 5 show that the concentration of the oxidizing agent has a significant impact on the solubility index. At low oxidizing agent concentrations, oxidized starches show a reduction in solubility compared to native starch. Above $[H_2O_2]$ = 0.2 M (Oxyam2, Oxpot2, Oxcas2, Oxcor2), the solubility of the resulting oxidized starches increases rapidly beyond the value of the corresponding native starch. The tendency of the solubility of oxidized starches to increase with increasing oxidizing agent concentration reflects a strong interaction of polar groups (COOH and CO). A high concentration of oxidizing agent weakens hydrogen and glycosidic bonds,

making the resulting molecular structure of oxidized starch more accessible to water. However, some authors Wang et al., (2023) [27], and Cahyana et al., (2019) [28] have shown that this increase in solubility could be explained by depolymerization or molecular rearrangement induced by the oxidizing agent.

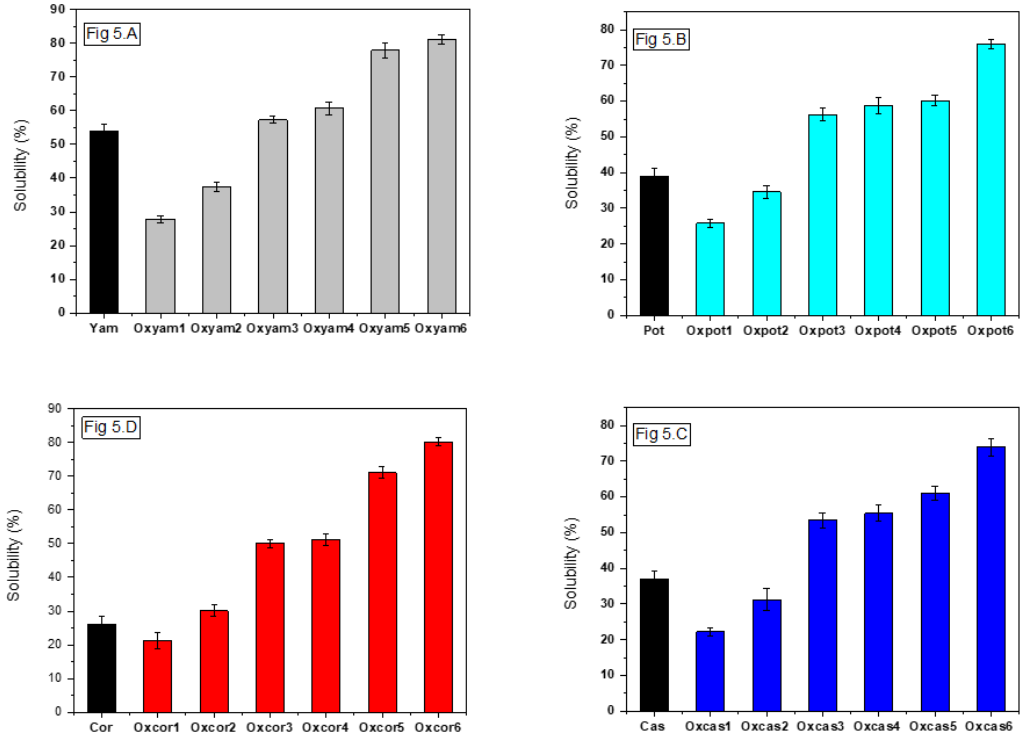

Fig 5. Effect of oxidizing agent concentration on solubility index

3.3.2 Waters absorption capacity

Figure 6 shows the variation in water absorption capacity of oxidized starches at different oxidizing agent concentrations. At $[H_2O_2] = 0.1$ M (Oxyam1, Oxpot1, Oxcas1, Oxcor1), there is a moderate reduction in absorption capacity compared with YAM (Figure 6**A**) and COR (Figure 6 **D**) native starches. This reduction is more pronounced in Pot native starch (Figure 6 **B**) and Cas native starch (Figure 6**C**). Above $[H_2O_2] = 0.1$ M, there is an overall tendency for the water absorption capacity of oxidized starches to increase with increasing oxidizing agent. However, with native Cas starch (Figure 6 **C**), this increase in the WAC of the resulting oxidized starches remains lower than that of native starch. Generally speaking, native starches have amorphous and crystalline regions. Crystalline regions limit water accessibility, while amorphous regions favor hydrolysis. The decrease in WAC observed at $[H_2O_2] = 0.1$ M chemical modification could be explained by a reorganization of amorphous regions linked to the introduction of groups (COOH and CO). Low oxidant concentrations below 0.1 M for Cor, 0.6 M for Yam and Pot and > 1 M for Cas, reduce the WAC of the resulting oxidized starches. The increase in WAC with increasing oxidizing silver is due to the destruction of the corresponding crystalline regions. This destruction is more marked at higher oxidant concentrations. The results obtained in this study are similar to Gupta and al., (2023) [29], which observed similar reductions in absorption capacity at moderate oxidant concentrations. However, this study presents a novelty by focusing specifically on differences between starch types (Yam, Pot, Cas, Cor) and examining the impact of optimal oxidant concentrations on the reorganization of crystalline and amorphous structures, an aspect less explored in previous studies.

