Processing and Utilization of Bio-Flocculant from Dent Corn in Food Wastewater

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Abstract

In the present research, native starch was prepared from dent corn *(Zea mays* L.) and the prepared native starch was modified by phosphorylation to get biodegradable bio-flocculants. The processed modified starch bio-flocculants were applied in the treatment of food wastewater. The physico-chemical properties of dent corn such as protein, fiber, fat, moisture, carbohydrate and ash contents were determined by AOAC (2000) method. The physico-chemical characteristics of native starch and modified starch (bio-flocculants) such as iodine test, bulk density, the degree of substitution, swelling power, amylose and amylopectin contents were determined. The flocculation efficiency of the processed bio-flocculants by using ferric laurate suspension and the optimal transmission percentage was investigated. The properties of food wastewater such as pH, colour, turbidity, total solids, dissolved solids and suspended solids before and after treatment with processes bio-flocculants were also determined.

Key words: Dent Corn, native starch, phosphorylation, modified starch, food wastewater

Introduction

Dent corn (*Zea mays* L.) is a variety of maize or corn with high soft starch content. It received its name because of the small indentation ("dent") at the crown of each kernel on a ripe ear of corn. It is a corn variety with kernels that contain both hard and soft and become indented at maturity. Dent corn is mainly used for making food, animal feed, and industrial raw sources. Yellow dent corn is primarily used for animal feed and for the production of ethanol and cooking oils. Dependent on their starch content, some yellow dent corn hybrids are grown and used in the production of food for human consumption. The production of maize crops is regularly in Northern Shan State, Mandalay Region and Ayeyarwaddy Region in Myanmar (http:// en.wikipedia.org/wiki/Dent_corn).

Starch is a polysaccharide originated from plants as renewable resources. It is an imperative carbohydrate for human and plays an important role in the food processing and can be modified to make it ideal for a number of uses. Starch is a natural carbohydrate consisting predominantly of two types of glucose namely amylose and amylopectin. Amylose is essentially a linear polymer of glucose linked together by α-1,4 bonds while amylopectin is a branched polymer consisting of both α 1,4 and α-1,6, glycosidic linkages, with the latter found at branch points. The amylose/amylopectin ratio, which is a function of the starch source, is significant as it affects some physicochemical properties of starch and in turn, influences its functionality and eventual applications (Cui, 2005).

Generally, amyloses have good arrangement structure due to the fact that they pack closely or form strong, rigid and insoluble material, whereas amylopectins have good thickening properties because they are readily soluble in aqueous systems. The proportion of amylase in starch depends on its botanical source and this may vary from 10% to 30% (Gilliard, 1987).

Starch can be modified by using inexpensive methods with the purpose of increasing their stability against excessive heat, acid, shear, time, cooling or freezing; of changing their texture; of decreasing or increasing their viscosity. Modified starches can be applied for food

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processing as thickener, stabilizer or emulsifier; for pharmaceutical fields as a disintegrant; for coated paper as binder (http://en:wikipedia.org/wiki/modified starch).

With an increasing awareness of environmental problems in recent years, versatile application has been found for starch in many areas such as flocculant, adhesives, biodegradable plastics and drug- delivery systems. Starch itself may be used as flocculant. As a flocculant, starch generally may be modified in order to obtain products with better flocculation efficiency. The modification can be carried out by chemical methods by introducing small amounts of ionic or hydrophobic groups into the molecules which change flocculation performance. Depending on whether can build anionic or cationic functional groups into the starch change, can get anionic or cationic flocculants. The starch derivative of produced with the proper reagent is non-toxic and indeed biodegradable (Hameed, 2014).

Phosphorylation is generally performed by treatment of granular starch with multifunctional reagents capable of forming either ether or ester intermolecular linkages between the hydroxyl groups of starch molecules. The main reagents used for phosphorylation are sodium trimetaphosphate, mono-sodium phosphate, sodium tripolyphosphate, phosphorly chloride, mixture of adipic acid, acetic anhydride, and vinyl chloride (Polnaya, 2012).

