CASSAVA STARCH-DERIVED NANOCARBON DOTS BY HYDROTHERMAL CARBONIZATION FOR DISTILLERY SPENT WASH TREATMENT

A Research Presented to

The Faculty of the College of Engineering and Technology

University of St. La Salle

Bacolod City

In Partial Fulfillment

Of the Requirements for the Degree

Bachelor of Science in Chemical Engineering

HANNAH MAE P. BACROYA

JAN HARRY A. JONDANERO

LUIGI P. LIMSIACO

September 28, 2019

UNIVERSITY OF ST. LA SALLE

COLLEGE OF ENGINEERING AND TECHNOLOGY

September 28, 2019

APPROVAL SHEET

This thesis entitled **"CASSAVA STARCH-DERIVED NANOCARBON DOTS BY HYDROTHERMAL CARBONIZATION FOR DISTILLERY SPENT WASH TREATMENT"** presented by **HANNAH MAE P. BACROYA**, **JAN HARRY A. JONDANERO**, and **LUIGI P. LIMSIACO**, in partial fulfilment of the requirements for the degree of **Bachelor of Science in Chemical Engineering** of the University of St. La Salle has been evaluated and approved by the panel of evaluators.

PANEL OF EVALUATORS

MARIE THERESE BERNADETTE F. SALES, RChE, PhD

Chair

FELIX R. QUERUBIN, RChE, MEE

Member

CHRISTER JOHN M. UY, RChE, MEE

Member

MARY ANN T. PANDAN, RChE, PhD

Adviser

ACKNOWLEDGEMENT

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF EQUATIONS

ABSTRACT

Distilleries are industries with various applications in different fields such as in beverages, pharmaceutical, and petroleum. However, distilleries are also considered as one of the most polluting industries where their effluents pose serious water pollution threats. This study aims to produce nanocarbon dots from cassava starch using microwave-assisted hydrothermal carbonization for the treatment of distillery spent wash. The spent wash treatment focused on the removal of BOD, color, TSS and the neutralization of pH and the extent of distillery spent wash treatment was compared with commercially available activated carbon. Extraction of starch from cassava showed that cassava contained 10.38% moisture and 21.22% starch. After hydrothermal treatment of one gram of starch dispersed in 25 cm^3 of distilled water with 7 cm^3 of 2M sulfuric acid using 700 W microwave oven for 3 min the solution turned yellowish in color and showed bright blue luminescence under UV light. The hydrochar from the hydrothermal treatment was characterized using Field Emission Scanning Electron Microscope, and the results showed that the nanocarbon dots were quasi-spherical in shape and had an average particle diameter of 62.86 nm. Three sand filter column set-ups were made to compare the extent of distillery spent wash treatment where set-up A contains activated carbon, set-up B contains the hydrochar and set-up C only contains sand. After filtering the spent wash sample using the set-ups there was an observable decrease in the measured parameters. Based on the t-test conducted at an alpha of 0.05, the P value for BOD, color, pH, and TSS were 0.038, 0.016, 0.656, and 0.067 respectively showing that there is a significant difference in the extent of removal of BOD and color from distillery spent wash between the nanocarbon dots and the commercially available activated carbon but no significant difference can be seen for the neutralization of pH and removal of TSS. The results of this study show that nanocarbon dots are effective adsorbing agents for filter columns in the treatment of distillery spent was, however it is recommended that prior treatment of the spent wash is required in order to improve the efficiency of the process and for the effluent to comply with environmental standards.

INTRODUCTION

This chapter provides a conceptual background and discusses selected studies which are related to the study. It provides a basic understanding on the production of cassava starch-derived nanocarbon dots using hydrothermal carbonization and its effect specifically on distillery spent wash. This chapter also discusses the objectives, scope and limitations, significance of the study, and the definition of terms.

Background of the Study

Distilleries are chemical industries that employ distillation processes to produce ethanol and other by-products which have grown extensively because of its widespread applications in various industries such as beverages, pharmaceutical and petroleum industries (Kharayat, 2012). In the Philippines, there are 10 accredited bioethanol distilleries according to the Department of Energy. Four of these bioethanol distilleries are situated in the Negros Island mainly because the island is a major producer of sugar and therefore, molasses as a by-product which is the main raw material used in fermentation for ethanol production.

However, distilleries are considered as one of the most polluting industries as 88% of its raw materials are converted into waste and discharged into bodies of water causing serious water pollution. It is estimated that for every liter of alcohol produced, about 15 liters of spent wash is released (Ravikumar et al., 2007). The spent wash generated from distilleries is dark brown in color and has a high temperature, low pH of about less than 4.0-4.5 and, high chemical oxygen demand (COD) ranging from 80,000

to 100,000 mg/L and biochemical oxygen demand (BOD) of 40,000 to 50,000 mg/L (Kharayat, 2012). According to the study by Kharayat (2012), the high amount of COD and BOD are attributed to the presence of organic compounds such as polysaccharides, reduced sugars, lignin, etc. from the manufacturing process. The amount of inorganic substances in the spent wash such as nitrogen, potassium, phosphates, calcium, and sulfates are also very high (Melamane et al., 2007 cited in Kharayat, 2012). According to Kharayat (2012) in India, various technologies have been tested for the treatment of spent wash, however, none of such technologies have been found effective and economically viable to achieve the standards set by the Indian Government Central Pollution Control Board.

The disposal of distillery effluent, especially the spent wash, is extremely detrimental to the quality of water where these effluents are discharged. The highly colored nature of the effluent blocks sunlight thus reducing oxygenation of water from photosynthesis and the high pollution load of inorganic substances can result to eutrophication of the contaminated water sources. Furthermore, the distillery effluent's high BOD and COD accelerates bacterial growth and consumes oxygen in the water (Kharayat, 2012).

Due to the hazardous impacts of industrial effluents to the bodies of water, the Philippine government has set standards regulating the quantity of harmful substances found in the wastes discharged by different industries as an action towards preventing, controlling and abating water pollution. The Department of Environment and Natural Resources (DENR) Administrative Order No. 2016-08 (DAO 2016-08) has set the important parameters that must be controlled for the effluent of ethanol producing

industries, which under the PSIC Code 20111 and 20114, include temperature, pH, BOD, Total Suspended Solids (TSS), ammonia, nitrate and sulfate. The standards for the parameters for effluents discharged to water bodies intended for a Class C Water Body Classification which are those bodies used for agriculture, irrigation, livestock watering, and propagation and growth of fish and other aquatic resources are as follows: a temperature change of 3C^{o}, the pH should range from 6 to 9.5, and the maximum amounts of BOD, TSS, ammonia, nitrate and sulfate are 50mg/L, 100 mg/L, 0.5 mg/L, 14 mg/L and 550 mg/L respectively as well as setting a standard for color of 150 True Color Units (TCU).

In order to conform by the set standards, ethanol-producing industries have been required to employ appropriate wastewater treatment methods. The usual methods used for distillery effluent treatment includes physical, chemical, and biological approach prior to disposal. Physical methods- which includes screening, flotation, sedimentation and adsorption-are for the removal of color, some organic pollutants, and TSS. Chemical methods are used to oxidize wastewater compounds to CO_2 and water. The biological methods can eliminate biologically removable organics by the application of biological systems.

Of the various wastewater treatment methods, adsorption is known to be very highly efficient according to Subha et al. (2015). Their study also defined adsorption as the result of the unsaturated and unbalanced molecular forces that are present on every solid surface. Adsorption is commonly used because it exhibits fast kinetics, high capacity, and preferable sorption towards wastewater.

According to Mukherjee et al. (2007), the most common adsorbent used is activated carbon (AC). Mukherjee et al. Added that extensive studies have shown that AC is very efficient in the adsorption of numerous bio-resistant organic pollutants from aqueous system. The study added that AC was even recommended by the United States Environmental Protection Agency (USEPA) as one of the best available technology. Furthermore, the USEPA emphasized the capital cost saving of using adsorption contactor such as the downflow gravity contactor. However, the use of AC is highly expensive for developing countries like Philippines. Locally available and cheaper adsorbents for the replacement of AC is continuously sought. With this, Villegas et al. (2016), recommended the use of nanoparticles as a substitute for AC.

Nanocarbon dots (NCDs) are spherical, nontoxic, biocompatible, and discrete particles less than 10 nm in diameter. Because of its ultra-compact nano size, it has gained interest from researchers in the recent years. Compared to AC, NCDs have a larger surface area which requires less material and cheaper cost (Mishra et al., 2018).

Synthesis of NCDs can be carried out using various processes such as laser ablation, electrochemical exfoliation, acidic oxidation, and hydrothermal treatments (Jelinek, 2018). Hydrothermal Carbonization, also known as HTC, is an induced coalification process which converts raw biomass, such as agricultural residues, into a coal-like product, called hydrochar, which has a high carbon content and high calorific value (Lucian, 2017). It is widely used in different carbonization researches due to its high carbon efficiency under low temperature conditions, low cost, environmentally friendly, and non-toxic route to produce carbon dots which later may be used as precursors of activated carbon for wastewater pollution remediation.

Recent studies give preference on microwave HTC over conventional HTC since according to Guiotoku et al. (2009) it is an innovative, technologically efficient and environmentally friendly method. Furthermore, according to Nizamuddin et al. (2018), hydrothermal carbonization with microwave heating makes thermal treatment greener, faster, and more efficient. Microwave-assisted HTC yields carbon-rich materials with oxygen substituted components suspended in an aqueous solution (Nizamuddin et al. 2016)

Biomass, the common raw material for Hydrothermal Carbonization, is the total mass of plant and animal organisms present in ecological systems. Examples of biomass include sugar, starch, lignocellulose, and oils or fats (Krysanova, 2017).

Starch is a carbohydrate from agricultural raw materials that is made up of large numbers of carbon molecules. Cassava, a good source and mainly constituted of starch at about 20-30%, is planted each year in approximately 120,000 hectares of agricultural land in the Philippines and producing about 1.8 million tons of cassava roots (Bacusmo, 2001). It is available locally and all-year round. Starch can be extracted from cassava in various ways. Common methods include the grinding of raw material, mixing with water, filtering and settling in order to produce starch such as discussed in Kaur et al. (2016).

Statement of the Problem

The study aims to produce nanocarbon dots from cassava starch using hydrothermal process. Specifically, the study aims to answer the following questions:

1. What is the percent yield of cassava starch from cassava?
2. What is the percent yield of nanocarbon dots from cassava starch?

3. What is the characteristic of the nanocarbon dots that will be produced in terms of:
    a. diameter?
    b. surface area?
    c. shape?
4. Is there a significant difference in the extent of distillery spent wash treatment of nanocarbon dots from the activated carbon in terms of:
    a. BOD removal?
    b. color removal?
    c. pH neutralization?
    d. TSS removal?

Hypothesis

Below are the null hypotheses of the study:

1. There is no significant difference between the nanocarbon dots that will be produced and the activated carbon in terms of BOD removal of the distillery spent wash.
2. There is no significant difference between the nanocarbon dots that will be produced and the activated carbon in terms of color removal from the distillery spent wash.
3. There is no significant difference between the nanocarbon dots that will be produced and the activated carbon in terms of pH neutralization from the distillery spent wash.

4. There is no significant difference between the nanocarbon dots that will be produced and the activated carbon in terms of the TSS removal of the distillery spent wash.

Scope and Limitation

This study is primarily focused on the production of nanocarbon dots from cassava starch- a product from processing cassava (*Manihot esculenta*)- using the methods stated in the methodology which was conducted in the University of St. La Salle – Bacolod, Bacolod City, Negros Occidental during the months of June and October 2019.

The use of PSB Cv-14 (CMP21-15) cassava variety was preferred for the study due to its high toxicity and therefore inedibility. However, such variety was no longer available and accessible to the researchers. Therefore, the study used commercially available cassava. The condition of the cassava such as age, moisture content, color etc. was dependent on the variety and the availability of the cassava in the commercial market, specifically the Libertad Market in Bacolod City, Negros Occidental where the material was collected.

