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Research paper

Gluconic Acid Production from Potato Peel Wastes by Oxidation Using Silver(I) Ion

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Abstract

Gluconic acid (GA) is a non-corrosive acid used in textile, food additives and pharmaceutical skin care products. Many synthetic approaches were proved costly to produce GA in bulk. Potato peel as domestic waste is rich in nutritional value as they could also be used as fertilizer for plantations. However, improper disposable of these waste could lead to serious environmental problems due to insufficient supply of oxygen leading to an anaerobic condition for the unwanted growth of harmful microorganisms. This bacterial pollution might lead to foul smell and contagious air pollution. An attempt was made by using this potato peel waste to produce GA chemically in normal experimental laboratory condition with high yields. In the process, it was also made to estimate the precious silver metal produced. In present study, potato peel was used to convert the starch in peel to GA and metal silver by oxidation using silver ions. Potato peel wastes were hydrolyzed in acidic medium, where the starch and cellulose in peel were converted into glucose. This glucose was converted into GA using ammonical solution of silver nitrate solution. GA was separated using water as a solvent. The yield of GA was quantified by physicochemical and spectrophotometric methods. The GA is quantified by titration and the yield was found as 68 ± 5% and the amount of silver metal powder was obtained 0.3±0.05 % per kilogram of potato peel waste. This process was simple, precise, accurate, environmental friendly, economical and meet the sustained development goals (SDG).

Keywords: *Acid Hydrolysis; gluconic acid; potato peel waste, gluconic acid, glucose; silver metal powder.*

1. Introduction

Gluconic acid (GA) is a chemically polyhydroxy acid produced from glucose by chemical synthesis from carbohydrate fermentation with bacteria or fungi (Datta and Henry.2006). GA derivatives such as sodium gluconate, calcium gluconate was reported with multiple applications in food industry, cosmetics and pharmaceuticals. (Ramachandran et al., 2017). Aqueous GA solutions are composed of cyclic ester of glucono-δ-lactone structure, which chelates metal ions and forms very stable complexes. In alkaline conditions, this agent exhibits strong chelating activities towards anions, i.e. calcium, iron, aluminium, copper, and other heavy metals (H. C. Ferraz et al., 2003). Glucose and other simple sugars are main precursors for the preparation of GA commercially. Microbial fermentation of GA is commercially done using fungal species like *Aspergillus Niger*, *Penicillium Luteum* or other bacterial species of the genera *Gluconobacter, Pseudomonas or Acetobacter* (M.Sauer,H.Marx 2013). Chemically bimetallic catalyst like (pd-Bi) was used for the oxidation of glucose on glassy carbon by means of electro-deposition. (M. Abdul Qadir, Sadia Atta And Faisal Jamshaid, 2011). It was also reported, where H_2O_2 was used as an oxidizing agent to convert glucose to GA (Ying Ming Mao, 2015). This process has better separation of the product over fermentation method. Many methods of synthesis of GA reported by oxidation of glucose using cesium-gold nanoparticle as catalyst (Robert Wojcieszak et al, 2016). A potato is being processed for skin peeling to generate about 6-10 % of potato peel waste (PPW). In 2012 in North America, 60% of processed potato production was generated large volume of PPW (NPC, 2012) and it was also proved that it is due to peeling and cutting procedures (Liang and McDonald, 2014). These wastes contain large amount of starch, which can be converted into value added products. (Liang et al.2014, 2015). About 25% of starch is present in PPW apart from non-starch polysaccharides, protein, lipids and lignin (Camire et.al 1997).It was published that lactic acid was produced using PPW by anaerobic sequencing batch fermentation of pure food carbohydrates (Shaobo Liang et al., 2015).

Glucose and other sugars are mostly utilized as an ideal substrate for GA production, however, the feed stack represents 30-40% of total operational cost to produce GA. These are produced by fermentation, metal catalyst and various synthetic approaches proved them cost rising, operational restrictions, critical fermentation process of natural potato peel. In the present study, GA was prepared by hydrolysis of starch obtained from fresh PPW using strong acid (8M HCl). Glucose was further oxidized using silver nitrate to get silver metal powder as a byproduct in simple chemical laboratory reaction. This method is feasible, eco-friendly environment, effective waste management and waste utilization to covert it chemically useful compounds like glucose and gluconic acid(GA).