Compared to other industrial sectors, food industry requires more water, used in throughout most of the plant operations, such as production, cleaning, sanitizing, cooling and material transport, among others. This wastewater contains environmental concerned parameters such as suspended and dissolved solids, turbidity, chemical oxygen demand (COD), biochemical oxygen demand (BOD), colour and dye. In addition to, food processing waste industry also contain large amount of organic materials such as proteins, carbohydrates and lipids (Shivani, 2017).

Flocculation is a process of bringing together smaller particle to form larger particles, and settling of colloidal particles from stable suspensions caused by the addition of chemicals known as flocculants in minute quantities. It is well known that the use of organic and inorganic flocculants can improve the efficiency of solid/liquid separation in wide range of papermaking, waste water treatment and mineral processing industries. Water-soluble synthetic polymers have a disadvantage of non-biodegradability and cost effective. Thus the demand for effective, cheap and environmentally friendly natural flocculants for wastewater treatment is increasing (Pang, 2013).

The main objective of this research work is the preparation of bio-flocculant from dent corn, sustainable agricultural resource for use as bio-flocculant in food wastewater. The specific objectives of this research work are:

- to study the nutritive values of dent corn
- to extract the native starch from dent corn
- to modify the prepared native starch by phosphorylation
- to study the physico-chemical properties of native and modified starch
- to study the flocculation efficiency of processed flocculant.

Materials and Methods

Materials

In this research work, dent corn was collected from Tuka Chan Thar Shop, Chan Aye Thar Zan Township, Mandalay Region. Sodium tripolyphosphate (Analar Grade, BDH England), sodium sulfate (Analar Grade, BDH England), sodium hydroxide pellet (Analar Grade, BDH England), lauric acid (Analar Grade, China) and ferric chloride (Analar Grade, China), were purchased from Able Chemical Shop, 76th Street between 27th & 28th Street, Chan Aye Thar Zan Township, Mandalay Region. Food waste liquor was collected from Win Win Taut (Mont Ti and Mohinga Industry), Gway Thee Gon Village, Mandalay Region.

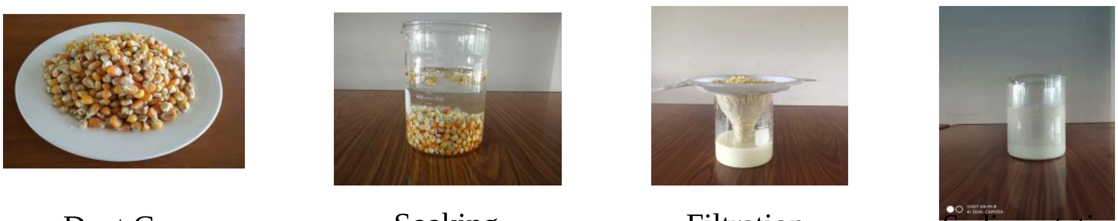
Methods

Preliminary Preparation and Nutritive Values of Dent Corn

Dent Corn husks were firstly removed and washed with water to remove some trash. After that, dent corn grains were gathered from the cob by hand. The nutritive values of dent corn such as moisture content, ash content, crude fiber content, crude fat content, protein content, carbohydrate content were determined by Association of Official Analytical Chemists (AOAC Methods , 2000).

Preparation of Native Starch

Dent corn grain 100 g was thoroughly washed to remove foreign materials. Then, the grains were steeped in 500 ml of water with 15 ml of 0.1N NaOH solutions for 24 hours and filtered and washed with water for two times. The grains were crushed using a blender and enough quantity of water was added to form slurry. The slurry was filtered through a filter paper (1.25 cm) to obtain starch solution. The native starch was prepared from starch solution by sedimentation and decantation of the supernatant fluid. Finally, the obtained starch was dried in an oven at 50°C for 1 hour and stored in an air tight container for further use.



