APPLICATION AND CHARACTERIZATION OF MICROPARTICLE-SIZE BIOSORBENT FROM PEEL WASTES OF CALAMANSI (*CITRUS MICROCARPA*) FOR THE REMOVAL OF COPPER (II) FROM CONTAMINATED WATER

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ABSTRACT

Copper pollution causes various health hazards and harmful biochemical effects to living creatures. The purpose of this study is to develop and characterize Microparticle-size Biosorbent from the peel wastes of Calamansi (*Citrus microcarpa*) for the removal of Copper from contaminated water. Waste peels were cleaned, shredded, dried and milled to create the Microparticle-size Biosorbent. Pretest-Posttest control Group design was followed in triplicates. Treatments: T1- 0.5g, T2- 1g and T3- 1.5g of Microparticle size Biosorbent were screened for the removal of copper from water using 1119 ppm Copper solution and at same time the untreated control was done. Using Acetylene-flame Atomic Absorption Spectrophotometer the Copper concentrations were analysed. One-way Analysis of Variance and Duncan's Multiple Range Test at 0.05 level of significance showed that the means are significantly different in terms of adsorption efficiency and capacity. T1 with 0.5g of Microparticle-size Biosorbent gained the highest adsorption efficiency with 60.17 % and highest capacity with 67.33mg/g. Pearson's Bivariate Correlation analysis revealed that the amount of the Microparticle-size Biosorbent is inversely proportional to its adsorption efficiency and capacity. Fourier Transform Infrared Radiation Spectroscopy revealed that the biomaterial is mainly composed of carboxylic acids and of carboxylates, while Field Emission Scanning Electron Microscopy showed that the particles have rough and irregular surfaces and irregular shapes with an average particle size of 36.41 μm. Therefore, the Calamansi peels Microparticle-size Biosorbent can be used or modified for the treatment of wastewater, for water filtration systems and for in situ remediation of Copper contaminated bodies of water.

Keywords: Calamansi; Microparticle-size; Biosorbent; Copper; Characterization.

INTRODUCTION

Copper can be released to our bodies of water naturally through wind-blown dusts, decaying vegetation and forest fire (Lenntech, n. d.), and by humans through the discharged effluents of industries of paints and dyes, pesticides, fertilizers, electroplating, metallurgy, mining and petroleum refining causing Copper pollution (Shrivastava, 2009). Even though Copper is an essential element it is still a heavy metal, and has a WHO Guideline level of 2 ppm (mg/L) and US EPA level of 1.3 ppm (mg/L) (Water Quality Association, 2013). According to the World Health Organization (2004) excessive exposure to copper in water, causes adverse health effects to humans ranging from mild to severe such as nausea, diarrhea, hepatocellular toxicity, gastrointestinal bleeding, acute renal failure and other diseases. In the same way it disrupts the aquatic environment by impairing the immune responses, the sense of smell and the migration capability of fishes, (Solomon, 2009), and it also causes harmful effects on the survival, growth, reproduction, brain function, enzyme activity, blood chemistry, metabolism, and even cause the death of aquatic organisms (US Environmental Protection Agency, 2016).

The Conventional treatment methods for these waters could be by precipitation, adsorption, membrane processes, ionic exchange, evaporation, electrodeposition, and coagulation. These techniques though, have natural limitations such as inefficiency, complex operative conditions, and the production of a secondary toxic sludge that requires expensive means of disposal, as stated by Abbas (2010).

On the other hand, biosorption is a promising biotechnology for pollutant removal and recovery. It is a physicochemical method in which pollutants are removed by biological materials from aqueous solution, which can comprise the use of microorganisms, plant materials and industrial and agricultural wastes. It gained its reputation because of its efficiency, simplicity and availability of biological materials (Fomina & Gadd, 2014). Biosorbents are dependent to different factors such as initial metal concentration, pH level, amount of biosorbent, and contact time (Abdel-Ghani & El-Chaghaby, 2014). Biosorbents from agricultural wastes and by-products contain lignin, pectin, and cellulose as major components and may also include polar functional groups as alcohols, aldehydes, ketones, carboxylic acids, phenolic and ether groups, and these groups have the ability to bind metal ions in aqueous solution (Saikaew, Kaewsarn & Saikaew, 2009).