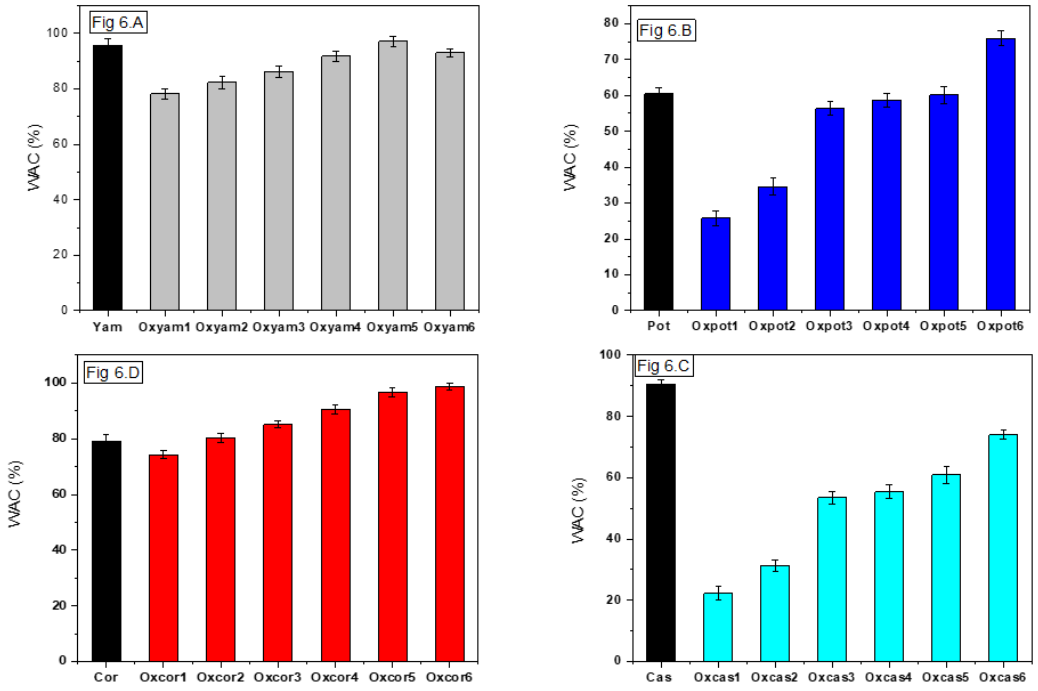

Fig 6. Effects of the concentration of the oxidizing agent on the absorption capacity

4 Conclusion

In this study, starches were extracted from various local biomasses and oxidized using hydrogen peroxide to improve their functional properties. Native and oxidized starches were characterized in terms of solubility index and water retention capacity. The results show that the optimum hydrogen peroxide concentration significantly influences the formation of functional groups and the properties of modified starches. A positive correlation between oxidizing agent concentration and improved solubility and water absorption capacity was observed. The innovation of this study lies in the detailed examination of behavioral differences between starches extracted from different biomasses, taking into account oxidant concentrations and their specific effect on the reorganization of amorphous and crystalline structures. Although low oxidation rates were observed, significant functional modifications were noted, confirming the effectiveness of oxidation in improving starch properties. However, the study has limitations, notably the absence of tests on other functional parameters such as viscosity and chemical reactivity of modified starches. It would be pertinent to further optimize the method, notably by adjusting the oxidation time and temperature, in order to maximize functional modifications without compromising starch stability. The results suggest that controlled oxidation could offer new prospects for industrial and food applications, such as in packaging or food manufacturing. Future research should explore more severe processing conditions to understand their effect on the durability and performance of modified starches under real application conditions.

References

1) Falua KJ, Pokharel A, Babaei-Ghazvini A, Ali Y, Acharya B. Valorization of Starch to Biobased Materials: A Review. *Polymers* . 2022;14(11):1–44. Available from: https://doi.org/10.3390/polym14112215.
2) Compart J, Singh A, Fettke J, Apriyanto A. Customizing Starch Properties: A Review of Starch ModificationsandTheirApplications. *Polymers*. 2023;15(16):1–20. Available from: https://doi.org/10.3390/polym15163491.
3) Zarski A, Kapusniak K, Ptak S, Rudlicka M, Coseri S, Kapusniak J. Functionalization Methods of Starch and Its Derivatives: From Old Limitations to New Possibilities. *Polymers*. 2024;16(5):1–46. Available from: https://doi.org/10.3390/polym16050597.
4) Sun X, Jiang F. Periodate oxidation-mediated nanocelluloses: Preparation, functionalization, structural design, and applications. *Carbohydrate Polymers*. 2024;341:1–24. Available from: https://doi.org/10.1016/j.carbpol.2024.122305.