The synthesis of NCDs was carried out using microwave-assisted hydrothermal carbonization. This was based on the study of Al-Douri et al. (2017) which used a 500W microwave. However, due to the unavailability of the said microwave, the researchers opted to use a 700W microwave which was locally available and more convenient. Further, the difference in the power rating in the microwave, the researchers made minor

revisions on the time for microwave heating based on the amount of microwave energy delivered by the oven to the suspended starch.

The production of NCDs was limited to the production of hydrochar from cassava starch using microwave-assisted hydrothermal carbonization and no further purification of the NCDs was conducted due to unavailability of apparatus and equipment. Therefore, the percent yield of nanocarbon dots from cassava starch, which was used in this study, was based on the mass of the hydrochar produced during the hydrothermal carbonization process.

The activated carbon used for spent wash treatment in comparison with the produced nanocarbon dots was bought commercially. The recovery or regeneration of the adsorbents is not within the scope of this study.

The results of the study were based on the parameters as mentioned in the problem statement which are the parameters of water quality monitored by the DENR as stated in DAO 2016-08. The measurements of spent wash quality parameters were determined and calculated by the researchers using the appropriate analytical methods, not necessarily standard methods due to financial and time constraints as well as the availability of equipment in the Chemical Engineering Laboratory of the University of St. La Salle, Bacolod City.

Furthermore, the Biochemical Oxygen Demand (BOD) of each replicate from each set-up used in the study cannot be determined by the researchers because the laboratory equipment can only have a maximum of 6 BOD analysis for a certain period and since the analysis for BOD must be done on the same day for the same sample, it was

not possible to perform all ten analysis. The researchers opted to conduct only one BOD analysis for the raw spent wash (pretest), one post-test analysis for the sand filtrate, two analyses for the AC filtrate, and two analyses for the NCD filtrate. The results of these analyses were taken to be representative of the pretest and for each set-up.

Moreover, the determination of the diameter and shape of the NCDs was done by the Advanced Device and Materials Testing Laboratory (ADMATEL), Taguig City using Field Emission Scanning Electron Microscope (FESEM).

Significance of the Study

The study is significant to the following sectors:

Distillery Industries. The study explored alternative methods for the treatment of distillery spent wash discharge. The results of this study would be beneficial for distillery companies that wish to improve their spent wash treatment methods and to control the conditions of their effluent in order to comply with environmental regulations.

Local Government Units (LGU) and National Government Agencies (NGA). National government agencies such as the Department of Environment and Natural Resources and the City Governments are mandated to enforce laws and regulations such as The Philippine Clean Water Act of 2004 and DAO 2016-08 which promotes the cleanliness of water sources and regulates effluent discharge. Therefore, the study would be advantageous to the LGU sectors as the study aimed to improve water quality by regulating the amount of harmful substances along the spent wash released by distilleries.

Community. Residents situated near distillery companies and water bodies directly affected by their waste discharge would benefit from the study as it would help

clean their water sources. Furthermore, this study would also benefit farming communities that grow cassava by providing another means of utilizing cassava.

Fisher Folks. The water bodies where distillery wastes are typically discharged are used by some residents as fishing grounds for source of income. A cleaner body of water promotes healthier ecological systems where fish and other aquatic organisms can thrive bringing more bountiful catch for the fisher folks.

Environment. The environment sector benefits the study as it provides cleaner technology process for the treatment of distillery spent wash. The study also promotes the welfare of the environment by providing means of decreasing pollutants being disposed to bodies of water.

Future Researchers. The study would significantly benefit future researchers who want to investigate other water treatment methods as well as other applications of nanocarbon dots in other industries.

Definition of Terms

The related and significant terms as used in this study was defined as follows:

Activated Carbon (AC). Refers to the microcrystalline material made from the thermal decomposition of carbonaceous materials. In this study, AC refers to the powdered activated carbon which will be used as a standard adsorbent in comparison with NCDs.

Biochemical Oxygen Demand (BOD). Refers to the amount of dissolved oxygen that must be present in water for microorganisms to decompose the organic matter in the

water, specifically the spent wash from distilleries. BOD will be used as a measure of the degree of pollution as well as a parameter for determining the extent of treatment.

Cassava. Refers to the species *Manihot esculenta* which will be the main raw material used in the extraction of starch for the production nanocarbon dots.

Color. Refers to the quality of darkness and lightness of the distillery spent wash.

Distillery. Refers to any chemical industry that produces ethanol and other by products as well as unwanted waste such as spent wash by means of distillation and other related processes.

Downflow Gravity Contactor. Refers to the laboratory-scale contactor where the adsorption takes place. This is also referred to as the filter column in some parts of this study.

Effluent. Refers to the wastewater discharge from distilleries which is passed into bodies of water such as rivers and seas.

Hydrochar. Refers to the solid product of hydrothermal treatment of cassava starch which contains the nanocarbon dots and other mass from the original biomass feed.

Hydrothermal Carbonization (HTC). Refers to the process used in this study to convert cassava starch into nanocarbon dots.

Nanocarbon Dots (NCDs). Refers to the product of this study which is used to treat distillery spent wash.

Spent wash. Refers to distillery spent wash; which is the main unwanted residual liquid waste generated during alcohol production in distilleries.

Total Suspended Solids (TSS). Refers to the dry-weight of suspended particles that are not dissolved, in a sample of water that can be trapped by a filter that is analyzed using a filtration apparatus. TSS will be used as a measure of the degree of pollution as well as a parameter for determining the extent of treatment.

Review of Related Literature

The review includes the conceptual and research literature which are related to the research problems. They are presented using the thematic approach.

Cassava Starch. Cassava production is an increasing trend of the agricultural sector in the Philippines because of the versatility of its application. Cassava is grown for human consumption and industrial uses such as alcohol production according to Mariscal et al. (2001).

According to the study of Bacusmo (2001), the Philippines is producing 1.8 million tons of cassava roots yearly, which is planted in about 120,000 hectares of agricultural land. The principal products from the processing of cassava are dried chips and starch. The study of Kaur et al. (2016) found that the starch content of cassava is about 25% dry weight. Choct and Morgan (2016) presented that the moisture content of cassava pulp is approximately 60% to 70%. Kaur et al. (2016) extracted starch from cassava by grinding 1 cm cubes of cassava for 5 minutes using a high-speed blender to obtain a pulp. The pulp was then suspended in water, about ten times its volume and was stirred for 5 minutes. Gujral et al. (2011) included in their study the increase in solubility of starch with the increase in temperature due to the degradation of amylopectin causing disruption of the granular structure resulting in higher solubility. Kaur et al. (2016) then filtered the suspended pulp using a double-fold cheese cloth. The filtrate was allowed to

settle for 2 hours so that the starch will be deposited at the bottom and the top liquid was decanted and discarded. Water was added to the sediment and the mixture was stirred again for 5 minutes. The mixture was filtered again using the same process and the resulting filtrate was allowed to settle for 2 hours. After decanting the top liquid, the sediment (starch) was dried at 55°C for one hour.

La Tondeña Distilleries Incorporated, a major consumer of molasses in the Philippines, has turned to cassava as an alternative raw material for the production of alcohol due to the unstable production of sugar in the country. Furthermore, new hybrid varieties such as KU-50, Rayong 5, and PSB Cv-12 (SM972-20) are rapidly being multiplied for San Miguel's Cassava project expansion in Negros Occidental (Mariscal et al., 2001).

From the adaptability trial at Ilijan, Bago City, Negros Occidental in 1999 provided by La Tondeña Inc. - PhilRootcrops (2000), PSB Cv-14 (CMP21-15) was the variety with the highest fresh root yield of 44.32 t/ha. However, PhilRootcrops (2000) found that PSB Cv-14 (CMP21-15) gave an HCN score of 8.0, using the Picrate rating scale of 1 to 9: 1= very low; 9 = very high, and ingestion of high levels of HCN have been proven to be fatal to humans.

Iodine Test. Mozo (2008) described iodine test as a test for the presence of starch in biological samples in which the sample turns blue-black in color when a few drops of potassium iodide solution are added on it. It was emphasized that the reaction is due to the formation of polyiodide chains from the reaction of starch and iodine. The amylose in starch forms helices where iodine molecules assemble, forming a dark blue or black color.

Muazu et al. (2011) adapted the classical way of performing the iodine test. One gram of starch was boiled with 15 mL of water and allowed to cool. A few drops of 0.1N Iodine solution was added. Color change of blue-black indicated the presence of starch.

Hydrothermal Carbonization (HTC). In the study of Li and Shahbazi (2015), hydrothermal carbonization is defined as thermochemical conversion process that converts raw biomass, such as starch, to coal-like product, called hydrochar, carried out under mild operating conditions in a sub-critical water medium.

During HTC, the solution of carbohydrate, typically glucose or starch, precursors is usually heated to 130-250℃ under self-generated pressures. HTC is advantageous method of producing nanocarbon dots since it omits the need to dry the wet feed stock and it operates in water at low reaction temperature. Furthermore, the products generally exhibit uniform chemical and structural properties.

The production of hydrochar, most importantly quantum carbon dots, through HTC can be done by several methods. One of which is microwave-assisted HTC. From the study of Guiotoku et al. (2011), the use of microwave on hydrothermal carbonization contributed to simplify and accelerate the process. They attributed this to the decrease in the reaction time compared when employing the conventional hydrothermal carbonization. Furthermore, they emphasized that with the use of microwave-assisted hydrothermal carbonization, the obtained products are usually homogeneous. Guiotoku et al. (2011) highlighted the advantages of using microwaves in contrast to conventional ovens such as the interaction of the material with electromagnetic radiation rather than radiant energy. This results to heat being generated by the material itself in its bulk and thus the heat reaches the entire volume and can be much faster and selective. These

characteristics, when properly monitored, result in a homogeneous material, with faster production, while providing a significant reduction in energy losses. According to the study of Yang et al. (2013), the use of domestic microwave ovens has been found successful in producing nanocarbon dots with less reaction time.

Al-Douri et al. (2017) synthesized carbon-based quantum dots, C-QD, by employing microwave-assisted hydrothermal carbonization to aqueous starch suspension mediated by sulfuric and phosphoric acid. The result of their experiment showed a blue luminescence color under UV light by treating 1 g of starch dispersed in 25 mL of water with 7 mL of 2M sulfuric acid with microwave energy at 500 W for 3–5 min, and changing the reaction produced green and yellow luminescence. Based on the analysis of their carbon-based quantum dots using T80^{+} UV-vis spectrometer, blue, green and yellow fluorescence of C-QDs obtained an average particle size of 10, 10.2, 15.4 nm respectively. The study also showed that C-QDs with UV light gave blue, green, and yellow luminescence colors. Furthermore, the effects of the carbonization process to the luminescence characteristics showed to be a function of heating energy (wattage), time, and pH of the solution.

Isnaeni et al. (2018) produced nanocarbon dots using microwave-assisted hydrothermal carbonization by placing the carbon source solution in a domestic microwave oven and found that 40 minutes microwave processing time is the optimum condition for synthesizing carbon dots from ginger and galangal herbs.

The study of Li and Shahbazi (2015) identified the influences of different parameters, namely temperature, residence time, precursor concentration, type of carbohydrate precursor, pH and pressure, to the size and size distribution of colloidal

carbon spheres prepared by HTC. The study stated that increase in temperature lead to uniform particle diameter but also increase in the diameter size, this is based on the hydrothermal carbonization of 0.5M pure glucose solution for 4.5h at different temperatures ranging from 170-230^{0}C. From the same study, increasing the residence time of the hydrothermal carbonization of 0.5M pure glucose solution at 160^{0}C led to higher reaction severity, lesser organic loss and increase in the particle diameter of the carbon dot product. The study also showed that the particle size of carbon dots produced using HTC increases with elevated concentration of solution but at certain degree of concentration the size becomes constant. Furthermore, the study stated that the carbohydrate precursors with more carbon per molecule yields a larger sized parameter and increasing the pH tends to decrease the particle diameter. Lastly, the study stated that pressure had no significant effect on promoting HTC conversion, because the HTC reaction occurred in the liquid phase.

