Adsorption Capability of Talisay (*Terminalia catappa*) Seed Husk Biochar for Removal of Cadmium in Contaminated Synthetic Water

Submitted in Partial Fulfillment of the Requirements in Practical Research II

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INTRODUCTION

A. Background of the Study

Water is becoming increasingly sparse that is projected to be one of the most valuable resources in the 21 st century. While the human population continues to grow, heavy industry and other sources are simultaneously polluting dwindling supplies of water. Excessive heavy metal concentration in water poses a significant risk to human health.

Activated carbon is a structure of carbon that has been administered with oxygen to create millions of tiny pores between the carbon atoms. Activated carbon treatment is typically installed to provide removal of compounds such as natural organic, taste, odor, and synthetic. Also, it has a capability of dissolving contaminants from water and then process gas-phase streams **(Jason C. 2014).** Therefore, activated carbon has the ability of adsorption where further chemical treatment enhances its aptness to adsorb.

According to **Palakshi, B. (2020),** biochar is also known as black carbon that is derived from organic materials by slowly heating biomass in a low-oxygen environment, until everything but the carbon is burned off. It has attracted widespread attention due to its high carbon content, abundant surface functional groups and porous structure. Moreover, Biochar brings beneficial effects where it increases agricultural productivity and provides protection against some foliar and soil-borne diseases.

Although known for its effectivity and beneficial effects, the average price for commercialized biochar in the US was $1.29 per pound or $2,580 per ton. In the near term, due to price point, biochar will likely only be used in high-end specialty markets, but there is growing interest in developing biochar into new products that take advantage of its unique chemical properties. **(Farm Energy, 2019).**

Wastewater treatment is a worldwide issue due to increment in both urbanization and industrialization where wastewater is used from any combination of domestic, industrial, commercial, and any sewer infiltration. Along with the current situation in Paracale, Camarines Norte where excessive mining activity is occurring that can trigger wastewater issue containing different harmful heavy metals. Moreover, water is one of the significant common factors and is basic for sustainability of life. On the other hand, toxic industrial effluents released into sewage systems and drains without treatment that deteriorating the water quality for drinking and irrigation.

Heavy metals are identified as being toxic and incorruptible where it will pose adverse health effects on humans. Excessive emissions of heavy metals are found in livestock wastewater and can cause serious environmental pollution **(Vhahangwele, M. Khathutshelo, M. 2018).** In addition, one of the heavy metals is highly toxic known as Cadmium that is present on earth's crust and its exposure in environment gives an extreme challenge to environmentalist for it is a non-degradable in nature where once released to the environment, stay in circulation. In environment, cadmium transfers from one trophic level to another and finally accumulated in human with toxic effects. Thus, there is an emergent need to remove the cadmium from environment.

Also, there are studies about tea waste and rice husk biochar that were used for the elimination of Hexavalent Chromium from wastewater titled as Adsorption-reduction performance of tea waste and rice husk biochars for Cr (VI) elimination from wastewater by **Usman K, Muhammad B, and et.al (2020)**. With the objectives to study the effect of pH (3–10), shaking time (0.016–24 h), sorbent dose (0.1–1.3 g L^{-1}) and initial concentration of Cr (VI) (10–250 mg L^{-1}). In addition, rice and corn husk biochar were used to remove selected heavy metal ions from industrial wastewater.

Talisay (*Terminalia catappa*), commonly known as Indian Almond, Tropical Almond Tree, or Java Almond, is a large tree up to 40 meters in height that grows mainly in Asia, Africa, and Australia. It is nocturnal with a trunk that can be either straight or bent, sometimes bolstered up to 3 m long. The leaves are long, flat, glossy, turn red and fall off twice a year. Greenish-white flowers are at the tip of the branches. The edible fruits are fibrous, with tender skin and a thin layer of sub acid juicy flesh. They are green and turn red when ripening. **(Fern, K. 2009**). This species has been extensively introduced into littoral habitats, coastal forests, gardens and parks to be used as an ornamental, shade tree, and sand-dune stabilizer (**Orwa et al., 2009; ISSG, 2017**).

Talisay (*T. catappa*) seed is known for its nutritional fruit and possesses medicinal benefits as well. Talisay (*T. catappa*) seed husk has been recognized for its medicinally essential phytoconstituents, such as phenol, flavonoid, and carotenoid. Numerous pharmacological investigations have confirmed this plant's ability to exhibit antimicrobial, anti-inflammatory, antidiabetic, antioxidant, hepatoprotective, and anticancer activities, all of which support its traditional uses **(Donoso, A.B.et al. 2018).**

Talisay (*T. catappa*) seed husks are practicable materials for biochar production with the ability of adsorption that can be used for the alteration of wastewater. In this manner, the economic and agricultural benefits of Talisay (*T. catappa*) seed husk biochar are to be established.

B. Significance of the Study

Water pollution is one of the major problems the world is facing. Wastewater effluents are released to a variety of environments, such as lakes, ponds, streams, rivers, estuaries, and oceans. As this water have harmful chemicals which result to the pollution of the environment and threating human life. Cadmium is formed from corrosion of galvanized pipes, erosion of natural deposits, discharge from metal refineries, and runoff from waste batteries and paints. It can cause short term-nausea, vomiting, diarrhea, sensory disturbances, liver injury and renal failure. Furthermore, it also has long term effect in the human health which can cause to kidney, liver, bone, and blood damage which is difficult to fix. In this study, the cadmium that is present in the synthetic wastewater or the adsorbate will be removed using the biochar made of Talisay (*T. catappa*) seed husk as the adsorbent.