2. Methods and Materials

2.1 Potato Peel Feed Stock and Chemicals

Holland Potato peel wastes were used for the synthesis of GA and silver metal powder as a by-product. The potato peel wastes were first cleaned with water and weighed. The peels were grinded adding variable amount of water to study the rate of hydrolysis of starch as shown in table-1 below. The potato peel was grinded using food processor machine till it turned into a thick paste. The paste was stored in frozen in an air tight container. All reagents like conc HCl, glucose, silver nitrate, ammonia, Fehling's solution, methanol, ethanol, diethyl ether, potato starch standard was purchased from Synertech Malaysia of reagent grade An easy way to comply with the paper formatting requirements is to use this document as a template and simply type your text into it.

Table 1: Amount of Potato Peel Wastes Grinded with Water

Trials	Weight of potato peel waste (g)	Amount of water added (g)	Total amount of potato peel wastes (g)
1	500	200	700
2	500	100	600
3	500	50	550

2.2. Quantification of starch

For qualitative analysis, the starch was detected using a solution of iodine (I_2) and potassium iodide (KI) in water by visually the color change from light orange-brown color to deep blue. It consists of two different types of polysaccharides that are made up of glucose units which are connected in two different ways. One is the linear amylose and the other is the branched amylopectin (Catharina Goedecke, 2016). For quantitative analysis, the unknown concentration of starch in kilogram of potato peel was calculated and compared with the standard starch of 5%, 10%, 15%, 20%, 25% and 30% of concentration respectively by adding Potassium Iodide and Iodine solution for quantification.

2.3. Hydrolysis of the Starch

Acid hydrolysis was performed using different concentration of HCl (2M, 4M, 6M, 8M, 10M and 12M). The amount of potato peel waste was kept constant. The reactor was incubated in a thermostatic water bath at different temperatures (70°C,75°C, 80°C,85°C,90°C and 95°C, 100°C) for designated time periods 15mins (Ying-Ming Mao ,2015). Samples were withdrawn periodically to test the presence of starch using KI and I_2 solution until no blue-black colour was formed. The mixture was cooled, and the pH of hydrolysed sample was tested. The mixture was neutralised using 0.0025 M NaOH to pH 7 using pH strips paper (M.B. Tasi´c et al., 2009). The neutralised mixture was separated using methanol, ethanol and diethylether separately using 100cm^3 of each. Presence of glucose was tested using Benedict's solution and compared with standard solution of glucose (1% to 10%).

2.4 GA production

GA was obtained by oxidation using 0.1M ammonical solution of silver nitrate of different volume to the methanol extract of 2 cm^3. The mixture was heated (30^{0}C, 40^{0}C, 50^{0}C, 60^{0}C, and 70^{0}C) to get silver metal deposits on the walls of flask. Oxidation was performed using 0.1M ammonical solution of silver nitrate of different volume (0.5,1.0,1.5,2,0, 2.5,3.0 ml) added drop wise to 2 cm^3 of separate sample. The respective samples were left oxidized under reflux at controlled temperature for 10 minutes. Silver was collected and weighed separately. The products were analysed using FTIR. At this point, GA and silver metal powder was formed. GA was separated using solvents water, petroleum ether or tetrahydrofuran and the result of each separations were compared.

2.5. Analytical methods

Potato peel waste was characterised using FTIR. Starch and glucose test was estimated. GA was also identified and characterised using FTIR techniques. Quantification of GA was done by titration method.

3. Results and Discussions

3.1. Characterization of Starch

The FTIR spectroscopy analysis was used to determine the vibrations of functional groups of starch present in the grinded potato peel waste (PPW). The FTIR spectra was recorded using a Perkin Elmer FTIR Spectrometer over the frequency range 4000-400 cm^{-1}. The FTIR spectra of the sample were shown in figure.1. The characteristic peak for PPW confirming the presence of starch as shown in table-2.