Nizamuddin et al. (2018) summarized the effects of different parameters of microwave HTC, such as the reaction time, reaction temperature, catalyst, feed type and its composition, and microwave power, on hydrochar yield. According to their study higher yields of hydrochar were obtained at lower reaction times. Furthermore, it was observed that there was a rapid decrease in mass yield of hydrochar with increase in temperature. The study also stated that higher mass yield was observed at lower microwave power.

The study of Sevilla and Fuertes (2009) used HTC to produce hydrochar from 2 and 16 grams of cellulose dispersed in 50 mL of water under the operating conditions of 200-250 ^{0}C maintained for 2 or 4 hours. The ratio of volume of solution/volume of

autoclave used in the study is 0.3. The study concluded that HTC of cellulose produced hydrochar of micrometer sized spheres (size~ 2-10μm).

The research conducted by Das et al. (2018) summarized different studies that synthesized carbon quantum dots using HTC from different carbon sources. Table 1 shows the different carbon source, HTC condition and particle diameter collated by study.

Table 1

Carbon dots derived from different natural resources (Das et al., 2018)

Carbon source	HTC Conditions	Carbon-Dots Diameter
Gelatin	200^0C for 3h	1.7 nm
Water Soluble Branched polyetheneimine	100-200^0C for 5-10h	3-4 nm
Saccharum offinarum juice	120^0C for 180 min	~3 nm
Grass	180^0C for 3h	3-5 nm
L- ascorbic acid	180^0C for 4h	2-2.5 nm
Dopamine	180^0C for 6h	3-8 nm
Pomelo peels	200^0C for 3h	2-4 nm
Ascorbic acid and Diethylenediamine	90^0C for 2h	6.2 nm
Orange juice with Ethanol	120^0C for 150min	1.5-4.5 nm
Cabbage	1400^0C for 5h	2-6 nm
Strawberry juice	180^0C for 12h	5.2 nm
Alanine and Diethylenediamine	200^0C for 6h	8 nm
Sweet potatoes	180^0C for 18h	No data

The studies generally hydrothermally treated the carbon sources by making 50 mL water mixture with the precursor and then used Teflon equipped stainless steel autoclave for the hydrothermal carbonization process.

Nanocarbon dots (NCDs). Carbon quantum dots or nanocarbon dots are a new class of fluorescent materials from nanocarbon family that are potential competitors of inorganic quantum dots and other toxic, heavy-metal based materials. (Soni, 2016) NCDs

were first discovered in 2004 through the purification of a single-walled carbon nanotubes by electrophoresis. Two years after, another method paved the way to produce NCDs which is via laser ablation. (Wang et al., 2014)

Presently, although the synthesis of NCDs can be carried through different processes such as chemical ablation, electrochemical carbonization, laser ablation, and microwave irradiation as laid out by Wang et al. (2014), hydrothermal treatment is preferred because it is cost-effective, non-toxic, and eco-friendly.

Li et al. (2012) stated that the interest for the use of NCDs in numerous researches was because of its superiority in water solubility, chemical inertness, low toxicity, and ease of functionalization. This was affirmed by Faddlan et al. (2016) through their study that focused on the production of NCDs from organic materials and waste materials in order to address the green earth issues today. These natural sources contain very high carbon bonds which may be a potential as base materials to produce NCDs. Al-Douri et al. (2017) proved this through their study which made use of starch extracts. From their research, four raw materials were used namely potato, cassava, rice, and yam. It was observed after the experiment that the group was able to produce NCDs from the starch extracts as precursors which exhibited strong luminescence and solubility.

Nanosizing. According to the United States National Nanotechnology Initiative, when particles are created with dimensions of about 1–100 nanometers, such as when NCDs are formed through HTC, the materials' properties change significantly from those at larger scales. Properties of materials are size-dependent in this scale range. Thus, when particle size is made to be nanoscale, properties such as melting point, fluorescence, electrical conductivity, magnetic permeability, and chemical reactivity change as a

function of the size of the particle. Furthermore, nanoscale materials have far larger surface areas than similar masses of larger-scale materials. As surface area per mass of a material increases, a greater amount of the material can come into contact with surrounding materials, thus affecting reactivity and as such, nanostructured materials also create better catalysts. Large surface area also makes nanostructured membranes and materials ideal candidates for desalination and water treatment.

Adsorption and Activated Carbon. There are many wastewater treatment methods, and each has its disadvantages and advantages depending on any factors such as to what specific purpose of treating wastewater does it serve. Adsorption is a wastewater purification technique for removing a wide range of compounds from industrial wastewater. It takes place when molecules in a liquid bind themselves to the surface of an adsorbent.

Adsorbents have a very high internal surface area due to its highly porous structure with pore volumes of up to 50% of total particle volume that permits adsorption and activated carbon is by far the most commonly used adsorbent, especially for organics, having a surface area of 300 to 1200 m^2/g and an average pore diameter of 10-60x10^{-10}m (EMIS 2010 and Geankoplis 1993). Geankoplis (1993) stated that the applications of liquid- phase adsorption include the removal of organic compounds from water or organic solutions, colored impurities from organics, and various fermentation products from fermenter effluents. Mazille (2018) described adsorption using activated carbon as the process in which contaminants adhere to the large surface carbon granules or become trapped in the small holes of the highly porous activated carbon during water filtration. According to the United States Environmental Protection Agency USEPA

(1973), using downflow carbon contactor for adsorption provides capital cost savings. The usual dimensions for the design of a cylindrical downflow carbon contractor as stated by this manual is 6ft in diameter and 25.83 ft in height packed with layers of filter block, gravel, and adsorbent with thickness 10 in, 12 in, and 15 ft respectively. From the study of Entrata et al. (2017), the researchers used 100 grams of biosand composite with 175mg of iron oxide microparticles to filter 300 mL of wastewater sample. The study of Entrata et al. (2017) concluded that, biosand composite has the ability to decrease the pH, chemical oxygen demand (COD), total suspended solids (TSS) of the wastewater sample to the extent that the filtered samples were able to pass the accepted range set by the DENR for Class C water.

A study conducted by Mwangi and Oguntimein in 2012 to investigate the wastewater treatment of discharges from a bioethanol production plant using the adsorption capabilities of activated carbon concluded that using activated carbon in a packed column containing sand resulted in the removal of dissolved organic compounds but the salts concentration from the ethanol production process was not significantly affected.

Agrawal et al. (2017) conducted a treatability study on wastewater to check out whether the activated carbon gives maximum removal of BOD, COD, pH, turbidity. In the study, raw wastewater was put under contact of activated carbon and was examined for the efficiency of the activated carbon for reducing the harmful parameters. The study tested the concentration of activated carbon that would yield a permissible concentration of the tested parameters after varying days and concluded that 4% concentration of the activated carbon after 14 days resulted to parameters that pass the set standards.

According to the study by Satyawali (2007), commercial activated carbons shows better performance of over 80% color removal when compared to other carbon samples. In the study, activated carbon treatment also showed reduction in chemical oxygen demand, total organic carbon, phenol and total Kjeldahl nitrogen. A similar study by Kumar et al. (2017) analyzed distillery spent wash which was found to be acidic (pH 4.7) and dark brown in color but when the researchers used activated charcoal purification, the distillery spent wash exhibited maximum reduction in COD (48.98%), TS (64%), TDS (55.26%), Mg (78.03%), Na (60%), Ca (80.91%), K (75.30%) and increase in pH toward pH 7.

Distilleries and its wastes. Adsorption technology has been used in distillery industries to treat its effluents because although alcohol is an important chemical used by different chemical industries, distilleries are meeting its high demand at the expense of producing large quantities of hazardous wastes. Distilleries produce alcohol mainly from raw materials such as sugarcane molasses and juice, barley malt, grains, and other cellulosic materials. The raw materials must undergo fermentation and distillation in order to produce alcohol.

The extent of the pollution problem brought by distilleries was emphasized in a study by Ravikumar et al., (2007) wherein the researchers highlighted that in developing countries, distilleries can be considered as one of the most polluting industries where 88% of its raw materials are converted into waste and discharged into bodies of water, causing water pollution. In the distillery, 15 liters of spent wash is released as waste water for every liter of alcohol produced. The spent wash generated from distilleries is dark brown in color and has a high temperature, low pH of about less than 4.0-4.5 and,

high chemical oxygen demand (COD) ranging from 80,000 to 100,000 mg/L and biochemical oxygen demand (BOD) of 40,000 to 50,000 mg/L (Kharayat, 2012). According to the study by Kharayat (2012), the high amount of COD and BOD are attributed to the presence of organic compounds such as polysaccharides, reduced sugars, lignin, etc. from the manufacturing process. The amount of inorganic substances in the spent wash such as nitrogen, potassium, phosphates, calcium, and sulfates are also very high (Melamane et al., 2007 cited in Kharayat, 2012). Ansari et al. (2008) found that untreated spent wash has a temperature of 70 - 100°C, a pH of 4.1, total dissolved solids concentration of 77,270 mg/L, total suspended solids amounting to 21,730 mg/L, chemical oxygen demand of about 70,400 mg/L, biological oxygen demand of 22,280 mg/L, and oil and grease concentration of 50 mg/L respectively higher than the permissible limit as per the standards set in India..

Chowdhary et al. (2017) stated that the effluent discharged by distilleries without proper treatment can cause serious environmental problems and health hazards in humans and animals. Mohana et al. (2009) stated that despite standards imposed on effluent quality, untreated or partially treated effluent very often finds access to watercourses. The study also gave importance to the serious threat to water quality in several regions around the globe brought about by the distillery wastewater with its characteristic unpleasant odor.

From the study of Kharayat et al. (2012), current treatment options used to treat distillery spent wash included physical, chemical, physicochemical and biological methods before its disposal where the researchers noted that the selection of treatment methods depends on various factors such as treatment efficiency, treatment cost, local

geography, climate, land use, regulatory constraints, and public acceptance of the treatment. Their study explored approaches in the treatment of distillery spent wash, however, in their discussion on the various physical treatments, the researchers highlighted the adsorption method. It was emphasized that adsorption is one of the most widely used physical method especially adsorption on activated carbon which is widely employed for removal of color and specific organic pollutants. Goyal and Bahgat (2012) affirmed with this in their study where they stated that even with several methods such as coagulation, aeration, oxidation have been used for the treatment of water, the AC adsorption has been found to be the best broad-spectrum technology currently available.

MATERIALS & METHODS

This section describes the components of the study which relate to research methodology such as the research design, research methodology, and statistical treatment.

Research Design

This study employed descriptive and experimental research methods in the production of nanocarbon dots. Experimental research method was used in the extraction of starch from cassava and in the preparation of the downflow gravity contactor set-up. Experimental research was also used in the measurement of the parameters of the study in both unfiltered and filtered distillery spent wash. Unfiltered spent wash referred to the fresh sample collected directly from Victorias Milling Company while the filtered spent wash referred to the filtrate after the sample was passed through downflow gravity contactor. The independent variable of this study was the concentration of NCDs in the filter media and the dependent variables were the change in BOD, color, pH, and TSS of the filtered distillery spent wash. Filtration of the distillery spent wash was administered using three set-ups with three replicates. Set-up A used commercial activated carbon as the adsorbing material. Set-up B used the nanocarbon dots as the adsorbing material in the downflow gravity contactor. Set-up C, the control set-up, only used sand as adsorbent for the spent wash filtration. Percent removal of BOD, color, and TSS, as well as, pH reduction in the distillery spent wash samples was evaluated using experimental method.

Research Methodology

This section explains in detail the research procedures for the extraction of starch from cassava, the hydrothermal carbonization into nanocarbon dots and its efficacy in treating distillery spent wash when used as an adsorbent in a laboratory-scale downflow gravity contactor in comparison to the control and the use of activated carbon as the adsorbent.

Figure 1 shows the flow diagram of the experimental procedure that was employed in this study.