Meanwhile, Calamansi or *Citrus microcarpa* is a hybrid plant cultivated in Southeast-Asia (Lim, 2012) and considered as a valuable citrus plant in the Philippines and now grown in a large scale because of its demand. It has variety of uses especially for culinary, cleaning and medicinal purposes (Philippine Council for Agriculture, Forestry and Natural Resources Research Development, 1999).Because of the mass production and usage of calamansi solid wastes are produced and this are the discarded peels, which are abundant.

In general this study aimed to apply and to characterize microparticle-size biosorbent from peel wastes of Calamansi (*Citrus microcarpa*) for the removal of Copper from water. Specifically, this work focused only on the determination of the adsorption efficiency and capacity of the different amounts of biosorbent, and also the relationship of the adsorption efficiency and capacity to the varying amounts of biosorbent. Furthermore to know the potential predominant mechanism of the biosorption process, its functional groups, its morphology, and its particle size and distribution.

METHODOLOGY

A. Research Design

A Pretest-Posttest Control Group Design was followed in this study. Pre-test or initial observation was done, it is before the application of the treatments. After the application of the treatments specifically the different amount of the microparticle-size biosorbent a final observation was made or known as the Post-test. The data that was gathered was needed for the calculation of the adsorption efficiency and capacity. The experiment was done in three replications. The independent variable was the different amounts of biosorbent while the dependent variable was the adsorption efficiency and adsorption capacity of the biosorbent in removing copper from contaminated water.

B. Materials and Equipment

This study required the use of the following materials: 100 g Calamansi peels, 1 L distilled water, 1 g Copper sulphate, 12 Whatman no. 42 filter papers.

The following equipment and apparatuses used in this study were: Laboratory drying oven, Analytical mill, Digital weighing scale, mechanical shaker, pH meter, timer, rotating funnel stand, 12 glass bottles and 12 plastic containers with associated caps, 12 glass funnel, 1 1000mL Volumetric flask, 1 graduated cylinder, spatula, 2 small beaker, 3 1500 mL plastic bottle, Acetylene - Flame Atomic Absorption Spectrophotometer (AAS) for the evaluation of the Copper concentrations, Field Emission - Scanning Electron Microscope (FE-SEM) and Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR) Spectrophotometer.

Main Procedures

Collection Waste peels and Preparation of Microparticle-sized Biosorbent

Waste Calamansi peels was collected from a Chicken Barbeque Vendor in Bago City. 100g Calamansi peels were separated from the other parts and shredded into smaller pieces manually, and then it was washed thoroughly using distilled water to remove unwanted materials. After that it was air dried for 15 minutes, then the materials were dried using laboratory drying oven in 100^0C for 24 hours enough to remove moisture and water. The dried materials was powdered using an Analytical mill. The biosorbent was then stored in a clean and closed container.

Verification of the Plant material

Fresh calamansi fruit samples collected from the same vendor where the peels wastes were acquired were brought to the Bureau of Plant Industry (BPI) National Plant Quarantine Services Division, Bacolod City for the verification of the plant's scientific name.

Preparation of Copper contaminated water

All reagents used were analytical grade. Copper sulphate (CuSO4) was used for the preparation of Copper in Contaminated water. One (1) g of Copper was dissolved in 1 L of distilled water with thorough mixing. For the Pretest Data the prepared solution with known amount of Copper was subjected to the Acetylene-flame Atomic Absorption Spectrophotometer and 1,119 ppm (mg/L) Copper sulphate solution was attained. Further adjustment to the pH of the solution using Sodium hydroxide (NaOH) or Hydrochloric acid (HCl) was not necessary because the pH was 5.3. The Simulated water was used for the screening. (Based on the procedures of Solidum, 2013).

Application of the Microparticle-size Calamansi Biosorbent

The Screening of the Microparticle-size Biosorbents was conducted at the Agro-based Laboratory of the Research, Development and Extension Department of the Sugar Regulatory Administration, Araneta St., Singcang, Bacolod City, Philippines. For the Pretest Data the prepared solution with known amount of Copper was subjected to the Acetylene-flame Atomic Absorption Spectrophotometer.