Specifically, this study benefits the following:

Community. Through this study, the community will appreciate the effectiveness of Talisay (*T. catappa*) seed husk as a biochar in wastewater treatment and have an awareness about how to prevent and treat a contaminated water.

People who live near bodies of water. Through this, they will have a knowledge on how to prevent a damage to a person's body because of heavy metals on contaminated water and they will also have an awareness on the possible effect of contamination and exposure to cadmium.

Philippines Economy. In this study, it will help the Philippine's economy to produce an alternative natural methods of wastewater treatment.

Researchers. In this study, the researchers may enhance their skills in research and have an improvement in their knowledge.

Wastewater Engineers. The findings in this study will give them an opportunity to have a development in wastewater treatment.

School. This study will serve as a reference material for discussion and learning.

Future Researchers. This study will serve as a reference for the future researchers who will study about wastewater management using a biochar.

C. Statement of the Problem

Heavy metals, among all contaminants, have attracted the most attention from environmental chemists due to its toxicity. Heavy metals are found in natural waters in trace quantities, but many of them are toxic even at extremely low concentrations. Even in limited amounts, metals such as arsenic, lead, cadmium, nickel, mercury, chromium, cobalt, zinc, and selenium are extremely toxic. The growing quantity of heavy metals in our resources is currently an area of greater concern, especially as a large number of factories discharge their effluent metals into fresh water without adequate treatment **(Masindi & Muedi, 2018)**.

Activated carbon is widely used to purify water. Both large-scale and small-scale products use activated carbon filters. They can eliminate impurities from both large-scale, community-wide water system and smaller scale, residential applications **(The Science Behind Activated Carbon Water Filters, 2018)**. Activated carbon is a very efficient adsorbent because it is a highly porous substance with a wide surface area for pollutants to adsorb to **(C. Johnson, 2014)**. However, despite being an outstanding adsorbent, it is also a costly adsorbent.

This study will examine the effectiveness of Talisay (*Terminalia catappa*) seed husk as a biochar for cadmium adsorption in wastewater. It will make a cost-efficient biomass material for biochar production. Also, it will identify the cadmium concentration in which the biochar is most effective. It can be used to prevent serious harm of heavy metal in the environment and in the health of people.

D. Objectives

This research study will focus on the efficacy of cadmium adsorption on synthetic wastewater using the Talisay (*Terminalia catappa*) Seed Husk as a biochar adsorbent produced from Talisay (*Terminalia catappa*) Tree to meet the following objectives:

1. To determine the effectiveness of Talisay (*Terminalia catappa*) Seed Husk as a biochar for Cadmium adsorption.

Hypothesis

1.1 Talisay (*Terminalia catappa*) seed biochar is effective in adsorbing cadmium in a "contaminated water."

1.2 Talisay (*Terminalia catappa*) seed husk is not effective in adsorbing cadmium in a "contaminated water."

2. To identify the cadmium concentration in which Talisay (*Terminalia catappa*) seed husk biochar is most effective.

Hypothesis

2.1 There is a significant difference in the effectivity of the biochar at different cadmium concentration.

2.2 There is no significant difference in the effectivity of the biochar at different cadmium concentration.

E. Research Questions

This study aims to determine the effectiveness of Talisay (*Terminalia catappa*) as a biochar for Cadmium adsorption.

Furthermore, the researcher seeks to answer the following questions:

1. What is the effect of 20 grams of adsorbent at:

1.1 10 ppm Cadmium Chloride concentration,

1.2 20ppm Cadmium Chloride concentration, and

1.3 30ppm Cadmium Chloride concentration?

2. What is the cadmium content after the treatment in the same setups in the following time intervals?

2.1 10 minutes;

2.2 20 minutes;

2.3 30 minutes?

3. Is there a significant difference in the cadmium content before and after the treatment to test the effect of constant adsorbent dose on varying cadmium chloride concentrations?

4. What are the challenges encountered by the researcher in the process during:

   4.1 pre-execution;

   4.2 during execution, and

   4.3 post-execution of the Talisay (*Terminalia catappa*) seed husk biochar for cadmium adsorption?

5. What makes the Talisay (*Terminalia catappa*) seed husk as a potential component for biochar in a cadmium adsorption method?

F. Scope and Delimitation

This study is primarily focused on the efficacy of cadmium adsorption on synthetic wastewater using the Talisay (*Terminalia catappa*) seed husk as a biochar produced from Talisay (*T. catappa*) trees. The researchers aim to identify the cadmium concentration in which Talisay (*T. catappa*) seed husk biochar is most effective. The materials will be collected in Vinzons Pilot High School, Vinzons, Camarines Norte.

With the modification and carbonization of Talisay seed husk, pyrolysis will be used with the help of the **Mines and Geosciences Bureau Region 5**. The physical and chemical characterization or the physicochemical testing of the produced Talisay seed husk biochar will be tested at **DOST- Forest Products Research and Development Institute.**

Due to the expensive laboratory test, the study will only be limited to testing and manipulating the effects of constant adsorbent dosage to varying cadmium chloride concentrations over time. Other factors that could affect the adsorption capacity will be tested and not manipulated instead they will remain constant.