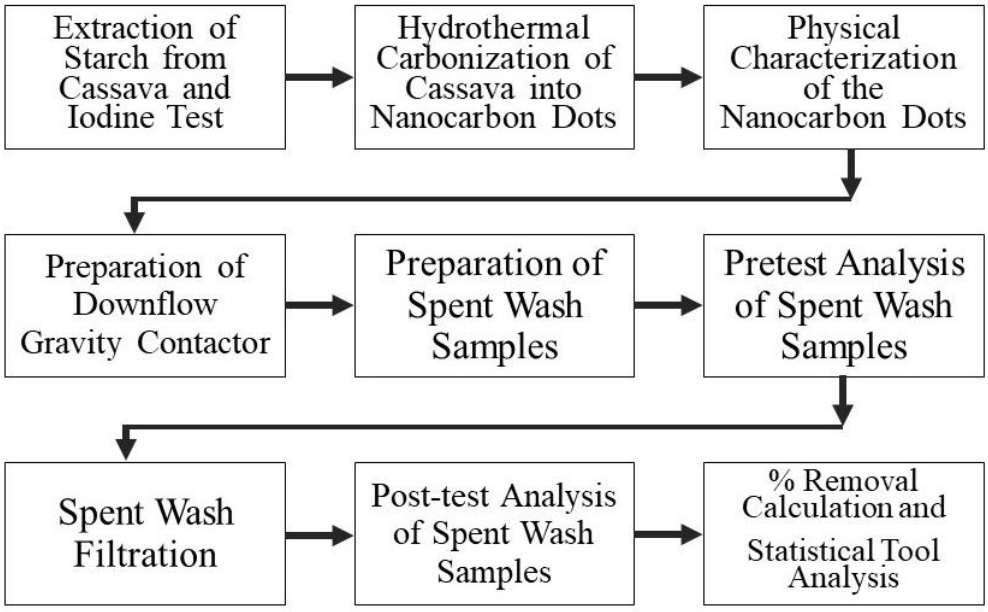

Figure 1. Schematic diagram of the experimental procedure

Extraction of Starch from Cassava. This process was adapted from the study of Kaur et al. (2016) with minor revisions. Two kilograms of cassava tubers was procured from Libertad Market in Bacolod City which was washed and peeled. A kilogram of prepared cassava was then chopped into cubes of approximately 1 cm and ground in a

high-speed blender for 5 minutes. The blended cassava was then dried in an air oven at 55°C for one hour. The obtained pulp was suspended in warm water at about 50°C, ten times of its volume, and was manually and continuously stirred for 5 minutes. The mixture was filtered using a double fold cheesecloth and the filtrate was allowed to stand for 2 hours for the starch to settle. After 2 hours, it was decanted, and the top liquid was discarded and disposed properly. The starch sediments after decantation were transferred to a pre-weighed pan and weight was recorded. The starch was dried at 55°C for 1 hour using an oven and was weighed. The percent yield of starch was calculated using the equation below:

$$yield_{starch}(\%) = \frac{m_{ds}}{m_{dc}} x100\% \quad (1)$$

where m_{ds} is the mass of the dried starch and m_{dc} is the mass of the dried cassava.

Starch Content Testing on Cassava Sediment. This process was adapted from Muazu et al. (2011) with minor revisions. One gram of starch was boiled with 15 mL of water and allowed to cool. Five drops of 0.1N Iodine solution was added to the solution and a color change of blue-black indicated the presence of starch.

Microwave-Assisted Hydrothermal Carbonization into Nanocarbon Dots. This process was adapted from Al-Douri et al. (2017) with minor revisions. One gram of starch was dispersed in 25 mL of distilled water with 7 mL of 2 M sulfuric acid in a 250 mL glass beaker. The beaker with the mixture was then heated using a 700 W microwave oven for 3 min. After microwave heating, the contents of the beaker were weighed and transferred to a test tube. The test tube was then placed in a dark room with a UV Light Emitter and a recording camera to determine the luminescence of the product. After the

luminescence test, the products were poured into an evaporating dish and dried in an oven at 105°C for 5 hours. The mass of dry NCD was recorded.

Percent yield of nanocarbon dots from cassava starch was calculated using the equation below:

$$yield_{NCD}(\%) = \frac{m_{NCD}}{m_{starch}} x(100\%) \quad (2)$$

where m_{NCD} is the mass of the dried NCD and m_{starch} is the mass of the dried starch.

Physical Characterization of the Nanocarbon Dots. The particle size in terms of shape, surface area and equivalent diameter, and image of the nanocarbon dots was analyzed using a Field Emission Scanning Electron Microscope (FESEM) by the Advanced Device and Materials Testing Laboratory (ADMATEL) in Taguig City.

Preparation of the Downflow Gravity Contactor. This process was adapted from Mwangi and Oguntimein (2012), the USEPA Process Design Manual for Carbon Adsorption (1973), and Entrata et al. (2017). Filtration column was made using clear cylindrical PET containers with diameters of 50 mm and heights of 160 mm. Perforated metal sheet with holes less than 5 mm in diameter was used as the flat bottom support system. Above the support was filter wool, gravel, and the adsorbing material for each set-up with a thickness of 5 mm, 6 mm, and 90 mm, respectively. The three set-ups were the sand-activated carbon composite, sand-NCD composite, and sand alone. For the sand composite, fine quarry sand was collected from Bacolod City, Negros Occidental and was sieved using No. 20 mesh. Two kilograms of sand was soaked in 8% v/v 0.5 M nitric acid solution overnight to displace any cations off the sand's cation exchange sites, rinsed

with distilled water to pH 5.0 and dried using an oven at 105°C. The adsorbents were introduced to 200 g of sand in a 6 L water bottle and was manually shaken for 15 minutes. A total of 9 downflow gravity contactors were prepared for three set-ups with three replicates each. Set-up A and set-up B contained 0.65 g of activated carbon and nanocarbon dots respectively.

Table 2 summarizes the composition of the set-ups used in the study.

Table 2

Composition of the set-ups used in the study

Composition	**Set-up A**	**Set-up B**	**Set-up C**
Adsorbent	AC	NCD	None
Concentration, g adsorbent/ g sand	0.65	0.65	0

Figure 2 shows an illustration of the downflow gravity contactor that was used in this study.

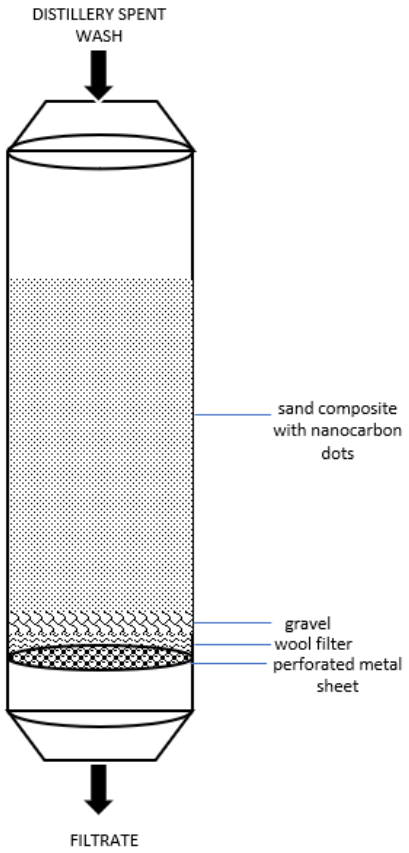

Figure 2. Illustration of the downflow gravity contactor.

Preparation of Spent Wash Samples. Twelve liters of distillery spent wash samples were collected in an ice bath from Victorias Milling Company Inc. Distillery Plant, Municipality of Manapla. It was divided into 9 containers containing 1.20 liter each.

Pretest Analysis of Spent Wash Samples. The methods of analyzing the spent wash parameters were summarized in Table 3 which shows the standard methods of analysis for water and wastewater set by DENR Memorandum Circular No. 012 Series of 2016 and the actual analysis method used by the researchers.

Table 3

Methods of analysis for water and wastewater used

Parameter	Standard Analysis Method	Analysis Method Used
BOD	5-Day BOD test at 20℃ in the dark.	5-Day BOD test at 20℃ in the dark.
Color	Visual Comparison with the Platinum Cobalt scale	Spectrophotometric Method
pH	Electrometric Method	Electrometric Method
Total Suspended Solids	Gravimetric Method at drying temperature of 103-105℃	Spectrophotometric Method

Spent Wash Filtration. The prepared 1.2 L of spent wash was poured into one set-up at a constant flow rate and was allowed to pass the adsorbing media until a 50 mL filtrate is obtained. Once finished, the filtrate was immediately processed for post-test analysis.

Post-test Analysis of Spent Wash Samples. The same methods used in the pretest analysis of spent wash sample was followed for the post-test analysis in the determination of BOD, Color, pH, and TSS.

Percent Removal and pH Reduction Determination. The percent removal of BOD, color, and TSS as well as the change in pH was calculated using the equations below:

For the percent removal of BOD. The procedure in calculating % removal of BOD will be adapted based on the formula given by the Water and Wastewater Courses (ND) where Ci is the BOD concentration in mg/L of the influent and Ce is the BOD concentration in mg/L of the effluent.

$$R_{BOD}(\%) = \frac{C_i - C_e}{C_i} x(100\%) \quad (3)$$

For the percent removal of color. The equation for the percentage removal of BOD holds for the calculation of the percent removal of color.

$$R_{color}(\%) = \frac{C_i - C_e}{C_i} x(100\%) \quad (4)$$

For the percent removal of TSS. The equation for the percentage removal of BOD holds for the calculation of the percent removal of TSS.

$$R_{TSS}AC(\%) = \frac{C_i - C_e}{C_i} x(100\%) \quad (5)$$

For the change in pH. The change in pH can be calculated by taking the difference between the pH of the influent (pHi) and the effluent (pHe).

$$\Delta pH = pH_i - pH_e \quad (6)$$

Statistical Tool Analysis. Mean was used to describe the data gathered for the three trials of the spent wash quality parameters. Standard deviation was used to determine how far the values are from the mean. To determine the significant difference in spent wash treatment between the sand-activated carbon composite and sand-NCD composite set-ups, T-test was used with 0.05 α. (Entrata et al., 2017).

RESULTS AND DISCUSSION

This section presents the data, analysis and interpretation based on the results of the experimentation conducted on the hydrothermal carbonization of starch produced from cassava including the qualitative data gathered. This section also presents the results of the characterization of the nanocarbon dots as well as the determination of the changes in the physical and chemical characteristics of spent wash when treated using sand filter, activated carbon-sand composite, and nanocarbon dots-sand composite. The experiment consisted of pretest and post-test analysis having three trials each. The results obtained were analyzed using statistical tool presented in this chapter.

Extraction of Starch from Cassava. Starch extraction methods patterned from Kaur et al. (2016) showed that after washing, chopping and blending of 1 kg of peeled cassava, 930.68 g of cassava pulp was produced which was white in color and is fine to the touch. The difference in weight of 69.32 g in pulp was primarily attributed to the pulp retained in the blender. After drying the pulp in the oven for 1 hour at 55^{o}C, the weight of the cassava pulp was 834.08 g.

The percent moisture of the cassava pulp was calculated to be 10.38%. The moisture content calculated is smaller than the value presented by Choct and Morgan (2016) which is about 60% to 70%. The large gap between the values was attributed to the difference in the methods used; the value presented by Choct and Morgan (2016) was based on the results of drying until constant weight whereas in this study, the calculated value was based on the masses before and after drying for one hour as presented by Kaur

et al. (2016). Furthermore, the researchers chose the methods of Kaur et al. (2016) over that of Choct and Morgan (2016) because of time constraints during experimentation and because the moisture content of the cassava will not affect the quality of starch produced and would only reflect a change in the results for the yield.

From the dimensions of the drying pan, which is 27.94 cm by 17.78 cm, and the thickness of the pulp, which about 23 cm, the approximate volume of the pulp was calculated to be 1142.58 mL and therefore, the volume of water added was about 11,430 mL. After stirring the mixture became cloudy white. After passing through the double-fold cheesecloth, 710.65 g of squeezed cassava pulp was discarded. The filtrate was cloudy yellow and after the settling period, a layer of white particles was visible at the bottom of the container. The mass of the wet sediment left after decantation was found to be 196.52 g. After oven drying, 177.01 g of dry sediment was obtained. The percent yield of cassava starch was calculated to be 21.22%. The percent yield obtained is lesser from that of the obtained value by Kaur et al. (2016) which is 25%, a deviation of 3.78%, which could be attributed to the difference on the variety of the cassava used.