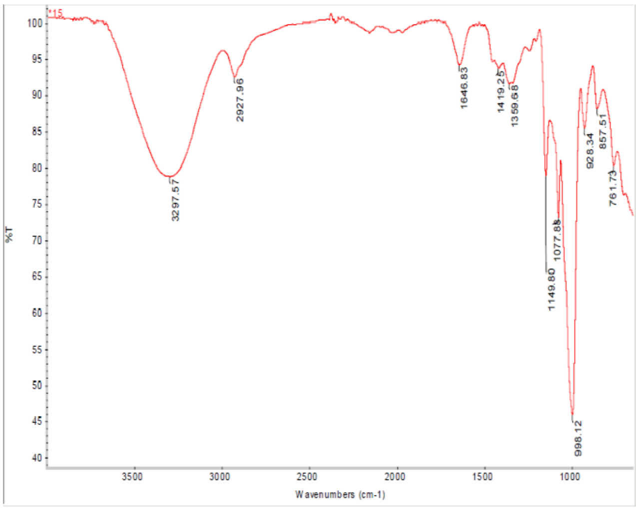

Fig. 1: FTIR Spectrum of starch in Potato Peel Waste

Table 2: Components Present in Starch of Potato Peel Waste

Functional Group	Type of Vibration	Sample, cm^{-1}	Standard, cm^{-1}
Carboxylic acid, R-COOH	Stretching	3297.57	2500-3300
Alcohol, O-H	Bending	1359.68	1330-1420
Tertiary alcohol, C-O	Stretching	1149.80	1124-1205
Primary alcohol, C-O	Stretching	1077.88	1050-1085
Alkene, C=C	Bending	988.12	985 - 995
Cis-alkene, C=C	Bending	731.73	665 - 730

3.2. Quantification of Starch

Starch was quantified using standard solution of I_2 + KI solution. It was obtained between 15-20%, when it was compared with standard starch solution. The color indicator was used for brown to blue black fall in the category of 15-20% of standard starch solution. Starch present in 1 kg of PPW is 150-200 g. PPW contained about 20% of starch compared with 19.4-27.4% reported by (Liang S. 2015) during Lactic acid production from Potato peel waste.

3.3. Acid Hydrolysis

The acid concentration was optimized using different molar solutions of HCl (2M, 4M, 6M, 8M, 10M and 12M) for the respective samples. The 8M HCl was found to be optimum concentration. Temperature was set and optimized at 90°C for hydrolysis of reaction in 15 minutes. Aliquot samples were taken out frequently to ensure the complete hydrolysis. Excess of HCl was neutralized with NaOH. Color changes and its observations were listed in a table 3 below.

Table 3: Effect of HCl concentration on Acid Hydrolysis (20 minutes)

Concentration of HCl (M)	Volume of HCl	Test for Starch Addition of (KI + I_2)		
		Sample 1	Sample 2	Sample 3
2	10	Blue	Blue	Blue
4	10	Blue	Blue	Blue
6	10	Light Blue	Light Blue	Light Blue
8	10	No color change	No color change	No color change
10	10	No color change	No color change	No color change

As temperature increased the α 1,4 and α 1,6 glycosidic bond cleaved to break and the hydrogen bonding between glucose molecules of the polymeric structures started to weaken at.90^0C - 95^0C. It was interpreted as the optimum temperature to break the glycosidic bond. Progeress of reaction was studied using I_2/KI solution for the disapperance of blue-black colour.(Wang S[1], Copeland L, 2015), as shown in table 4.