Chapter II

A. Review of Related Literature

Wastewater has been a global issue, which is a byproduct of domestic, industrial, commercial, or agricultural activities. It is defined as used water. It includes substances such as human waste, food scraps, oils, soaps, and chemicals. It is composed of 99.9% water and the remaining 0.1% is what is removed. This 0.1% contains organic matter, microorganisms, and inorganic compounds. Wastewater effluents are released to a variety of environments, such as lakes, ponds, streams, rivers, estuaries, and oceans. Wastewater also includes storm runoff, as harmful substances wash off roads, parking lots and rooftops (**Tuser C., 2020**). At a global level, around 80% of wastewater produced is discharged into the environment untreated, causing widespread water pollution.

Treatment plants reduce pollutants in wastewater to a level nature can handle. If wastewater is not properly treated, then the environment and human health can be negatively impacted. These impacts can include harm to fish and wildlife populations, oxygen depletion, beach closures and other restrictions on recreational water use, restrictions on fish and shellfish harvesting and contamination of drinking water. Wastewaters contain high loads of organic matter and nutrients, constituting a severe problem. These wastewaters, after the application of an appropriate treatment, can be used for food production, improving its yield and quality. The use of reclaimed water for irrigation has been often recommended by several organizations, namely, the Environmental Protection Agency (EPA), World Health Organization (WHO), and European Union

(EU) as a suitable solution for setting up water management strategies (**Prazeres et al., 2017**).

Water pollution by heavy metal ions is a crucial environmental issue worldwide because these ions are acutely toxic, nondegradable, and bioaccumulative. Cadmium (II), Lead (Pb) and mercury (II) are the most important toxic elements in the liquid wastes of several industries, including those that produce fertilizers, batteries, electronics, textiles, and petrochemicals, as well as tanneries and pesticide mills. Much research is focused on lead (Pb) and cadmium (Cd) ions which are *extremely* toxic at low concentrations and considered as carcinogenic heavy metals (**Sönmezay *et al.* 2012**). These heavy metals are poured into water and groundwater from mining and petrochemicals industries (**Li *et al.* 2019**). The toxicity of Cd (II) may lead to carcinogenesis, renal dysfunction, lung damage, and various syndromes in humans.

Many commercial materials such as commercial activated carbon have since being used in the removal of these heavy metals, mainly by the process of adsorption. But the use of these materials is usually expensive and involves a number of technicalities. (**P.R.O. Edogbanya, and Y. Apeji, 2013**). Biochars have great potential to be used for wastewater treatment. Biochar can be used as an adsorbent to remove different pollutants in water and wastewater. It can be used for adsorbing metals/metalloids and purifying water (**Agrafioti et al., 2013**), applied to soils for improving soil fertility and crop productivity (**Yoo et al., 2018**), employed for clean energy production to partially replace the fossil fuels (**Fang et al., 2018**), and utilized as adsorbent and catalysts to various pollutants and reduce greenhouse gas emission (**Xiong et al., 2017**). Long term exposure to heavy metals in the aqueous phase can cause serious health threats even at low concentration (Ahmed et al., 2016).

Increased evidence suggests that biochar obtained from plants and animal residues can effectively adsorb heavy metals in water and wastewater (Higashikawa et al., 2016). In addition, several studies have also suggested biochar's applications for adsorption of organic matter for water treatment. Biochar production has many benefits, it includes; offset greenhouse gas emission because it stores carbon in a stable form, preventing the release of greenhouse gases into the atmosphere from biomass degradation (**Creamer and Gao, 2016**) and biochar is an effective, low-cost, and environment-friendly adsorbent (**Cha et al., 2016**), which is related to its relatively large surface area and abundant surface functional groups (SFG) (**Wang et al., 2017**).

B. Review of Related Study

In the following study, the heavy metal that was adsorb by the different biochar is Cadmium (II): *Adsorption of Cadmium (II) onto Oxidized Activated Carbon Derived from Mahogany (Swietenia macrophylla King) Pericarp: Equilibrium, Thermodynamics, and Kinetics (2021), Removal of Cd (II) ion from wastewater by adsorption onto treated old newspaper: kinetic modeling and isotherm studies (2013), Cadmium adsorption by biochar prepared from pyrolysis of silk waste at different temperatures (2018), Investigation on cadmium ions removal from water by different raw materials-derived biochars (2020.), and Adsorption of Cadmium Using Biochars Produced from Agro-Residues (2020)* while in the study of **Baguio R., and Decatoria M. (2018),** *The Adsorption Ability of Talisay (Terminalia* *catappa) Leaves for Removal of Hexavalent Chromium in Aqueous Solution,* they used hexavalent chromium in an aqueous Solution.

Furthermore, in the study conducted by **Canlas, J. et. al (2019)**, they tested the lead (II) ions in an artificial contaminated soil, while in the study of *Application of laboratory prepared and commercially available biochars to adsorption of cadmium, copper, and zinc ions from water (Bioresource Technology, 2015)*, they tested various heavy metals such as cadmium, copper and zinc ions from water.