Dent Corn   Soaking   Filtration   Sedimentation

Figure (1) Preparation of Native Starch

Preparation of Modified Starch by Phosphorylation (Cross -Linking)

Sodium tripolyphosphate (STPP), 7 g was dissolved in 100 ml of water containing 7 g of sodium sulfate. The pH of the solution was adjusted to 11 by adding 10% aqueous HCl or NaOH. 100g of native starch was dispersed in the solution. Slurry was stirred for 60 min at room temperature and dried to 10-15 % moisture at 50˚C in an oven. To affect the phosphorylation, the dried starch cake in the dish was heated for 2 hr at 130˚C in an oven. The phosphorylated starch was cooled to ambient temperature and washed with clean water for three times and then dried at 50°C. The dried modified starch (bio-flocculant) was stored in the air tight container.

Effect of Ingredients on the Characteristics of Modified Starch

Effect of Concentration of Sodium Tripolyphosphate (STPP)

To determine the most suitable concentration of sodium tripolyphosphate used as phosphorylating agent, the concentrations were varied in the range of (6 to 8) % while the other variables were fixed using the same method mentioned above. The effect of concentration of STPP on the degree of substitution, colour and yield percentage of modified starch was determined.

Effect of Reaction Temperature

The effect of reaction temperature on the degree of substitution, colour and yield percentage of modified starch was investigated as the same procedure mentioned above except variable of reaction temperature in the range of (120 to 140) ˚C.

Effect of Reaction Time

The effect of reaction time on the degree of substitution, colour and yield percentage of modified starch was carried out as the same procedure mentioned above except variable of reaction time in the range of (40 to 80) min.

Physico-chemical Characteristics of Processed Native Starch and Modified Starch

The Physico-chemical characteristics of native starch and modified starch such as moisture content (AOAC method 2000), bulk density (Musa, 2010), swelling power, iodine test (Lugo’s iodine test), degree of substitution (DS) (Rahim, 2013) and amylase and amylopectin content (Williams, 1990) were determined.

Determination of Flocculation Efficiency of Processed Bio-Flocculant

Preliminary Preparation of Ferric Laurate Suspension

Lauric acid (1g) was dissolved in 100 ml of distilled water and 10 % NaOH and 10% ferric chloride solution were added into it to get pH 10 and heated at 60-70˚C by stirring for 5 min. Then it was cooled down to room temperature (Hebeish, 2013).

Preliminary Preparation of Bio-Flocculant Solution

Modified starch (1g) was mixed with 90 ml of distilled water by stirring and heating at 100˚C for 10 min and adjusted to 100 ml of distilled water (Hebeish, 2013).

Determination of Flocculation Efficiency

Ferric laurate suspension (50ml) was placed in a beaker and different doses of bio-flocculant solution (1, 3 and 5) ml was added into the above beaker and stirred at 200 rpm for 10 sec. Then its liquor was settled for 20 min and supernatant liquid was measured for the transmission of suspended solution (%) at 620 nm and the results are recorded.

Treatment of Food Wastewater by using Process Bio-flocculant Solution

Effect of Bio-flocculant Dose on the Characteristics of Treated Food Wastewater

The effect of bio-flocculant solution dose on the characteristics of treated food wastewater was conducted using various bio-flocculant solution doses in the range of (2 to 4) ml for 100 ml of food wastewater at constant pH of flocculation medium. The mixture was agitated with magnetic stirrer at a constant speed of 500 rpm at room temperature for 10 min contact time. After 10 min contact time, the treated food wastewater samples were settled. The settling time and removal percentage of suspended solids and dissolved solids of treated food wastewater were determined and recorded.

Physico-chemical Characteristics of Food Wastewater before and after Treatment with Processed Bio-flocculant

Physico-chemical characteristics of food wastewater such as pH (pH meter, HANNA instruments, waterproof tester), colour (digit logging colorimeter, HACH - DR/890), turbidity (digit logging colorimeter, HACH - DR/890), total solids (American Public Health Association, 1988), dissolved solids and suspended solids (digit logging colorimeter, HACH -DR/890) were determined and recorded.