Table 4: Effect of Temperature on Acid Hydrolysis (20 minutes)

Tempera-ture(°C)	Volume of HCl (8M)	Test for Starch Addition of (KI + I_2)		
		Sample 1	Sample 2	Sample 3
60	10	Blue	Blue	Blue
70	10	Blue	Blue	Blue
80	10	Light Blue	Light Blue	Light Blue
90	10	No Color change	No Color Change	No Color change
100	10	No Color change	No Color change	No Color change

Concentrated acid is required to break the polymer structure into monomer molecule. Hydrochloric acid (8M) required for the complete disappearance of blue-black color at the reaction time of 15 minutes (Adenise Lorenci Woiciechowski[1]; Saul Nitsche[1]; Ashok Pandey[2] and Carlos Ricardo Soccol, 2002). The data obtained with PPW under acidic conditions is shown in Table 3. Evidently the best acid hydrolysis conditions were optimized using 8M hydrochloric acid with reaction time of 15 minutes. The temperature of 90°C has resulted 200 g of reducing sugars from 1Kg of PPW. Acid hydrolysis has more advantages over enzymatic hydrolysis in terms of cost of chemicals and less energy consumption was reported (Adenise Lorenci Woiciechowski[1]; Saul Nitsche[1]; Ashok Pandey[2] and Carlos Ricardo Soccol, 2002).

3.4. Separation of Glucose

The content of hydrolysis was neutralized. Glucose obtained from hydrolysis process was found to be best separated using methanol as a solvent compare to ethanol and diethyl ether for all three samples as per table 5.

Table 5: Comparison of Solvents Used in Separation of Glucose

Samples	Volume of hydrolyzed PPW (ml)	Solvents used	Solubility	Observation
A	150	Ethanol, C_2H_5OH	Soluble	Less salts formed
B	150	Methanol, CH_3OH	Very Soluble	More salts formed
C	150	Diethyl ether, $(C_2H_5)_2O$	Slightly Soluble	Less residue formed

Methanol gave better separation with high amount of salt separation among the three above solvents. Due to its greater polar character methanol separated glucose more effectively than the other two solvents. As glucose contain polyhydroxy group both methanol and ethanol can separate glucose from salt. However, due to the more non-polar nature diethlyether is a poor solvent. Due to polyhydroxyl group glucose is found to be highly soluble is Methanol. (Angeles Farran et al, 2015)

3.5. Production of Gluconic acid

Presence of glucose was confirmed using Benedicts reagent. Color changes from blue to red confirmed the conversion of presence of glucose. Ammonical solution of silver nitrate was used as an oxidizing agent to oxidize glucose to gluconic acid. Silver formed as a byproduct and collected from the walls of the flask. 0.30 grams of silver was obtained from 0.34g of silver nitrate upon oxidation reaction. Tollen's reagent responds with aldehyde, and converts it to carboxylic acid . The elemental silver precipitates out of solution, occasionally onto the inner surface of the reaction vessel, giving a characteristic "silver mirror". GA was extracted from the reaction mixture using water, petroleum ether and tetrahydrofuran. Water is proven to be the best solvent when kept for 24hours in separating funnel. The carboxylate ion on acidification will give its corresponding carboxylic acid as shown in Figure 2.

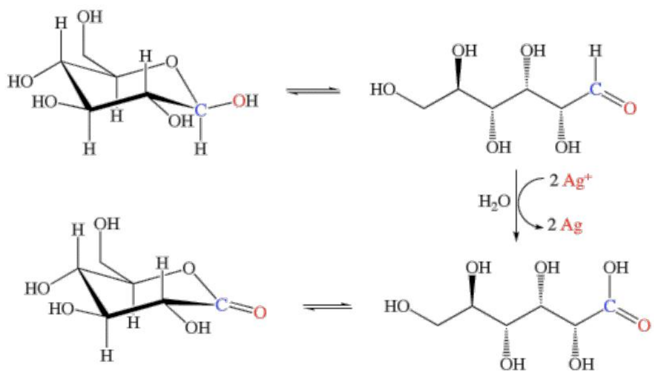

Fig. 2: Oxidation Reaction of Glucose with silver (I) ions

Silver (I) ion can be used as homogenous catalyst during oxidation of aldehydes in water. More than 50 aliphatic and Aromatic aldehydes, were test for oxidation reaction using Ag(I) ions with high yields ((Mingxin Liu,Haining Wang,Huiying Zeng,and Chao-JunLi). Table 6 indicates percentage of products form during chemical reactions.