In the study conducted by **Canlas, J. et. al (2019)**, *Talisay (Terminalia catappa) seed husk biochar for adsorption of lead (II) ions in artificially contaminated soil,* it investigates the efficacy of biochar from Talisay (*Terminalia catappa*) seed husks in long-term adsorption of Lead in a synthetic contaminated soil in which the results showed that the biochar had a satisfactory adsorption. Furthermore, according to the immobilization experiment the soil amended with biochar immobilized Pb, lowering its concentration by 99.47 percent. Therefore, as result, the biochar produced is sufficient for Pb remediation in contaminated soils. On the other hand, in the study of **Baguio R. and Decatoria M. (2018)**, *The Adsorption Ability of Talisay (Terminalia catappa) Leaves for Removal of Hexavalent Chromium in Aqueous Solution,* the researchers investigated the adsorption ability of talisay *(Terminalia cattapa*) leaves for the removal of hexavalent chromium in aqueous solution. According to the findings, the chromium content in the aqueous solutions was eradicated after the procedure. Due to its high porosity and surface area, the Talisay (*Terminalia catappa*) leaves was proved to be an efficient adsorbent.

In addition, in the study of **Granada, J. R. N., et. al (2021)**, *Adsorption of Cadmium (II) onto Oxidized Activated Carbon Derived from Mahogany (Swietenia macrophylla King) Pericarp: Equilibrium, Thermodynamics, and Kinetics.* The adsorption of Cd (II) ions onto oxidized activated carbon derived from mahogany pericarp was studied in terms of thermodynamics and kinetics. Adsorption equilibrium studies showed that as the degree of oxidation of carbon material increased, the overall adsorption potential for Cd (II) also increased. According to the results of kinetic studies, the adsorption of Cd (II) ions onto oxidized activated carbon is restricted by film diffusion, while Cd (II) adsorption on unmodified carbon is limited by intraparticle diffusion.

Moreover, in the study, *Investigation on cadmium ions removal from water by different raw materials-derived biochars,* biochar from sludge (SB), cow dung (DB), corn stalk (CB) and willow branches (WB) were synthesized and activated by potassium hydroxide (KOH), and these biochars were used as adsorbent to remove divalent cadmium ion (Cd (II)) from water, while in the study of *Adsorption of Cadmium Using Biochars Produced from Agro-Residues (2020),* biochars made from the pyrolysis of various agro-residues, such as coffee husk, quinoa straw, and oil palm kernel shell, are discussed here. Also, in the study of *Cadmium adsorption by biochar prepared from pyrolysis of silk waste at different temperatures (2018),* biochars (BC300, BC500 and BC700) were produced from silk waste through pyrolysis under oxygen-limited condition at 300, 500 and 700 °C, respectively.

In addition, in the study, *Removal of Cd (II) ion from wastewater by adsorption onto treated old newspaper: kinetic modeling and isotherm studies (2013),* This research studies the effects of initial Cd (II) concentration. Chakravarty et al., who studied the use of treated old newspaper (TNP) as an adsorbent for removing heavy metal ions from aqueous solution, found that current research into the use of TNP as an adsorbent for removing zinc and copper ions from aqueous solution is extremely limited. Furthermore, the study of *Application of laboratory prepared and commercially available biochars to adsorption of cadmium, copper and zinc ions from water (2015),* conducted to compare and evaluate the two biochars (made from Sida hermaphrodita – BCSH/laboratory developed and made from wheatstraw – BCS/commercially available) for their ability to adsorb heavy metal ions Cd (II), Cu (II), and Zn (II) from water. The effect of solution pH and interfering ions on sorption kinetics and isotherms, as well as the influence of solution pH and interfering ions, were investigated. The adsorption capacity of biochars was affected by its physico-chemical properties. In all of the metals tested, BCHS had a higher adsorption efficiency than BCS. **(Bogusz, A. et al., 2015)**.