5) Tolvanen P, Mäki-Arvela P, Sorokin AB, Salmi T, Murzin DY. Kinetics of starch oxidation using hydrogen peroxide as an environmentally friendly oxidant and an iron complex as a catalyst. *Chemical Engineering Journal*. 2009;154(1-3):52–59. Available from: https://doi.org/10.1016/j.cej.2009.02.001.
6) Thuppahige VTW, Moghaddam L, Welsh ZG, Wang T, Xiao HW, Karim A. Extraction and characterisation of starch from cassava (Manihot esculenta) agro-industrial wastes. *LWT*. 2023;182:1–12. Available from: https://doi.org/10.1016/j.lwt.2023.114787.
7) Barbosa JV, Martins J, Carvalho L, Bastos MMSM, Magalhães FD. Effect of peroxide oxidation on the expansion of potato starch foam. *Industrial Crops and Products*. 2019;137:428–435. Available from: https://doi.org/10.1016/j.indcrop.2019.05.045.
8) Muflihati I, Marseno DW, Pranoto Y. Oxidation of Oven-Dried Cassava Starch Using Hydrogen Peroxide and UV-C Irradiation to Improve Frying Expansion. *Journall of Indonesian Food and Nutrition Progress*. 2019;16(1):9–14. Available from: http://eprints.upgris.ac.id/id/eprint/1483.
9) Pham TTH, Nguyen TT, Nguyen VK, Nguyen TD, Pham TT, Nguyen TH, et al. Effect of oxidation on physicochemical characteristics of thermoplastic canna starch. *Vietnam Journal of Chemistry*. 2024;62(S1):15–22. Available from: https://doi.org/10.1002/vjch.202300260.
10) Zhang JY, Xiong JW, Chen ZP, Cui N. Physicochemical properties of potato starches oxidised by different concentrations of sodium hypochlorite, and their application in yogurt. *International Food Research Journal*. 2022;29(3):582–592. Available from: https://doi.org/10.47836/ifrj.29.3.11.
11) Dorantes-Fuertes MG, López-Méndez MC, Martínez-Castellanos G, Ángel Meléndez-Armenta R, Jiménez-Martínez HE. Starch Extraction Methods in Tubers and Roots: A Systematic Review. *Agronomy* . 2024;14(4):1–27. Available from: https://doi.org/10.3390/agronomy14040865.
12) Achudan SN, Mohamed AMD, Rashid RSA, Mittis P. Yield and physicochemical properties of starch at different sago palm stages. *Materials Today: Proceedings*. 2020;31(Part 1):122–126. Available from: https://doi.org/10.1016/j.matpr.2020.01.341.
13) Jariyah, Susiloningsih EKB, Nilasari K. Glycemic Index Biscuits Formulation of Pedada Flour (Sonneratia caseolaris) with Tubers Starch. In: The 2nd International Joint Conference on Science and Technology (IJCST) 2017;vol. 953 of Journal of Physics: Conference Series. 2018;p. 1–7. Available from: https://doi.org/10.1088/1742-6596/953/1/012246.
14) Fakorede J, Badoussi ME, Loko LEY, Sanoussi F, Dassou GA, Tchekessi CKC, et al. Evaluation Of The Functional And Rheological Characteristics Of Instant Pounded Yam (Dioscorea Rotundata) Flours Obtained From Tubers Of Cultivars Used As Parents In A Breeding Program In Benin. *Biotechnology, Agronomy and Society and Environment*. 2021;25(2):71–88. Available from: https://doi.org/10.25518/1780-4507.18951.
15) Zhang J, Tao H, Tan C, Yuan F, Guo L, Cui B. Effects of biomass additives on mechanical strength and water resistance of corn starch straws. *Industrial Crops and Products*. 2023;205. Available from: https://doi.org/10.1016/j.indcrop.2023.117584.
16) Rashwan AK, Younis HA, Abdelshafy AM, Osman AI, Eletmany MR, Hafouda MA, et al. Plant starch extraction, modification, and green applications: a review. *Environmental Chemistry Letters*. 2024;22:2483–2530. Available from: https://doi.org/10.1007/s10311-024-01753-z.
17) Oriola KO, Raji AO. Physical properties of cassava (Manihot esculenta Crantz) root. *Acta Horticulturae*. 2014;1054:197–204. Available from: https://doi.org/10.17660/ActaHortic.2014.1054.23.
18) Oriola K, Raji A. Effects of Tuber Age and Variety on Physical Properties of Cassava [Manihot Esculenta (Crantz)] Roots. *Innovative Systems Design and Engineering*. 2013;4(9-Special Issue):15–25. Available from: https://doi.org/10.1111/jfpe.13923.