Table 6: Amount of Starch, Glucose, Gluconic acid and Silver formed

S.No	PPW+ Water ratio (g)	Amount Starch (%)	Amount of glucose (%)	% conversion Gluconic acid	% silver
1	5:2	20	80	69.992	0.3
2	5:1	20	70	64.899	0.26
3	5:0.5	20	70	63.761	0.25

Acid hydrolysis is more effective when the ratio of PPW to water is more as the acid dissociation rate increases with dilution. There is not much significant change with 5:1 and 5:0.5 ratio (Marija B. Tasi ´c, Budimir V. Konstantinovi ´c, Miodrag L. Lazi´c, Vlada B. Veljkovi). As the reaction time is constant for 15 minutes, the amount of glucose formed is more in diluted sample. With the result GA production is greater in 5:2 PPW to water ratio. Maximum silver is formed in the PPW to water (5:2) ratio. The byproducts like silver, ammonia and water are produced and recycled for further use, this is greener process compared to other conventional process. Silver (I) ions oxidizes glucose and get reduced to silver mirror .Silver formed can be purified and reused.

3.6. Separation and Purification of Gluconic Acid

The products of oxidation were separated. Silver formed as silver mirror were deposited on the walls of reactor. Ammonia formed was neutralized using 0.05 M HCl. Excess of silver ion precipitated with HCl as silver chloride and ammonium chloride and settled down the flask.

3.7. Characterization of Gluconic Acid

The FTIR analysis spectroscopy was used to determine the vibration of functional groups of GA present in the remaining residue remains from the oxidation process. Characteristic peak of carboxylic acid group is present at 1633.67cm^{-1} and also between 3200 cm^{-1} to 3300 cm-^{1} due to OH group of acid. GA formed was titrated against 0.1M NaOH. About 70% of GA is quantified using titration method.

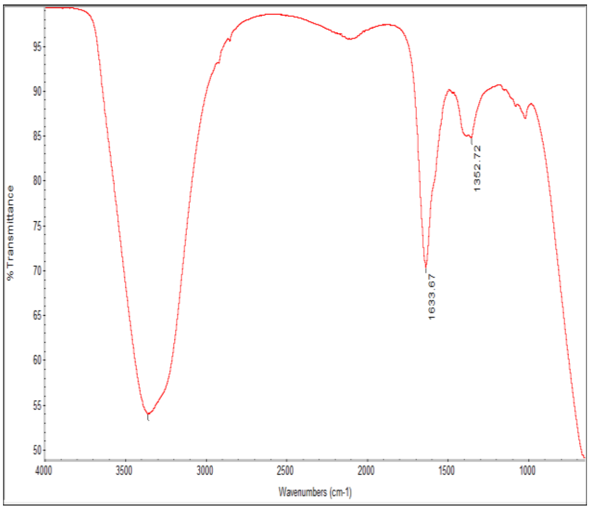

Fig.3: The FTIR spectrum of Gluconic acid

Table 7: Data Tabulated Comparing Produced Gluconic acid acid and Standard Gluconic acid

Functional Group	Type of Vibration	Sample, cm^{-1}	Standard, cm^{-1}
Carboxylic acid group	Stretch	1633.74	1630 - 1690
Hydroxyl group	Stretch	3200	2800 - 3300

4. Conclusion

PPW and other domestic waste can be converted into value added products by simple chemical reactions. Acid hydrolysis is more economical compared to enzymatic hydrolysis. In terms of time acid hydrolysis has more advantages due to shorter hydrolysis time of 15 minutes. Tollen's reagents is a very good oxidising agent to oxidise glucose giving silver as a by-product. Formation of solid silver saves the separation cost during production. Water and Ammonia formed during reaction can be easily distil off and get separated. Production of value added products like GA, silver, ammonia and water from waste can close the chemical loop for sustainable development. . The formation of GA required mild temperature of 40°C - 50°C with the reaction time of 10 minutes. Silver nitrate required to oxidise is very low amount so more economical process. The GA yield was calculated as 68 ± 5% and the amount of silver metal powder was obtained 0.3±0.05 % per kilogram of potato peel waste.

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