Starch Content Testing on Cassava Sediment. Iodine test was used to confirm the presence of starch in the sediments obtained from cassava. This test states that after the addition of iodine solution, a color change of blue-black indicates the presence of starch.

After adding 5 drops of 0.1N iodine solution to 1 gram of starch which was brought to a boil with 15 mL of water, the color changed to bluish black which confirmed the presence of starch. The color change was similar to the study of Muazu et al. (2011) wherein the method for the confirmatory test was adapted.

Microwave-Assisted Hydrothermal Carbonization into Nanocarbon Dots. After the starch was dispersed in water, the solution turned cloudy but became slightly clearer after the addition of sulfuric acid. While in the microwave, rising vapor was observed as a result of water evaporating. The resulting product was black in color along with a clear yellowish liquid and a pH of 2.95. The product was weighed and transferred to a test-tube where the solid black particles settled at the bottom. When test-tube was put in a sealed box with an Ultraviolet Light Emitter and a recording camera, the video showed luminescence of the liquid with emission of a slightly bright blue color. This luminescence is similar to the result of Al-Douri et al. (2017) where they were able to produce blue luminescence using cassava as the starch source and 2M H_2SO_4 as the acid, indicating the presence of NCD with particle size of 10 nm.

For 15 batches of Microwave-Assisted Hydrothermal Carbonization, a total of 15.0 g of starch was used and the total volume of water and sulfuric acid used were 375 mL and 105 mL, respectively. The average mass of wet NCD for the 15 trials was 9.77 ± 1.12 g. The total mass of wet hydrochar produced was 146.48 g. After drying, the mass of dry hydrochar obtained was 10.44 g.

The percent yield of NCD obtained from 15.0 g of starch was 69.60%. The yield, as defined in the scope and limitations of this study, is based on the amount of hydrochar. Other relevant literature expresses this yield in terms of the quantum yield.

Physical Characterization of the Nanocarbon Dots. The results of the Field Emission Scanning Electron Microscope by the Advanced Device and Materials Testing Laboratory (ADMATEL) in Taguig City are available in Appendix B Table B.2, which present the diameter of the NCDs found using a Dual Beam Helios Nanolab 600i

instrument with a beam current of 0.17 nA and a FESEM Accelerating Voltage of 5.0 kV after oven-drying the sample at 100^{o}C for one hour. Furthermore, the surface area of the synthesized NCDs were calculated by the formula given in Dune Sciences, Inc. (2011)

The data indicates that the average particle diameter was 62.8615 nm, with the largest particle having a diameter of 114.20 nm and the smallest having 38.08 nm, which is much larger than the particle size Al-Douri et al. (2017) obtained for NCD with blue fluorescence with UV light (10 nm). The increase in particle size was due to having the hydrochar as the subject for FESEM analysis rather than the NCD dispersed in the aqueous solution. The product fits the description of a nanoparticle given by the United States National Nanotechnology Initiative (ND) and the International Organization for Standardization (2008) which considers a particle to be in nanoscale if it is in the size range of 1 nm to 100 nm. The average surface area of the NCDs was 13,357.2135 nm^2 which was larger than the results of the study by Abong et al. (2018). As discussed by the United States National Nanotechnology Initiative (ND), a larger surface area results in greater amount of contact with surrounding materials and makes the material a candidate for water treatment.

Figure 3 shows the SEM images of the NCD sample taken at 100,000x magnification.

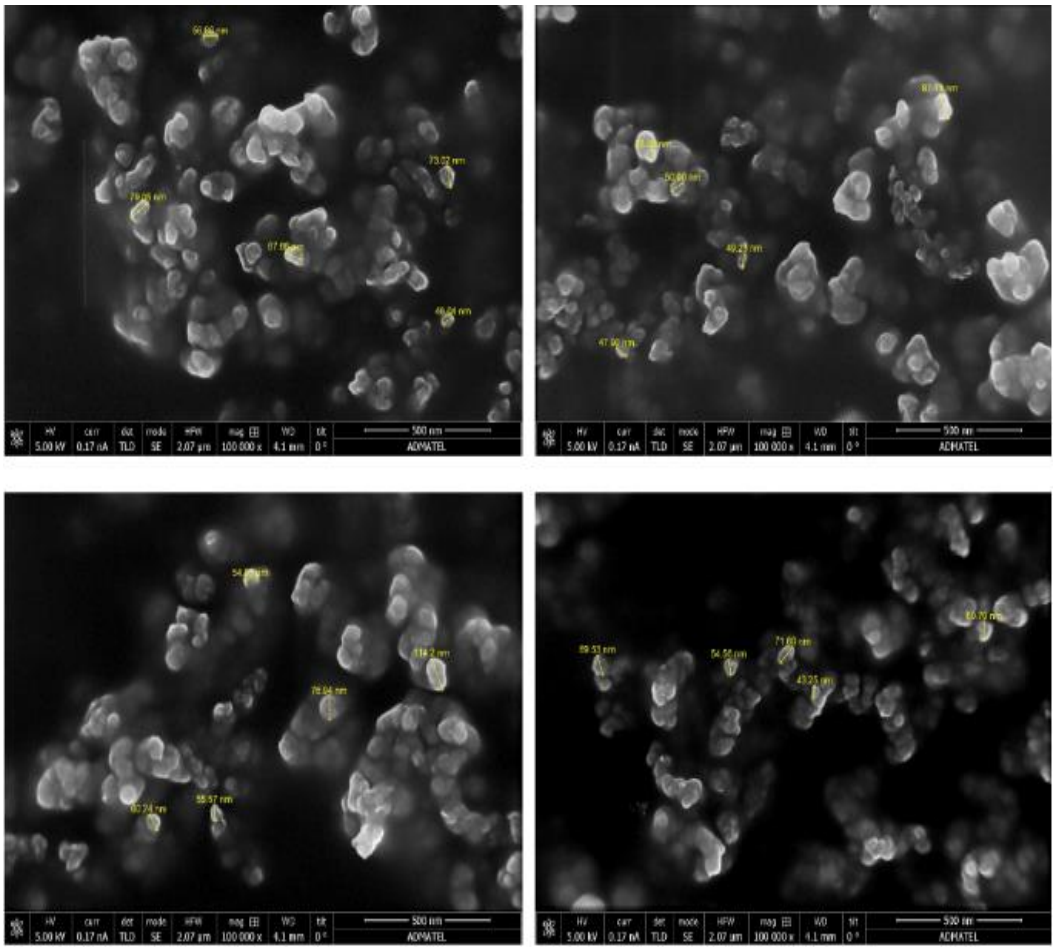

Figure 3. FESEM images of Nanocarbon Dots sample taken at 100,000x magnification.

It can be observed from figure 3 that the resulting NCD produced from Microwave-Assisted Hydrothermal Carbonization was quasi-spherical in shape, have rough surfaces and are varying in sizes which was the same as that of the results of Abong et al. (2018).

Preparation of the Downflow Gravity Contactor. The sand used for the assembly of the downflow contactor was composed of fine sand after it was passed through the No. 20 mesh Tyler sieve. Upon mixing the sand with the adsorbents, the NCD and AC were no longer distinguishable from the sand. The downflow gravity

contactors were completely assembled by adding wool filter (5 mm), gravel (6 mm), and sand (90 mm).

Preparation of Spent Wash Samples. The fresh spent wash was dark brown in color and had a strong sweet odor. The 12 liters of spent wash was divided into 9 containers having 1.20 liter each for each set-up and the rest was used for the pretest analysis.

Pretest Analysis of Spent Wash Parameters. The BOD concentration of the sample was higher than what was described by Kharayat (2012). The color reading indicates that the spent wash is very dark. The pH for the raw spent wash was less acidic than the results found by the study of Kumar et al. (2017) with a difference in pH of 0.43 as well as that of the results by Ansari et al. (2008) with a pH difference of 1.03. The TSS of the raw spent wash is relatively large as compared to the results by Ansari et al. (2008) which is only about 21,730 mg/L. All values indicate a more polluting spent wash than those describe in literature because the source of the raw spent wash used in this study. Furthermore, all values of the parameters exceed the limits set by the DAO 2016-08.

Spent Wash Filtration. The spent wash from the containers were poured into the filter through faucets attached to the container which resulted in a constant laminar flow pattern. The spent wash filled the filter as observed at the sides of the transparent filter. After about the same amount of time, 50 mL of the filtrate for all three set-ups were collected. For the three set-ups, it was observed that the filtrate turned from a light brown to a dark brown liquid as the filtration went on. The color returned to dark brown as the filtration continued due to the large number of color-contributing particles of the spent

wash that the adsorbents in filter column became quickly saturated and could no longer remove color before the filtrations were finished.

Post-test Analysis of Spent Wash Parameters. Table 4 summarizes the results of the pretest and post-test conducted on the spent wash using the methods found in the methodology of this study.

Table 4

Pretest and post-test results of the spent wash parameters

	Spent Wash Parameter			
Set-up	**BOD, mg/L**	**Color, mg/L**	**pH**	**TSS, mg/L**
Pretest	58,123	109,764	5.13	44,367
AC	19,227	80,444	6.00	1,989
NCD	20,774	56,134	5.90	1,619
Sand	56,756	85,748	5.50	3,315

Post-test results indicated that set-up A, which contained AC as the adsorbent, showed better performance in removing BOD and reducing pH against the other set-ups. On the other hand, Set-up B, which contained NCD as the adsorbent, had better performance in removing both color and TSS from the spent wash compare to set-ups A and C.

Percent Removal Calculation and pH Reduction Determination. Figure 4 summarizes the percent removal of the spent wash parameters by the three different set-ups which were calculated using equations 3, 4, and 5. Using equation 6, the pH reduction in the AC set-up, NCD set-up, and sand set-up is 0.84, 0.74, 0.37 respectively. The pH of the filtrates for all set-ups improved with set-up A having the highest

neutralization and set-up C having the lowest. This suggested that the adsorbents contribute to the neutralization of the acidic spent wash.

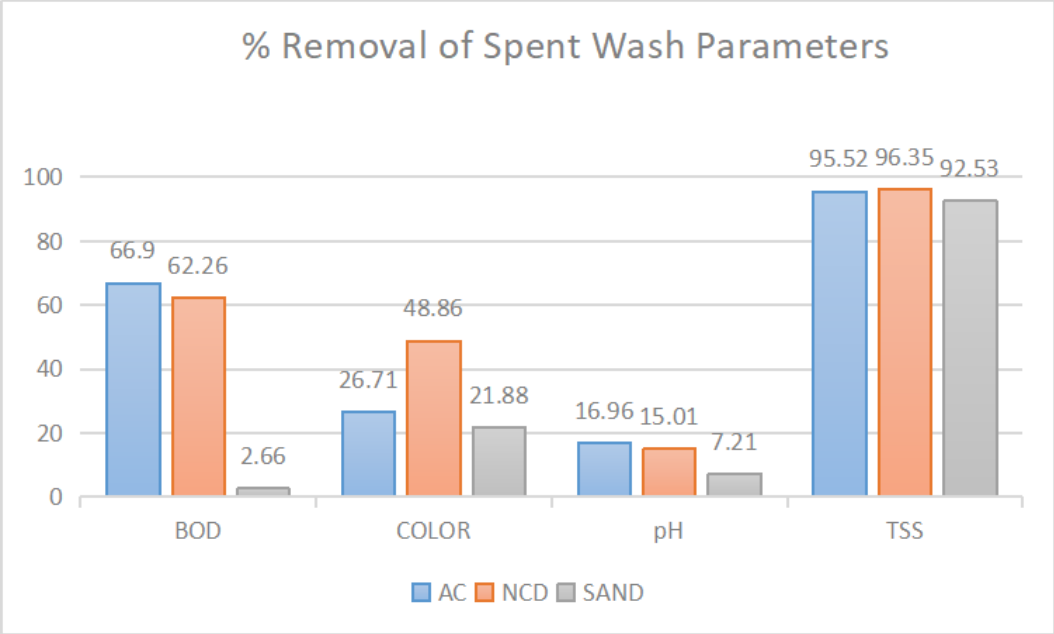

Figure 4. Summary of the percent removal on the spent wash parameters.