C. Conceptual Framework

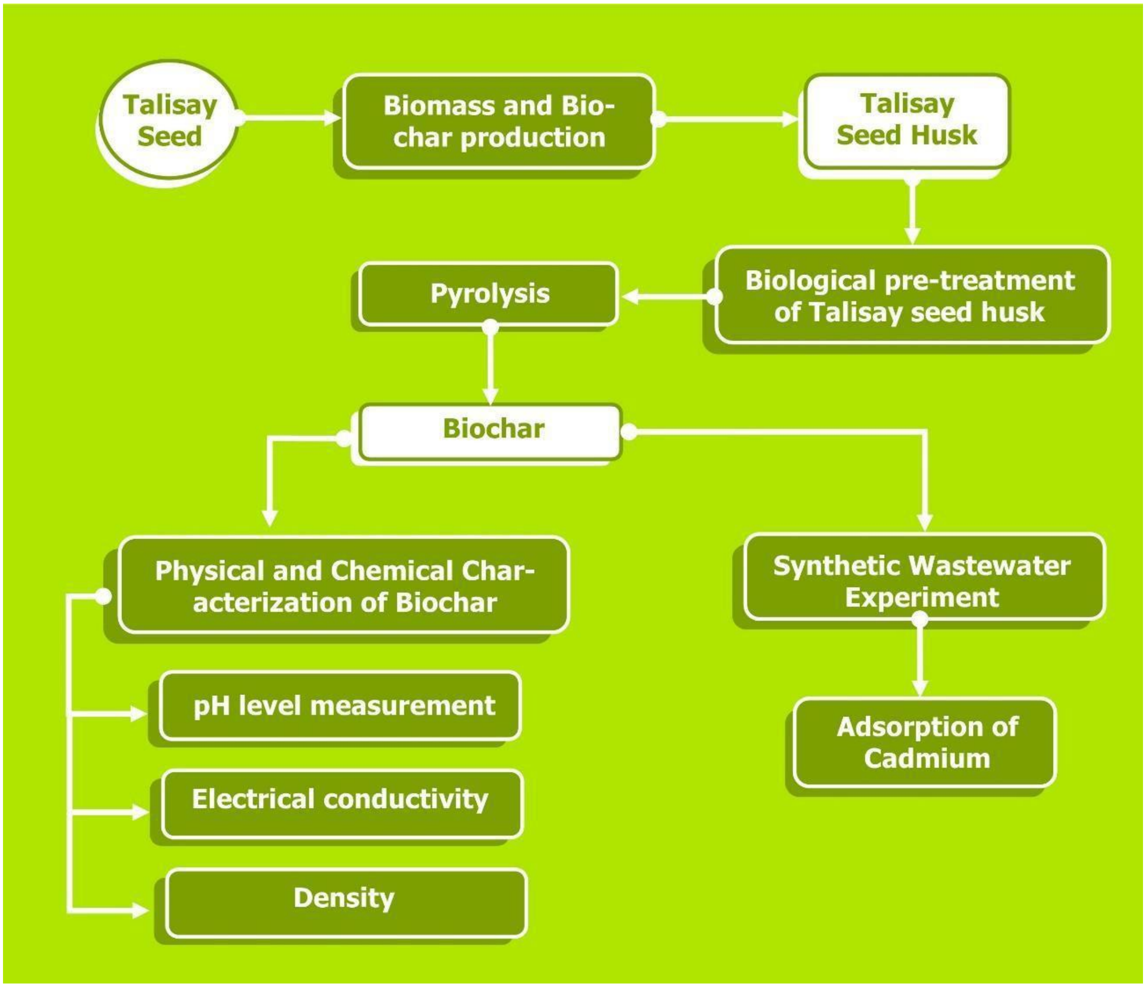

Figure 1. Conceptual Framework

In this study, the collected **Talisay (*Terminalia catappa*) Seed Fruit** will undergo the **biomass and biochar production** in which it will go through the decorticator machine where the seed will be manually separated from the husk.

From **Talisay (*Terminalia catappa*) seed husk**, **biological pre-treatment** will be the first step in the production of biochar. Biological pre-treatment allows for the removal of microorganisms.

Then the **Talisay (*Terminalia catappa*) seed husk** will undergo **pyrolysis process** for the **modification and production of biochar**.

For the **physical and chemical characterization of biochar; pH level** will be determined for its acidity and basicity of the biochar, **electrical conductivity** gives an indication of the availability of nutrients, or presence of excess ash/salt, and **density of biochar** will also be determined where the mass per unit volume displaced by the envelope of the particle, including internal pores will be measured. After testing the physicochemical property of biochar, it will be subjected to **synthetic wastewater** wherein there is a presence of Cadmium chloride in the solution. And **adsorption** is the process of removing the Cadmium from the contaminated wastewater.