Results and Discussion

The nutritive values of dent corn were determined and comparatively mentioned with literature value in Table (1). From the results in Table (1), it could be seen that carbohydrate content on dent corn was 80. 20 % and protein content was lower than literature value and thus it was better for starch extraction. Another crucial component is fat content. The role of lipid is that it can affect the swelling properties of starch. Quite low content of fat was found in dent corn and also lower than that of literature value. All these compositions could be depended on cultivar, region and climatic conditions.

The effect of concentration of sodium tripolyphosphate (STPP) on the characteristics of modified starch is shown in Table (2). It was observed that phosphorylation of starch at pH 11, with 7 % STPP, reaction temperature 130˚C for reaction time 60 min, provided the highest degree of substitution (DS), 0.05 (indicated the highest level of cross-linking), swelling power and solubility. Thus it was the most suitable concentration of sodium tripolyphosphate for preparation of the flocculant. Furthermore, effect of reaction temperature on the characteristics of modified starch was studied and shown in Table (3).

The reaction temperature 130˚C was designated as the most suitable temperature due to the highest degree of suspension with the highest yield. From the result in Table (4), It was observed that reaction time 60 min was the most suitable time which also provided the highest degree of suspension and the longer the reaction time, the lower the DS was observed. It was clearly determined that phosphorylation of starch at pH 11, with 7 % STPP, reaction temperature 130˚C reaction time 60 min, provided the highest DS, 0.05 (indicated the highest level of cross-linking), swelling power and solubility. Thus it was the most suitable condition for preparation of the best bio-flocculant. The yield percentage of native dent corn starch was 68% but 87.5% for phospholyated modified starch.

The physico-chemical characteristics of processed native and modified starch were comparatively studied and described in Table (5).The native starch had 10.5 % moisture content and modified starch had 8.9 % moisture. The different in moisture contents will depend on the extent of drying. Swelling capacity of phosphorylated starch was increased with increased in DS. These improvements facilitated a more enhanced holding capacity as flocculant. Bulk density of native starch was 0.5 g/ml and modified starch was 0.68 g/ml. Bulk density is a function of particle size of starch; particle size is inversely proportional to density.

The effect of bio-flocculant solution dose on the transmission percentage of ferric laurate suspension was studied. The optimal transmission percentage was occurred using 3 ml of bio-flocculant solution dose per 50 ml of ferric laurate at pH 6. The transmission was 86.8% and hence it was emphasized the processed bio-flocculant undergo better flocculation efficiency on this suspension as shown in Table (6).

The effects of bio-flocculant solution dose on the percentage reduction of suspended solids and dissolved solids of food wastewater as shown in Table (7). The highest removal efficiency was 90.87% and 85.47% within 30 min settling time, by using 3ml of 3 % flocculant dose per 100 ml of food wastewater. The characteristics of food waste liquor before and after treatment with processed bio-flocculant are shown in Table (8). It could be clearly seen that the pH of treated food wastewater increased and dramatically decreased in colour, turbidity, and total solids of food wastewater due to effectiveness of environmentally friendly bio-flocculant.

Table (1) Nutritive Values of Dent Corn

Sr. No.	Compositions	Dent Corn	Literature Value*
1	Moisture (% w/w)	8.0	-
2	Ash (% w/w)	1.08	1.3-1.6
3	Protein (% w/w)	2.23	3-5.5
4	Crude fiber (% w/w)	2.01	2
5	Crude fat (% w/w)	3.0	3.3-5.6
6	Carbohydrate (% w/w)	80.20	70-80

*(Peplinski, 1991)

Table (2) Effect of Concentration of Sodium Tripolyphosphate (STPP) on the Characteristics of Modified Starch

Amount of native starch = 100g Temperature = 130˚C Catalyst = 7 % Na_2SO_4

pH = 11 Reaction time = 60 min

Sample No.	Concentration of STPP (% w/w)	Characteristics		Yield Percent %(w/w)
		Degree of Substitution	Colour	
1	6	0.027	Pale yellow	86.0
2	7*	0.050	Pale yellow	87.2
3	8	0.025	Pale yellow	86.0

*****the most suitable concentration of STPP

Table (3) Effect of Reaction Temperature on the Characteristics of Modified Starch