It can be observed from the results in Figure 4 for BOD that the use of sand filter alone was insufficient for the removal of BOD and that both AC and NCD showed high % removal of BOD. It can be concluded that the adsorption sites of adsorbents are very effective in removing organics from wastewater. The percent removal of color for the treated spent wash was lower compared to the results from the study of Satyawali (2007) which was 80%. The lower color reduction was attributed to the combination of sand and the adsorbents contrary to Satyawali (2007) who used pure activated carbon. The set-up with NCD showed the largest reduction in color among the three set-ups and the control having the least. The filtration set-ups showed an increasing trend in the removal of TSS from distillery spent wash with set-up C having the lowest removal and set-up B having

the highest percentage of TSS removal. The higher % of removal by the NCD is due to its large surface area although this attribute was not maximized in the study since the NCD used was in the form of a wet hydrochar. Despite the increasing trend in percent removal, it can also be observed that the results from each set-up are relatively close with each other indicating that adsorbents do not greatly improve the removal of TSS in the filtration set-ups. This is because the particles associated for TSS is significantly larger compared to that of BOD and color thus it can easily be removed from water using filtration even without the presence of adsorbents.

Statistical Tool Analysis. Statistical analysis was used to compare the differences in the percent removal of BOD, color, pH, and TSS between Set-up A and Set-up B. T-test for two independent means was utilized to determine a significant difference in the performance of the adsorbing media used. Based on the t-test conducted at an alpha of 0.05, the P value for BOD, color, pH, and TSS was 0.038, 0.016, 0.656, and 0.067 respectively. This result indicated that there is a significant difference in the extent of distillery spent wash treatment of nanocarbon dots from the activated carbon in terms of the removal of BOD and color while no significant difference in terms pH neutralization and TSS removal. AC removed BOD significantly higher than NCD which was attributed to the NCD being wet causing the nanoparticles to agglomerate and reducing the exposed surface area of the NCD as well as its active binding sites. In terms of color, there was a significantly large difference in the extent of removal using NCD compared to AC because of its smaller pore sizes which enabled it to trap more color. Furthermore, there was no significant difference between the pH neutralization of set-up A and set-up B since both NCD and AC are composed of carbon elements differing only in size. Lastly,

the results also showed that even though NCD scored higher % removal of TSS than AC, there is no significant difference in their ability to remove suspended solids. With these results the first and second null hypotheses which states that there is no significant difference between the nanocarbon dots and the activated carbon in terms of BOD and color removal were rejected. Moreover, the third and fourth null hypotheses that states that there is no significant difference between the nanocarbon dots and the activated carbon in terms of pH neutralization and TSS removal were accepted.

CONCLUSION

This chapter presents the summary of findings in the experimentation of this study. In addition, this chapter offers recommendations for further research in a similar field.

Cassava contained 21.22% cassava starch which was used as the biomass source for the microwave-assisted hydrothermal carbonization for the production of nanocarbon dots. Its presence was indicated by the color change into blueish black during iodine test.

Microwave-assisted hydrothermal carbonization of cassava starch produced NCD with a yield of 69.60%. The synthesized NCD showed bright blue luminescence with UV light. Based on the results from FESEM imaging, the NCD produced was quasi-spherical in shape and had a mean particle diameter of 62.8615 nm, and the computed average surface area was 13,357.21 nm^2.

There were significant differences between the nanocarbon dots produced and the activated carbon in terms of the percent removal of color and BOD while there is no significant difference between the NCD and the activated carbon in terms of the pH neutralization and TSS removal when used as adsorbing agent for distillery spent wash treatment using T-test statistical tool. Based on the statistical analysis, the hypotheses stating that there are no significant differences between the produced nanocarbon dots and the activated carbon in terms of BOD and color removal were rejected. On the other hand, the hypotheses stating that there are no significant differences between the

produced nanocarbon dots and the activated carbon in terms of pH neutralization and TSS removal were accepted.

In light of the results of this experiment, the researchers would like to make some recommendations in similar fields related to this study. The researchers recommend to experiment on the effects of the size of NCD to the amount the particle can adsorb in a filtration set-up. The filtration set-up using NCD as the adsorbent is effective in removing color, BOD and TSS, and in increasing pH however the values does not comply with DAO 2016-08, therefore further researches on possible pretreatment methods to improve the efficiency of this set-up to be applied for industrial practice can be conducted as well as the research on the combination of biological treatment and the used of NCD for the treatment of spent wash. The researchers also recommend to further explore on the adsorption properties of nanocarbon dots to maximize the efficiency of filtration systems using NCD. Further studies can be conducted by comparing the efficiency of NCD derived from different precursors and different synthesis methods to wastewater treatment. Lastly, the researchers recommend to explore on other possible industrial uses for NCD.

REFERENCES

Abong G, Develos C, Jimenea Y, Tambolero M, Torres K, Yema K (2018). Synthesis of Iron (II, III) Oxide Nanoparticles Using Rice Hull as Reducing and Capping Agent for Hexavalent Chromium Removal in Water

Al-Douri Y, Badi N, & Voon C (2017). Synthesis of carbon-based quantum dots from starch extracts: Optical investigations. Luminescence, 33(2), 260-266. doi: 10.1002/bio.3408

Ansari FA, Khan AH, Singh DP (2008). Physio-chemical Characteristics of Spent-Wash of Distillery Industry. Pollution Research, 27(1) pp. 125-128

Agrawal V, Vairagade V, Kedar A (2017). Activated carbon as Adsorbent in Advance Treatment of Wastewater. Journal of Mechanical and Civil Engineering. 14(4) pp. 36-40

American Public Health Association (1992) Standard Methods for the Examination of Water and Wastewater. 18th edition.

Bacusmo J. (2001). Status and Potentials of the Philippine Cassava Industry. (unpublished data). pp. 84-101

Chowhary P, Khan N, Bharagava RN. (2017). Distillery Wastewater: it's Impact on Environment and Remedies. Department of Environment Microbiology, India, 1(2), pp. 1-2.

Choct M, Morgan N (2016). Cassava: Nutrient Composition and Nutritive Value in Poultry Diets. Animal Nutrition, 2(4), pp. 253-261.

Das R, Bandyopadhyay R, Pramanik P (2018) Carbon Quantum Dots from Natural Resources: A Review, Materials of Today Chemistry, 8(1), pp. 96-109

Department of Energy (ND). List of Accredited Bioethanol Producers. Retrieved from https://www.doe.gov.ph/renewable-energy/list-bioethanol

Department of Environment and Natural Resources (2016). Environmental Management Bureau Memorandum Circular No. 012. EMB Approved Methods of Analysis for Water and Wastewater

Department of Environment and Natural Resources (2016). DENR Administrative order No. 2016-08. Water Quality Guidelines and General Effluent Standards of 2016.

Dune Sciences Inc. (2011). Particle Size analysis of nanomaterials using ImageJ/Fiji [PDF File]. Retrieved from: http://www.dunesciences.com/files /Particle_Size_Analysis_SOP.pdf

EMIS (2010) Adsorption Techniques. Retrieved from https://emis.vito.be/en/ techniekfiche/adsorption-techniques

Entrata J, Escordial T, Russel G, & Villagracia S (2017). Green Synthesis and Characterization of Iron Oxide Microparticles using Sugarcane (Saccharum Officinarum) Bagasse as Capping and Reducing Agent and Its Application as Novel Biosand Filter for Industrial Wastewater Treatment. Asian Journal of Basic and Applied Sciences, 4(1). Retrieved from https://www.omicsonline.org/open-access/removal-of-chromium-from-industrial-wastewater-by-adsorption-usingcoffee-husk-2169-0022-1000331.php?aid=88350

Fadlan A, Marwoto P, Aji M.P, Susanto, Iswari R.S. (2016). Synthesis of Carbon Nanodots from Waste Paper with Hydrothermal Method. AIP Conference Proceedings, 1(1), pp. 1-7.

Geankoplis C (1993). Principles of Transport Processes and Separation Processes. pp. 760-770

Goyal M and Bahgat M (2012). Application of Adsorbents for Water Pollution Control. Retrieved from http://www.eurekaselect.com/104515/chapter/activated-carbon-adsorption-for-waste-water-treatment

Guiotoku M, Rambo C, Maia C, and Hotz, D. (2018). Synthesis of carbon-based materials by microwave assisted hydrothermal process. Microwave Heation, doi:10.5572/20089

Gujral HJ, Kaur H, Sharma P, Singh J. (2011). Physiochemical, Pasting, and Thermal Properties of Starch Isolated from Different Barley Cultivars. Retrieved from https://www.tandfonline.com/doi/full/10.1080/10942912.2011.595863

ISO/TR 27628. (2008). Nanotechnologies — Terminology and definitions for nano-objects — Nanoparticle, nanofibre and nanoplate.

Jelinek R (2018). Carbon Quantum Dots. 1st ed. Switzerland: Springer, pp.5-27.

Kharayat Y (2012). Distillery wastewater: bioremediation approaches. Journal of Integrative Environmental Sciences, 9(2), pp.69-91.

Kaur K, Ahluwalia P, Singh H (2016). Cassava: Extraction of Starch and Utilization of Flour in Bakery Products. Retrieved from

https://www.researchgate.net/publication/316459045_Cassava_Extraction_of_starch_and_utilization_of_flour_in_bakery_products?fbclid=IwAR2ditzzIay25-1JV1RWBbq8Dc4Fxl3H_5LQdmYVGlyOwXElHdc1IbXHsaA

Kumar B, Gola D, Singh G, Bisht RS. (2017). Purification of Distillery Spent Wash by Using Activated Charcoal. EPH- International Journal of Applied Sciences. 2(2) pp. 10-21

Krysanova KO, Krysanov ON, Krylova A, Zaitchenko VM. (2017). Hydrothermal Carbonization of Peat. Solid Fuel Chemistry. 51(4). pp. 214-215

Li R, Wang L, and Shahbazi A (2015). A Review of Hydrothermal Carbonization of Carbohydrates for Carbon Spheres Preparation. Trends in Renewable Energy, 1(1), pp.43-56.

Li H, Kang Z, Liu Y, & Lee S (2012). Carbon nanodots: synthesis, properties and applications. Journal of Materials Chemistry, 22(46), 24230. doi: 10.1039/c2jm34690g

Martin MA, Raposo F, Borja R, Martina A. (2002). Kinetic Study of Anaerobic Digestion of Vinasse Pretreated with Ozone, Ozone Plus Ultraviolet, and Ozone Plus Ultraviolet Light in the Presence of Titanium Dioxide. Process Biochem. 33. pp. 699-706

Manisankar P, Rani C, Viswanathan S (2004). Effect of Halides in the Electrochemical treatment of Distillery Effluent. Chemosphere. 57(8). pp. 961-966.

Mazille F (2018). Adsorption (Activated Carbon). Retrieved from https://sswm.info/sswm-university-course/module-6-disaster-situations-planning-and-preparedness/further-resources-0/adsorption-%28activated-carbon%29

Melamane XL, Strong PJ, Burgess JE (2007). Treatment of Wine Distillery Wastewater: A Review with Emphasis on Anaerobic Membrane Reactors. S Afr Enol Vitic. 28(1). Pp 25-36

Mohana S, Archaya B, Madamwar D (2009). Distillery Spent Wash: Treatment Technologies and Potential Applications. Retrieved from https://www.sciencedirect.com/science/article/pii/ S0304389408009746

Muazu, Jameel & Musa, Hamidu & Isah, Ab & Bhatia, Pg & Tom, Gm. (2011). Extraction and characterization of Kaffir Potato Starch: A potential Source of pharmaceutical raw material. J. Nat. Prod. Plant Resour. 1.