D. Theoretical Framework

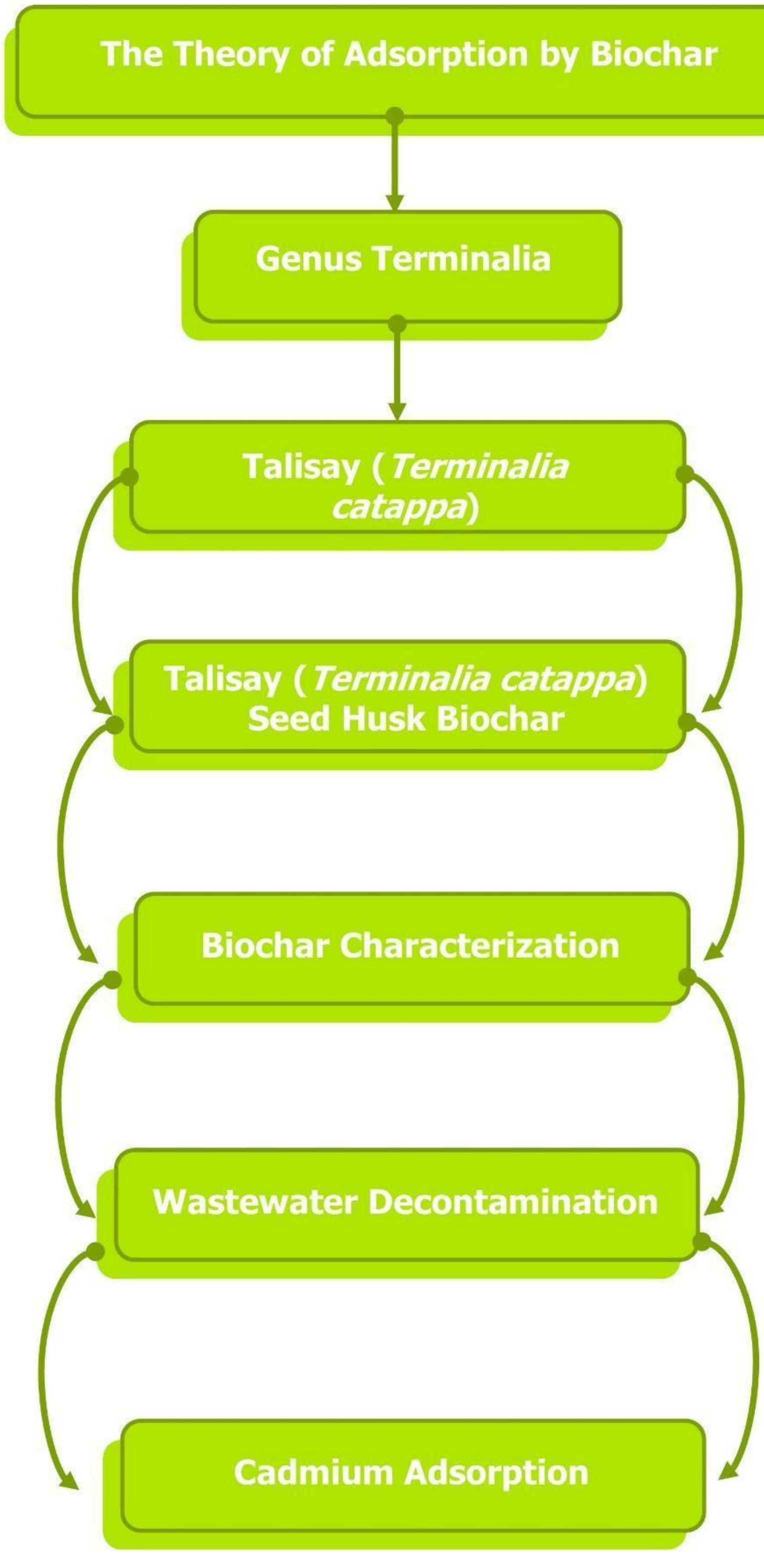

Figure 2. Theoretical Framework

The Theory of Adsorption by Biochar is applied to this study.

Terminalia is a genus of large flowering trees with the classification of the **Talisay tree** also known as Indian almond with the scientific name of ***Terminalia catappa***. Moreover, **Talisay (*Terminalia catappa*) seed husk biochar** will be used to remove the heavy metal, Cadmium that can induce health risks. Biochar produced from trees are one form of activated carbon aiding in removal of heavy metals. Related studies have shown that activated carbon can be produced from Talisay (*Terminalia catappa*) seed husk with the potential to remove the heavy metal Cadmium through the process of adsorption.

The properties of biochar depend upon the pyrolysis temperature with the biochar characterization. They showed that the pore size and the specific surface areas of biochar increase proportionally with the pyrolysis temperature. **Chen et al. (2012)** as well as **Ahmad et al. (2012)** proposed that the presence of carbonized matter, surface area, pores and hydrophobicity of biochar increased when the temperature was increased. Moreover, the efficiency of biochar as a biosorbent of heavy metals can be increased by reducing the particle size, exposing the inner pores and their functional groups. **(Fahmi A. 2018)**

The inherent biochar properties such as surplus surface binding sites (hydroxyl, carboxyl, phenolic hydroxyl and carbony groups), porous surface, high cation exchange capacity and its surface area, this organic amendment be utilized as an efficient and practical sorbent for remediation. The pyrolysis conditions such as temperature, rate of heating and residence time are all critical factors influencing the potentiality of metal sorption on biochar. In addition, changes in sorption potential can also be obtained through physico-chemical techniques.

Moreover, another parameter that affects the adsorption of heavy metals like Pb, Cu, Zn and Cd is the composition of the feedstock. Although prepared at the same pyrolysis temperature, biochars obtained from different feedstocks exhibit different adsorption capacity of heavy metals. It should be related to the presence and absence of minerals like CO2−3, PO3−4 in the feedstock, which affects the adsorption capacity of biochar. These minerals can contribute to the formation of active sites that enhance the adsorption of heavy metals from wastewater. **(Cao et al. 2009; Xu et al. 2013).**

Thus, Talisay seed husk biochar will enable us to remove heavy metals from contaminated wastewater by adsorption that can initiate negative effects if consumed by humans, animals and absorbed by plants.

E. Definition of Terms

The researchers defined the following terms operationally and conceptually for clearer understanding of this study.

Adsorbate - Any substance that has undergone adsorption on a surface. Refers to the Cadmium in this experiment.

Adsorbent - a substance that adsorbs another. Refers to the Talisay seed husk biochar in this experiment.

Adsorption - A process in which material (adsorbate) travels from a gas or liquid phase and forms a superficial monomolecular layer on a solid or liquid condensed phase (substrate).

Heavy metal - Any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations.

Wastewater - Any water that has been affected or changed due to human activity. It is a liquid waste which has water as its largest component along with various types of impurities like sewage from houses, offices, factories, hospitals etc.

Decorticator machine - A Machine that peels off the fibrous husk, bark or outer layer of some agricultural products.

Biomass - A collective term for all plants and animal material that can be burned or digested to produce energy.

Spectrophotometry – The method of measuring how much a chemical substance absorbs light by measuring the intensity of the light as a beam of light passes through sample solution.

Diphenyl carbazide colorimetric method - The method used in the study to determine the changes in color of the solution using diphenyl carbazide solution.

Lagergren Pseudo-First Order (PFO) kinetic models – The rate of change of solute uptake with time is directly proportional to difference in saturation concentration and the amount of solid uptake with time, which is generally applicable over the initial stage of an adsorption process.