19) Hung DP, Nam TT, Phuc MV, Hiep NA, Thanh TV, Vuong NT. Oxidized Maize Starch: Characterization and Effect of It on the Biodegradable Films I. Characterization of Maize Starch Oxidized By Sodium Hypochlorite. *Vietnam Journal of Science and Technology*. 2016;54(3):347–355. Available from: https://doi.org/10.15625/0866-708X/54/3/7101.
20) Hung DP, Van Phuc M, Hiep NA, Van Thanh T, Vuong NT, Nam TT, et al. Oxidized Maize Starch: Characterization and Effect of It on the Biodegradable Films. Part II Infrared Spectroscopy, Solubility of Oxidized Starch and Starch Film Solubility. *Vietnam Journal of Science and Technology*. 2017;55(4):395–
402. Available from: https://doi.org/10.15625/2525-2518/55/4/7919.
21) Valerio O, Pin JM, Misra M, Mohanty AK. Synthesis Of Glycerol-Based Biopolyesters As Toughness Enhancers For Polylactic Acid Bioplastic Through Reactive Extrusion. *ACS Omega*. 2016;1(6):1284–1295. Available from: https://doi.org/10.1021/acsomega.6b00325.
22) Sumardiono S, Kusumawardani NI, Abdurahman AU, Arland A, Jos B, Pudjihastuti I. The modification of sago (Metroxylon Sagu) starch by combination of lactic acid hydrolysis and H_2O_2 oxidation methods to increase baking expansion. In: Proceedings Of 2nd International Conference On Chemical Process And Product Engineering (ICCPPE) 2019;vol. 2197, Issue 1 of AIP Conference Proceedings. AIP Publishing. 2020. Available from: https: //doi.org/10.1063/1.5140940.
23) Garrido LH, Schnitzler E, Zortéa MEB, Rocha TS, Demiate IM. Physicochemical Properties Of Cassava Starch Oxidized By Sodium Hypochlorite. *Journal of Food Science and Technology*. 2012;51(10):2640–2647. Available from: https://doi.org/10.1007/s13197-012-0794-9.
24) Lovera M, de Castro GMC, da Rocha Pires N, do Socorro Rocha Bastos M, Holanda-Araújo ML, Laurentin A, et al. Pyrodextrinization of yam (Dioscorea sp.) starch isolated from tubers grown in Brazil and physicochemical characterization of yellow pyrodextrins. *Carbohydrate Polymers*. 2020;242:1–8. Available from: https://dx.doi.org/10.1016/j.carbpol.2020.116382.
25) Barua S, Rakshit M, Srivastav PP. Optimization and digestogram modeling of hydrothermally modified elephant foot yam (Amorphophallus paeoniifolius) starch using hot air oven, autoclave, and microwave treatments. *LWT*. 2021;145. Available from: https://dx.doi.org/10.1016/j.lwt.2021.111283.
26) Fonseca LM, Gonçalves JR, Halal SLME, Pinto VZ, Dias ARG, Jacques AC, et al. Oxidation of potato starch with different sodium hypochlorite concentrations and its effect on biodegradable films. *LWT - Food Science and Technology*. 2015;60(2):714–720. Available from: https://dx.doi.org/10. 1016/j.lwt.2014.10.052.
27) Du Y, Chu J, Wang R, Zhang C, Zhang J, Zhi K. Efficient encapsulation of fat-soluble food-derived biofunctional substances (curcumin as an example) in dual-modified starch-based nanoparticles containing large conjugated systems. *International Journal of Biological Macromolecules*. 2023;242(P3):125078. Available from: https://dx.doi.org/10.1016/j.ijbiomac.2023.125078.
28) Cahyana Y, Pratiwi PA, Marta H, Djali M, Halim IR, Urrohmah S, et al. Oxidation by Hydrogen Peroxide Changes Crystallinity and Physicochemical Properties of Banana Flour. *IOP Conference Series: Earth and Environmental Science*. 2019;292(1):012007. Available from: https://dx.doi.org/10.1088/ 1755-1315/292/1/012007.
29) Gupta S, Prajapati A, Kumar A, Acharya S. Synthesis of silica aerogel and its application for removal of crystal violet dye by adsorption. *Watershed Ecology and the Environment*. 2023;5:241–254. Available from: https://dx.doi.org/10.1016/j.wsee.2023.10.003.