Weight of native starch = 100g Amount of STPP = 7 g Catalyst = 7 % Na_2SO_4

pH = 11 Reaction time = 60 min

Sample No.	Temperature (˚C)	Characteristics		Yield Percent % (w/w)
		Degree of Substitution	Colour	
1	120	0.031	Pale yellow	85.8
2	130*	0.050	Pale yellow	87.5
3	140	0.050	Pale yellow	77.2

*****the most suitable reaction temperature

Table (4) Effect of Reaction Time on the Characteristics of Modified Starch

Weight of native starch = 100g Amount of STPP = 7 g Catalyst = 7 % Na_2SO_4

pH = 11 Temperature = 130˚C

Sample No.	Reaction time (min)	Characteristics		Yield Percent % (w/w)
		Degree of Substitution	Colour	
1	40	0.028	Pale yellow	84.8
2	60*	0.050	Pale yellow	87.5
3	80	0.042	Pale yellow	84.2

*the most suitable reaction time

Table (5) Physico-chemical Characteristics of Processed Native Starch and Modified Starch

Sr. No.	Characteristics	Native Starch	Modified Starch
1	Moisture, (%w/w)	10.5	8.9
2	Degree of substitution	0.004	0.05
3	Iodine test	positive	positive
4	Bulk density, (g/ml)	0.50	0.68
5	Swelling power, (g/g)	14.8	17.6
6	Amylose (%)	25	20
7	Amylopectin (%)	70	73
8	Yield percent (%w/w)	68	87.5

Figure (2) Native Starch

Figure (3) Modified Starch

Table (6) Effect of Processed Bio-flocculant Dose on the Percentage Transmission of Suspended Solution

Suspended solution (ml) = 50 ml

Suspension medium = Ferric Laurate (pH= 6)

Sample	Bio-flocculant Dose (ml)	Transmission of Suspended Solution (%)(620nm) (Ferric Laurate)
1	1	83.1
2	3*	86.8
3	5	52.8

*the most favourable bio-flocculant dose

Figure (4) Treatment of Food Wastewater by using Processed Bio-flocculant

I = Food wastewater

II = treatment of food wastewater using 1ml bio-flocculant dose

III = treatment of food wastewater using 3ml bio-flocculant dose

IV = treatment of food wastewater using 5ml bio-flocculant dose

Table (7) The Effect of Bio-flocculant Solution Dose on the Characteristics of Treated Food Wastewater

pH of food wastewater = 5.4

Concentration of bio-flocculant solution = 3%

Sample No.	Bio-Flocculant Dose (ml/100ml)	Characteristics of Food Wastewater			
		Suspended Solids (mg/l)	Removal Efficiency of Suspended Solids (%)	Dissolved Solids (mg/l)	Removal Efficiency of Dissolved Solids (%)
1	2	980	74.07	965	67.40
2	3*	345	90.87	430	85.47
3	4	365	90.34	454	84.66

*the most suitable bio-flocculant dose

Table (8) Characteristics of Food Wastewater before and after Treatment with Processed Bio-flocculant

3% bio-flocculant solution dose = 3 ml/100ml of food wastewater

Sr. No.	Characteristics	Food Wastewater	
		Before Treatment	After Treatment
1	pH	5.4	6.2
2	Colour (Pt-Co)	800	300
3	Turbidity (NTU)	710	-
4	Total solids (mg/l)	6740	775
5	Dissolved solids (mg/l)	2960	345
6	Suspended solids (mg/l)	3780	430

Conclusions

Due to high in carbohydrate content, 80.20% in dent corn, it is invaluable source of starch. Phosphorylation improved the some unstable properties of native dent corn starch. Swelling power, amylopectin content, degree of substitution and bulk density became higher due to modification. The highest removal efficiency of suspended solids and dissolved solids were 90.87% and 85.47% by using 3 ml of 3 % flocculant dose per 100 ml of food wastewater with 30 min settling time. Thus, it can be used as effective biopolymer based flocculant in treatment of food wastewaters.

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