Ho’s Pseudo-Second Order (PSO) kinetic models - A term describing the reaction rate of a chemical reaction in which the rate is proportional to product of the concentration of two of the reactants, or the square of the molar concentration of the reactant if there is only one.

Chapter III

Methodology

This part of the paper discusses the specific procedures or techniques used to identify, select, process, and analyze information about the research topic. **(Libguides, 2020).**

Research Design

A. Experimental Design

In this study, the researchers will use an experimental research design that involves collecting quantitative data and performing statistical analysis during research that integrate a quantitative research design **(Formplus blog, 2020).** It is necessary to utilize this type of design since the proponents are dealing with scientific concepts and variables in the study. As the effect can be easily seen on the dependent variable due to independent variable manipulation **(Center for Innovation in Research and Teaching, n.a).**

B. Materials and Methods

The materials and methods section of this paper describes in detail all the materials that will be used to conduct the study as well as the procedures.

Procedures that have been developed by experts will be used in the development of this research. This research will take five steps to develop the biochar and removal of cadmium in contaminated wastewater. The steps are as follows: 1) Biomass and biochar production 2) Modification of biochar 3) Physical and chemical characterization of biochar 4) Synthetic preparation of wastewater, and 5) Cadmium chloride solution experiment.

B.1 Biomass and Biochar Production

Talisay (*Terminalia catappa*) Fruit nuts will be harvested in Camarines Norte, the fruit nuts will be selected from potentially clean areas as a biomass material for biochar production. The Talisay (*Terminalia catappa*) fruit nuts will be dried, and the dried fruit nuts will be cracked using a decorticator machine. The Talisay (*T. catappa*) seeds will be separated manually from the husks.

B.1.1 Pre-treatment of Talisay seed husk

Pre-treatment will be the first step in the production of biochar from collected Talisay (*T. catappa*) seed husk. Physical pre-treatment will be used in this study that includes drying, crushing, sieving, and washing of the Talisay seed husk.

B.2 Modification of biochar

B.2.1 Pyrolysis

Pyrolysis is the main thermal process that will be used in converting the Talisay (*T. catappa*) Seed Husk into a biochar. The sieved biomass will be contained in a closed fire assay clay crucible and subjected to pyrolysis using a muffle furnace. Pyrolytic conditions for each batch of 400, 500, and 600 ºC with solids residence time of 1 hour were set to determine the optimum pyrolytic temperature of the biochar. The produced biochar will then be cooled to room temperature, weighed, collected, and labeled distinctively.

B.3 Physical and chemical characterization of biochar

The physical and chemical characterization of Talisay (*T. catappa*) seed husk biochar will be conducted by the method of **Rezende F. and et.al (2019).**

B.3.1 Measuring of the pH level of Biochar

A crushed air-dry biochar sample is mixed with five times its weight of distilled water, shaken for 1 hour, and the pH is measured using an electrode àpH(H20) or pHw.

A dilute concentration (0.01M) of calcium chloride (CaCl2) can be used in place of water. The results are expressed as pH (CaCl2) or pHCa.

B.3.2 Electrical conductivity of Biochar

When biochar is placed in water some of its salts will be dissolved and the water will be able to conduct electricity. Electrical conductivity is a measure of total dissolved salts (TDS), and gives an indication of the availability of nutrients, or presence of excess ash/salt.

Electrical conductivity can be measured, like pH, by making a slurry of the ground biochar in distilled water and measuring with an EC or TDS meter.

B.3.3 Density of biochar

These terms can apply to biochars, soils or biomass feedstocks.

Bulk density: Mass of a unit volume of a collection of particles or pieces. It is not an intrinsic property of the material, but depends on size, shape and compaction of the particles. It is important in materials handling, production yield and application considerations.

Biochars: 0.06 – 0.7 g/cm^3

Particle density: The mass per unit volume displaced by the envelope of the particle, including internal pores.

B.4 Synthetic Wastewater Preparation

B.4.1 Wastewater Contamination

The cadmium chloride will be analytical grade. All laboratory glassware will be soaked in 10% (v/v) nitric acid (Merck) for at least 48 hours and will be rinsed 3 times with distilled water prior to use to keep the testing solution to the nominal level of Cd. All chemical stock solutions will be made volumetrically using distilled water. Cadmium Chloride will be firstly dissolved in distilled water and then the desired volume of the solution was mixed in distilled water to obtain the corresponding cadmium chloride concentrations (10ppm, 20ppm, 30ppm) **(Ahmadpour, A. 2019).**

B.5 Cadmium Chloride Solution Experiment

The Cadmium Chloride solution experiment will be conducted according to the method by **Baguio R., and Decatoria M. (2018).**

Cadmium Chloride solution will be used in this experiment to recreate actual raw wastewater containing the heavy metal cadmium. Also, since Cadmium dichloride or Cadmium Chloride is a Cadmium coordination entity in which cadmium(2+) and Cl(-) ions are present in the ratio 2:1. Cadmium chloride is a white crystalline solid and is soluble in water and is noncombustible. Furthermore, Cadmium Chloride is purchasable and available in the local market to carry on with this experiment.

Experiment 1. *Effect of 20 grams of Talisay (Terminalia Cattapa) seed husk on varying Cadmium Chloride concentrations.*

In this method, it tests the significant difference between the setups of different cadmium chloride concentrations; 10 ppm, 20ppm, 30ppm will be treated with a constant 20 grams of Talisay (*T. catappa*) seed husk. Each of the cadmium solutions will be placed in different beakers. The sample will be tested under the spectrophotometry every 10 minutes.