Mukherjee S, Kumar S, Misra A, Fan M (2007). Removal of Phenols from Water Environment by Activated Carbon Bagasse Ash and Wood Charcoal. Chemical Engineering Journal 129. pp. 133-142.9

Mwangi G and Oguntimein G (2012). Study of an Activated Carbon System for the Treatment of Fermentation Wastewater from a Bioethanol Production Process. The West Indian Journal on Engineering. 35(2)

Nizamuddin S, Shrestha S, Athar S, Ali BS, Siddiqui MA (2016). A Critical Analysis on Palm Kernel Shell from Oil Palm Industry for Solid Char Production. Rev Chem Eng 32:489-505

Nizamuddin S, Baloch HA, Siddiqui MT, Mubarak NM, Tunio MM, Bhutto AW, Jatoi AS, Griffin GJ, Srinivasan MP. (2018), An Overview of Microwave Hydrothermal Carbonization and Microwave Pyrolysis of Biomass. Environmental Science and Bio/Technology. 17(4), pp.813-817, doi:10.1007/s11157-0189476z

Perry R and Green D (2008). Perry's Chemical Engineers' Handbook. 8(16). pp. 4-38

Ravikumar R, Saravanan R, Vasanthi NS, Swetha J, Akshaya N, Rajthilak M, Kannan KP. (2007). Biodegradation and decolorization of biomethanated distillery spent wash. Indian J Sci Technol. 1(2), pp. 1–6.

Satyawali Y (2007). Removal of Color from Biomethanated Distillery Spent Wash by Treatment with Activated Carbon. Retrieved from https://www.researchgate.net /publication/6424068_Removal_of_Color_from_Biomethanted_Distillery_Spent wash_by_Treatment_with_Activated_Carbon

Sevilla M and Fuertes A (2009). The production of carbon materials by hydrothermal carbonization of cellulose. Carbon, 47(9), pp.2281-2289.

Subha R, Sridevi OA, Aritha D, Sudha D (2015). Treatment Methods for the Removal of Phenol from Water – A Review. International Conference on Systems, Science Control, Communication, Engineering and Technology. pp. 199-203

United States National Nanotechnology Initiative (ND) What's So Special About the NanoScale? Retrieved from https://www.nano.gov/nanotech-101/special

United States Environmental Protection Agency USEPA (1973). Process Design Manual for Carbon Adsorption. Cincinnati, Ohio. pp 24-93

Wagh M and Nemade P (2015) Treatment of Distillery Spent Wash by Using Coagulation and Electro-coagulation [EC]. Retrieved from https://www.researchgate.net/publication/281242154_Treatment_of_Distillery_Spent_Wash_by_Using_Coagulation_and_Electrocoagulation_EC

Wang Y, & Hu A (2014). Carbon quantum dots: synthesis, properties and applications. Journal of Materials Chemistry C, 2(34), 6921. doi: 10.1039/c4tc00988f

Water and Wastewater Courses (ND). Wastewater Math Practice Problem – Percent Removal Efficiency. Retrieved from https://www.waterandwastewatercourses.com/wastewater-math-practice-problem-percent-removal-efficiency/

Yang Z, L, Z, Xu M, Ma Y, Zhang J, Su Y, Gao F, Wei H, and Zhang L (2013) Controllable Synthesis of Fluorescent Carbon Dots and Their Detection Application as Nanoprobes. Nano-Micro Letter*,* 5(4), pp 247-259, doi:10.5101/nml. v5i4.

Zhen, J, Liu X, Yang Y, Liu X, and Xu B (2018) Rapid and green synthesis of fluorescent carbon dots from starch for light emitting diodes. New Carbon Materials*,* 33(3), pp. 276-288. doi:10.1016/s1872-5805(18)60339-7

APPENDIX A

Documentation

Acquisition of Cassava

Washing and Peeling of Cassava

Size Reduction of Cassava using Knife and High-Speed Blender

Suspension of Pulp in Warm Water

Filtration using double fold cheesecloth

Decanting of Cassava Pulp Mixture

Drying of Cassava Starch

Microwave-assisted Hydrothermal Carbonization

UV Light Testing for Luminescence

Dried Nanocarbon Dots

Sieving and Drying of Sand

Preparation of Downflow Gravity Contactor

Preparation of Set-ups with Replicates

Treatment of Distillery Spent wash

Spent Wash Parameter Testing

APPENDIX B

Raw Data

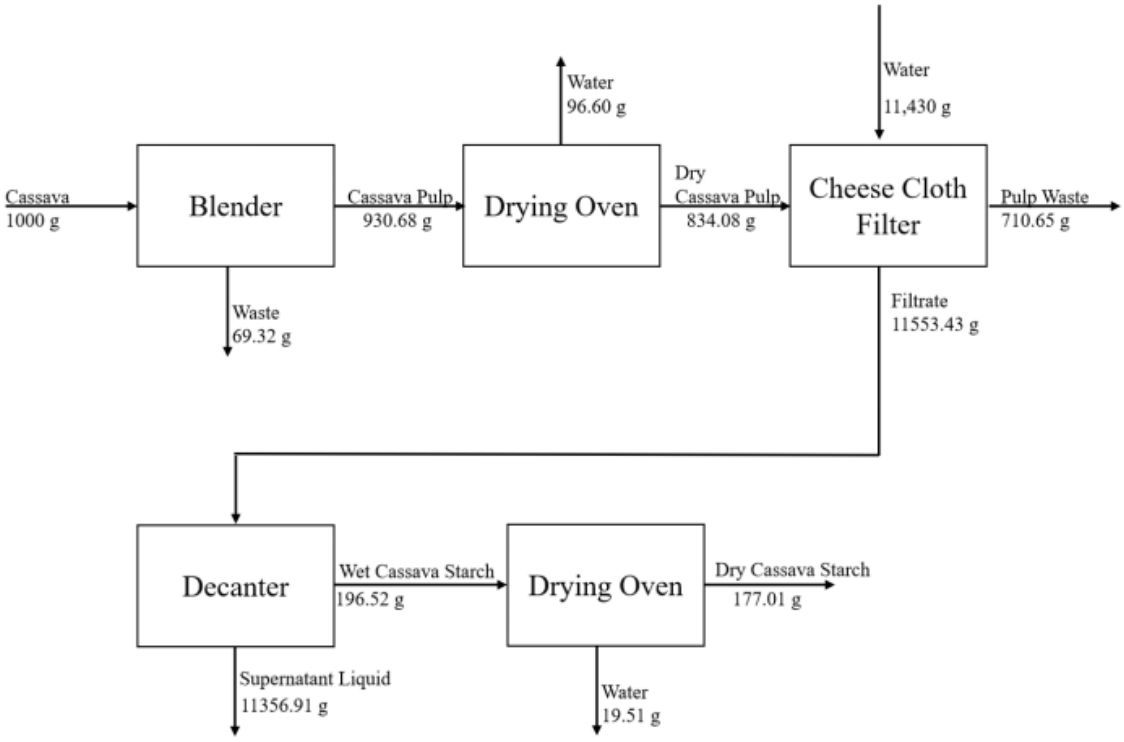

Figure B.1. Flow process diagram of the starch extraction process.

Table B.1

Mass of Wet NCD Produced in Each Microwave-Assisted Hydrothermal Carbonization

Batch	Mass, g
1	7.54
2	7.92
3	9.84
4	8.18
5	9.14
6	9.66
7	9.73
8	10.34
9	9.74
10	10.84
11	11.26
12	10.12
13	9.96
14	10.95
15	11.26
Total Mass, g	**146.48**
Average Wet NCD per Batch, g	**9.77**

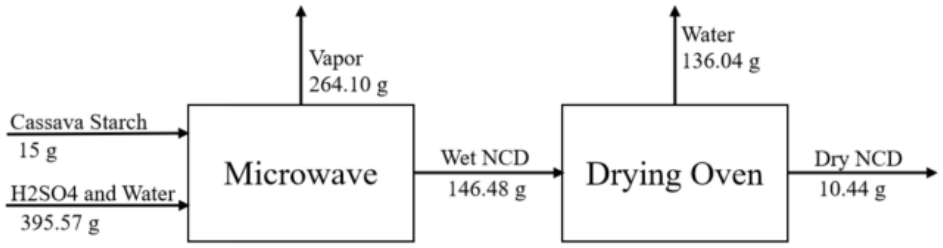

Figure B.2. Flow process diagram of the microwave-assisted hydrothermal carbonization.

Table B.2

FESEM Analysis on Particle Diameter and the Corresponding Surface Area

Particle No.	Particle Diameter, nm	Surface Area, nm^2
1	56.66	10085.63
2	79.05	19631.51
3	73.02	16750.72
4	67.66	14381.82
5	46.04	6659.18
6	87.17	23781.73
7	38.08	4555.58
8	50.90	8139.27
9	49.23	7613.94
10	47.90	7208.10
11	54.93	9479.14
12	114.20	40971.52
13	76.94	18597.49
14	55.57	9701.32
15	60.24	11400.39
16	69.53	15187.78
17	54.56	9351.87
18	71.60	16105.56
19	43.25	5876.55
20	60.70	11575.17
Average	**62.8615 nm**	**13357.2135 nm^2**

Table B.3

Pretest results for spent wash parameters.

Parameter	Diluted Sample	Actual Result
BOD, mg/L	263	58,123
Color, mg/L	496	109,764
pH	5.13	5.13
TSS, mg/L	200.76	44,367

Table B.4

Post-test results for spent wash parameters.

Parameter	Set-up A		Set-up B		Set-up C	
	Diluted Sample	**Actual Result**	**Diluted Sample**	**Actual Result**	**Diluted Sample**	**Actual Result**
BOD, mg/L	263	19,227	94	20,774	256	56,756
Color, mg/L	496	80,444	254	56,134	388	85,748
pH	5.13	6.00	5.90	5.90	5.50	5.50
TSS, mg/L	200.76	1,989	7.33	1,619	15	3,315

Table B.5

T-test Result for Spent Wash Treatment in terms of BOD removal

Variable	n	Mean	SD	df	T-ratio	p
Activated Carbon	2	87.0	1.41	2	4.950	0.038
Nanocarbon dots	2	94.0	1.41			

Table B.6

T-test Result for Spent Wash Treatment in terms of color removal

Variable	n	Mean	SD	df	T-ratio	p
Activated Carbon	3	364.0	26	2.124	7.217	0.016
Nanocarbon dots	3	254.0	4.58			

Table B.7

T-test Result for Spent Wash Treatment in terms of pH Neutralization

Variable	n	Mean	SD	df	T-ratio	p
Activated Carbon	3	6.0	0.20	4	0.480	0.656
Nanocarbon dots	3	5.9	030			

Table B.8

T-test Result for Spent Wash Treatment in terms of TSS removal

Variable	**n**	**Mean**	**SD**	**df**	**T-ratio**	**p**
Activated Carbon	3	9.00	1.00	4	2.50	0.067
Nanocarbon dots	3	7.33	0.58			

APPENDIX C

Calculations

Computation for % moisture in cassava pulp:

$$\%_{H_2O\_in\_cassava\_pulp} = \frac{m_{wc} - m_{dc}}{m_{wc}} x(100\%) = \frac{930.68 - 834.08}{930.68} x(100\%) = 10.38\% \quad (7)$$

Computation for yield of starch and NCD:

$$yield_{starch} = \frac{m_{ds}}{m_{dc}} x(100\%) = \frac{177.01}{834.08} x(100\%) = 21.22\% \quad (8)$$

$$yield_{NCD}(\%) = \frac{m_{NCD}}{m_{starch}} x(100\%) = \frac{10.44}{15.00} x(100\%) = 69.60\% \quad (9)$$

Computation for the % removal of BOD:

$$R_{BOD}AC(\%) = \frac{C_i - C_e}{C_i} x(100\%) = \frac{58{,}123 - 19{,}227}{58{,}123} x(100\%) = 66.92\% \quad (10)$$

$$R_{BOD}NCD(\%) = \frac{C_i - C_e}{C_i} x(100\%) = \frac{58{,}123 - 20{,}774}{58{,}123} x(100\%) = 64.26\% \quad (11)$$

$$R_{BOD}Sand(\%) = \frac{C_i - C_e}{C_i} x(100\%) = \frac{58{,}123 - 56{,}576}{58{,}123} x(100\%) = 2.66\% \quad (12)$$