		Readings (Interval of 10 Minutes)			
Amount of Cadmium Chloride Concentrations		Initial	10 minutes	20 Minutes	30 minutes
10 ppm	Trial 1				
	Trial 2				
	Trial 3				
20 ppm	Trial 1				
	Trial 2				
	Trial 3				
30 ppm	Trial 1				
	Trial 2				
	Trial 3				

Table 1. Readings of Talisay (*Terminalia cattapa*) seed husk biochar on varying Cadmium Chloride concentrations.

C. Methods of Data Collection

In this section of the research paper, the sequence on how the researchers will gather the data is stated.

The experimental research design chosen is the randomized complete block design (RCBD). This type of research design is suited for field experiments where the number of treatments is limited and there is an existing conspicuous factor based on which homogenous sets of experimental units can be identified.

C.1 Data gathering process:

C.1.1 Test for Talisay (Terminalia *catappa*) seed husk biochar adsorption capabilities

1. Spectrophotometer Reading
2. Statistical Treatment
3. Metal Uptake
4. Removal Percentage

C.1.2 Test for cadmium absorption in constant cadmium concentration

1. Adsorption Kinetics Experiment

Treatment 1 -> 10ppm - 10min. (3 trials)

Treatment 2 -> 10ppm - 20min. (3 trials)

Treatment 3 -> 10ppm - 30min. (3 trials)

Treatment 4 -> 20ppm - 10min. (3 trials)

Treatment 5 -> 20ppm - 20min. (3 trials)

Treatment 6 -> 20ppm - 30min. (3 trials)

Treatment 7 -> 30ppm - 10min. (3 trials)

Treatment 8 -> 30ppm - 20min. (3 trials)

Treatment 9 -> 30ppm - 30min. (3 trials)

2. Adsorption Isotherm Experiment

The researchers will tabulate the data gathered and then will be thoroughly analyzed.

D. Data Procedure

A. Spectrophotometer Reading

In this study, diphenyl carbazide colorimetric method will be used to read the cadmium chloride solutions. The cadmium chloride solution will be determined by the reaction with diphenyl carbazide in acid solution.

B. Statistical Treatments

The statistical instrument that will be used in this study is t – tests. In order to test if differences between the pre-test and post-test are significantly different from each other.

C. Amount of Adsorption per unit mass of Talisay (*T. catappa*) seed husk (Metal Uptake)

To determine the quality of the biochar according to how much cadmium chloride it can adsorbed. The purpose of this is to determine the cadmium chloride uptake of biochar.

The Cadmium Chloride uptake will be calculated from mass balance and difference between initial and final cadmium chloride concentrations by using the formula:

$$Q = \frac{Co - Ce}{M} (V) \qquad (1)$$

Where:

Q = metal uptake

C_o = Initial Cadmium Chloride concentration

C_e = Final Cadmium Chloride concentration

M = mass of biochar

V = Volume of the Cadmium Chloride Solution

D. Removal Percentage

The removal of cadmium chloride will be calculated using the formula:

$$\text{Cd removal \%} = \frac{100\,(C0 - Ce)}{C_o} \qquad (2)$$

Where:

Cd removal % - is the percentage removed Cadmium from the solution.

C_o = Initial Cadmium (Cd) concentration

C_e = Final Cadmium (Cd) concentration

E. Adsorption kinetics experiment

Lagragren's pseudo-first order (PFO) and Ho's pseudo-second order (PSO) kinetic models will be applied to the experimental data to determine the adsorption kinetics of cadmium chloride.

For kinetics experiments, batch adsorption had initial Cadmium Chloride concentration of 10ppm, 20ppm, and 30ppm. The samples will be taken at various times 10 minutes, 20 minutes, and 30 minutes with three trials each to determine the extent of adsorption.

The adsorption kinetics will be fitted with equation (3) for pseudo-first order (PFO) model and equation (4) for pseudo-second order (PSO) model.

$$Q_t = Q_e\,[1 - \exp(-k_1 t)] \qquad (3)$$

$$\frac{1}{Q_t} = \frac{1}{(k_2 Q_e^2)} + \frac{t}{Q_e} \qquad (4)$$

Where:

t – The time of adsorption

Q_e – The equilibrium adsorption capacity

Q_t – The adsorption time at time t

K_1 and K_2 – rate constants

F. Adsorption isotherm experiment

Adsorption isotherm pertains to the relationship between the amount of adsorbed substance by an adsorbent and the equilibrium concentration of substance at constant.

The following equations will be used to pertain the relationship between the amount of adsorbed substance by an adsorbent and the equilibrium concentration of substance at constant.

The equation is commonly expressed as:

$$Q_e = K_f C_e^{\frac{1}{n}} \quad (5)$$

and a linearized form is expressed as equation:

$$\log \log Q_e = \log \log K_f + \frac{1}{n} \log \log C_e \quad (6)$$

Where:

C_e = equilibrium concentration (mg/L),

Q_e = amount of adsorbed metal ion per unit mass of adsorbent (mg/g),

K_f = Freundlich constant (relative adsorption capacity) and;

1/n = function of strength of adsorption in the adsorption process

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