Computation for the % removal of color:

$$R_{color}AC(\%) = \frac{C_i - C_e}{C_i} x(100\%) = \frac{109{,}764.07 - 80{,}444}{80{,}444} x(100\%) = 26.71\% \quad (13)$$

$$R_{color}NCD(\%) = \frac{C_i - C_e}{C_i} x(100\%) = \frac{109{,}764.07 - 56{,}134}{80{,}444} x(100\%) = 48.86\% \quad (14)$$

$$R_{color}Sand(\%) = \frac{C_i - C_e}{C_i} x(100\%) = \frac{109{,}764.07 - 85{,}748}{80{,}444} x(100\%) = 21.88\% \quad (15)$$

Computation for change in pH:

$$\Delta pH_{AC} = pH_i - pH_e = 5.13 - 6.00 = -0.87 \quad (16)$$

$$\Delta pH_{NCD} = pH_i - pH_e = 5.13 - 5.97 = -0.77 \quad (17)$$

$$\Delta pH_{Sand} = pH_i - pH_e = 5.13 - 5.5 = -0.37 \quad (18)$$

Computation for the % removal of TSS:

$$R_{TSS}AC(\%) = \frac{C_i - C_e}{C_i} x(100\%) = \frac{44{,}367.07 - 1{,}989.00}{44{,}367.07} x(100\%) = 95.52\% \quad (19)$$

$$R_{TSS}NCD(\%) = \frac{C_i - C_e}{C_i} x(100\%) = \frac{44{,}367.07 - 1{,}619.93}{44{,}367.07} x(100\%) = 96.35\% \quad (20)$$

$$R_{TSS}Sand(\%) = \frac{C_i - C_e}{C_i} x(100\%) = \frac{44{,}367.07 - 3{,}315.93}{44{,}367.07} x(100\%) = 92.53\% \quad (21)$$

APPENDIX D

Republic of the Philippines
Department of Science and Technology
INDUSTRIAL TECHNOLOGY DEVELOPMENT INSTITUTE
ADVANCED DEVICE AND MATERIALS TESTING LABORATORY
DOST Cpd., General Santos Ave., Bicutan, Taguig City
Tel.: (02) 837-0461 Email: services@admatel.com
http://www.admatel.com/

PAB Accredited Testing Laboratory
PNS ISO/IEC 17025:2005
LA-2015-272A

REPORT OF ANALYSIS

Reference No.	:	**ADMATEL 1908 – 1622**
Customer	:	**Hannah Mae Bacroya** University of Saint La Salle
Sample Label	:	Nano Carbon Dots – Hydrochar mixture - Black in color solid form
Analysis Requested	:	FE - SEM Imaging
Date Received	:	August 19, 2019
Date Tested	:	August 20, 2019

I. Test Description

The analysis was done using the following parameters:

Instrument	: Dual Beam Helios Nanolab 600i
FESEM Accelerating voltage	: 5.0 kV
Beam Current	: 0.17 nA

II. Summary

The SEM images of the Nano Carbon Dots sample are presented in Figures 1 to 4. The particle size measurements are shown in Figure 5 and summarized in Table 1.

Republic of the Philippines
Department of Science and Technology
INDUSTRIAL TECHNOLOGY DEVELOPMENT INSTITUTE
ADVANCED DEVICE AND MATERIALS TESTING LABORATORY
DOST Cpd., General Santos Ave., Bicutan, Taguig City
Tel.: (02) 837-0461 Email: services@admatel.com
http://www.admatel.com/

PAB A accredited
Testing Laboratory
PNS ISO/IEC 17025:2005
LA-2015-272A

III. Results

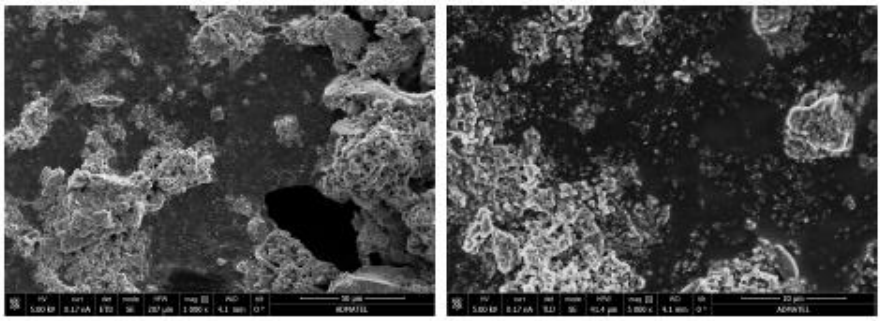

Figure 1. SEM images of Nano Carbon Dots sample taken at 1,000 and 5,000x magnifications

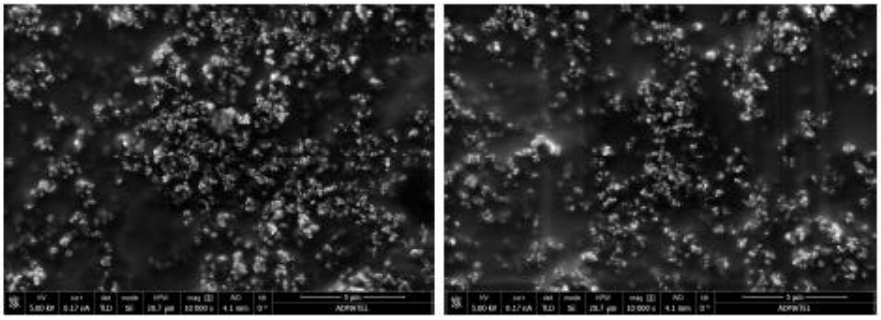

Figure 2. SEM images of Nano Carbon Dots sample taken at 10,000x magnification

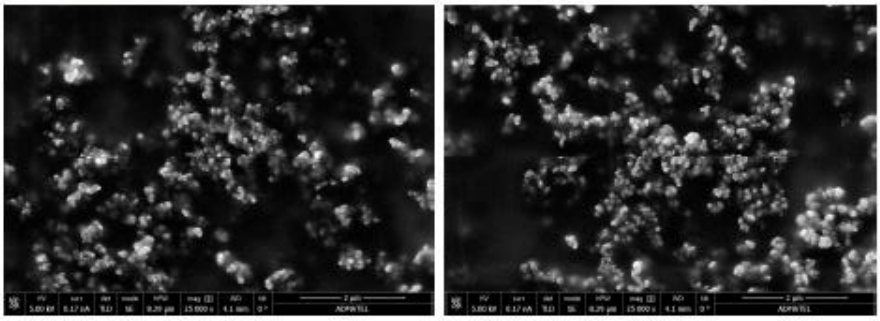

Figure 3. SEM images of Nano Carbon Dots sample taken at 25,000x magnification

Republic of the Philippines
Department of Science and Technology
INDUSTRIAL TECHNOLOGY DEVELOPMENT INSTITUTE
ADVANCED DEVICE AND MATERIALS TESTING LABORATORY
DOST Cpd., General Santos Ave., Bicutan, Taguig City
Tel.: (02) 837-0461 Email: services@admatel.com
http://www.admatel.com/

PAB A accredited
Testing Laboratory
PNS ISO/IEC 17025:2005
LA-2015-272A

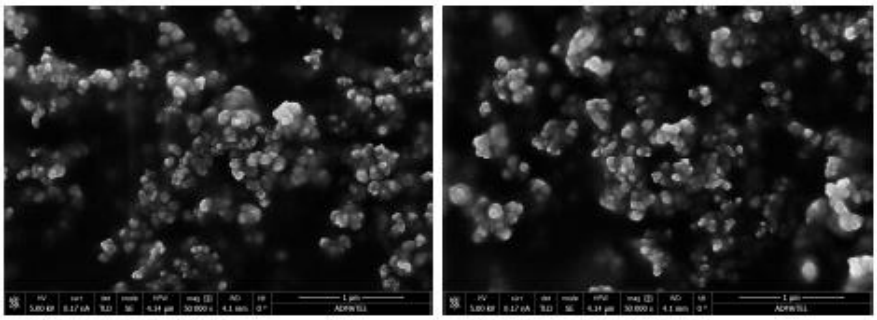

Figure 4. SEM images of Nano Carbon Dots sample taken at 50,000x magnification

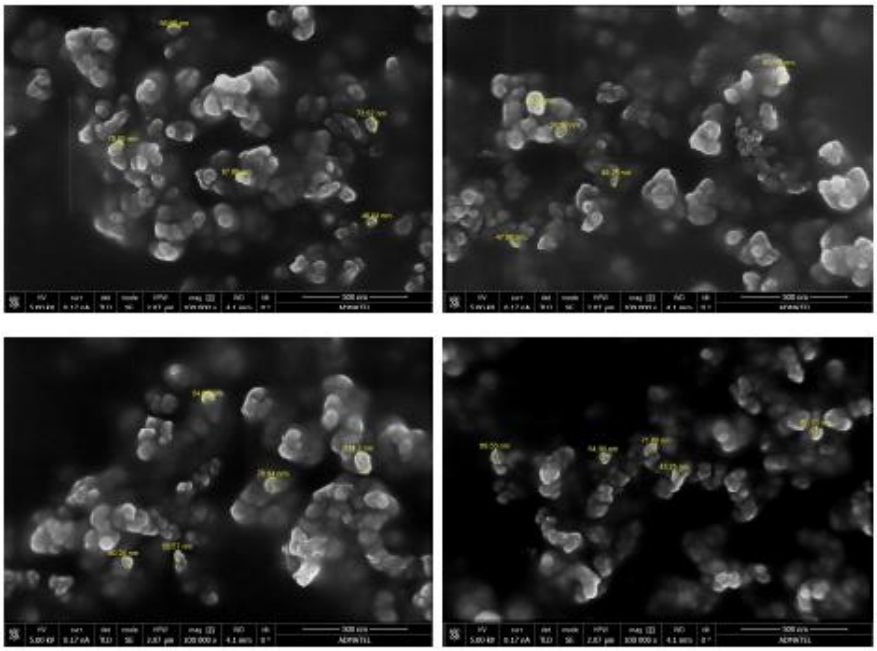

Figure 5. SEM images of Nano Carbon Dots sample taken at 100,000x magnification

Republic of the Philippines
Department of Science and Technology
INDUSTRIAL TECHNOLOGY DEVELOPMENT INSTITUTE
ADVANCED DEVICE AND MATERIALS TESTING LABORATORY
DOST Cpd., General Santos Ave., Bicutan, Taguig City
Tel.: (02) 837-0461 Email: services@admatel.com
http://www.admatel.com/

PAB Accredited
Testing Laboratory
PNS ISO/IEC 17025:2005
LA-2015-272A

Table 1. Particle measurements of the Nano Carbon Dots

Particle No.	Measurement, nm	Particle No.	Measurement, nm	Particle No.	Measurement, nm	Particle No.	Measurement, nm
1	56.66	6	87.17	11	54.93	16	69.53
2	79.05	7	38.08	12	114.2	17	54.56
3	73.02	8	50.90	13	76.94	18	71.60
4	67.66	9	49.23	14	55.57	19	43.25
5	46.04	10	47.90	15	60.24	20	60.70

IV. Remarks

Sample was oven-dried at 100°C for one hour prior to SEM imaging.

VALIDITY OF THE REPORT: The test results are those obtained at the time of the test and pertain only to the sample/s received by ADMATEL.

PRINCESS JOYCE R. ANTONIO
Analyst

for
MARIANNE THERESE A. BAUCA
Laboratory Head

Issued under the authority of:

ARACELI M. MONSADA, Dr. Engg
Laboratory Manager

Form: AL-21-F25a
Issue: June 2017
Revision: 01

APPENDIX E

October 7, 2019

To Whom It May Concern,

This is to certify that the undergraduate thesis titled “Cassava Starch-Derived Nanocarbon Dots by Hydrothermal Carbonization for Distillery Spent Wash Treatment” by Hannah Mae P. Bacroya, Jan Harry A. Jondanero, Luigi P. Limsiaco for the degree in Bachelor of Science in Chemical Engineering has been edited by the undersigned faculty member of the University of St. La Salle, Bacolod City.

Thank you very much,

Truly yours,

Annabelle A. Chavez, Ph.D.