Twelve (12) clean Glass bottles were labelled using designated codes for the treatments and the control (**T1, T2, T3, and C**), Three (3) bottles every code.

The Glass bottles were used to contain the Biosorbent and Copper contaminated water, The Treatments; 0.5 g, 1 g and 1.5 g of Calamansi Biosorbent were be placed in separate glass bottles having three replicates in each treatment. The Glass bottles that were labelled as **T1 (Treatment 1)**were placed with 0.5 g of Calamansi biosorbent, then the glass bottles that were labelled as **T2 (Treatment 2)** were placed with 1 g of Calamansi biosorbent and the

glass bottles that were labelled as **T3 (Treatment 3)** were placed with 1.5 g of Calamansi biosorbent. The remaining three (3) glass bottles received no application of any amount of biosorbent and were labelled as **C (Untreated Control)**. Then, 50 ml of the Copper Contaminated water was poured individually to the glass bottles. The Glass bottles were sealed using their associated caps and shaken using a mechanical shaker in a period of 60 min.

While shaking, Twelve (12) plastic containers were labelled using the same codes of the previous glass bottles (**T1, T2, T3, and C**). After shaking, the Samples were filtered separately using Whatman no. 42 filter paper in a glass funnel with the help of a Rotating funnel stand. And, the filtrates were placed inside the labelled plastic containers.

The filtrates were subjected to the Acetylene - Flame Atomic Absorption Spectrophotometer for the post-test data, necessary for the Adsorption efficiency and capacity calculation. Based on the procedures of Solidum (2013).

Characterization of the Microparticle-size Calamansi Biosorbent

The Microparticle-size Calamansi Biosorbent was sent Department of Science and Technology- Industrial Technology Development Institute (DOST-ITDI), Standards and Testing Division, Gen. Santos Ave., Bicutan, Taguig, Metro Manila 1631 to undergo **(ATR-FTIR) Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy** to determine the presence of functional groups in the material, which is essential for the elucidation of the biosorptive mechanisms of the material.

Also, it was sent to the Advance Material Testing Laboratory of the Department of Science and Technology and was subjected to **Field Emission - Scanning Electron Microscopy (FE-SEM)** to define its particle size, particle size distribution and surface morphology.

Proper Safety Precautions and Waste Disposal

Appropriate clothing such as Lab gown, plastic gloves, face mask, and closed footwear were followed by the researcher throughout the laboratory activities in-order to insure the safety of the researcher especially in handling the chemicals.

The water samples were disposed appropriately at the disposal unit (special pit) of the laboratory and the unused leftover chemical solutions were recycled for future use. The used microparticle-size biosorbent were kept for future experimentations like for the Desorption of Copper from the material.

Data Gathering and Analysis

The final concentration of the Copper ions in the contaminated water were analyzed using an Acetylene-flame Atomic Absorption Spectrophotometer (AAS).The concentration of Copper ions in the water were expressed in part per million (ppm). Then the Data were subjected, for calculation to determine the adsorption efficiency and capacity to the equation:

$$\text{Adsorption efficiency} = (C_i - C_f) / C_i \times 100\%$$

$$\text{Adsorption capacity} = (C_i - C_f) V / W$$

Where C_i is the initial concentration and C_f is the final concentration of Copper ions in the contaminated water, and **V** is for the volume of solution in liters and **W** is the weight of the

Biosorbent in grams. Based on the procedures and equation used of Saleem and Bhatti (2011).

Statistical Data Analysis

Data were analyzed using the IBM Statistical Package for Social Science (SPSS) Software 22. Mean was used as a descriptive tool to establish the average adsorption efficiency and capacity of the treatments. While One-way Analysis of Variance (ANOVA) was used as an inferential tool to determine if there are significant differences among the mean both control and experimental groups. Followed by Duncan's Multiple Range Test (DMRT) which was used as an inferential tool to determine which of the means are equal and which are significantly different. Pearson Bivariate Correlation was used to identify the relationship between the amounts of the biosorbent to the resulting adsorption efficiencies.

RESULTS

After the application of the Microparticle-size Biosorbent using the 1119 ppm Copper solution, the amount of Copper in the treated water were analyzed and the data obtained are presented in Figure 1.
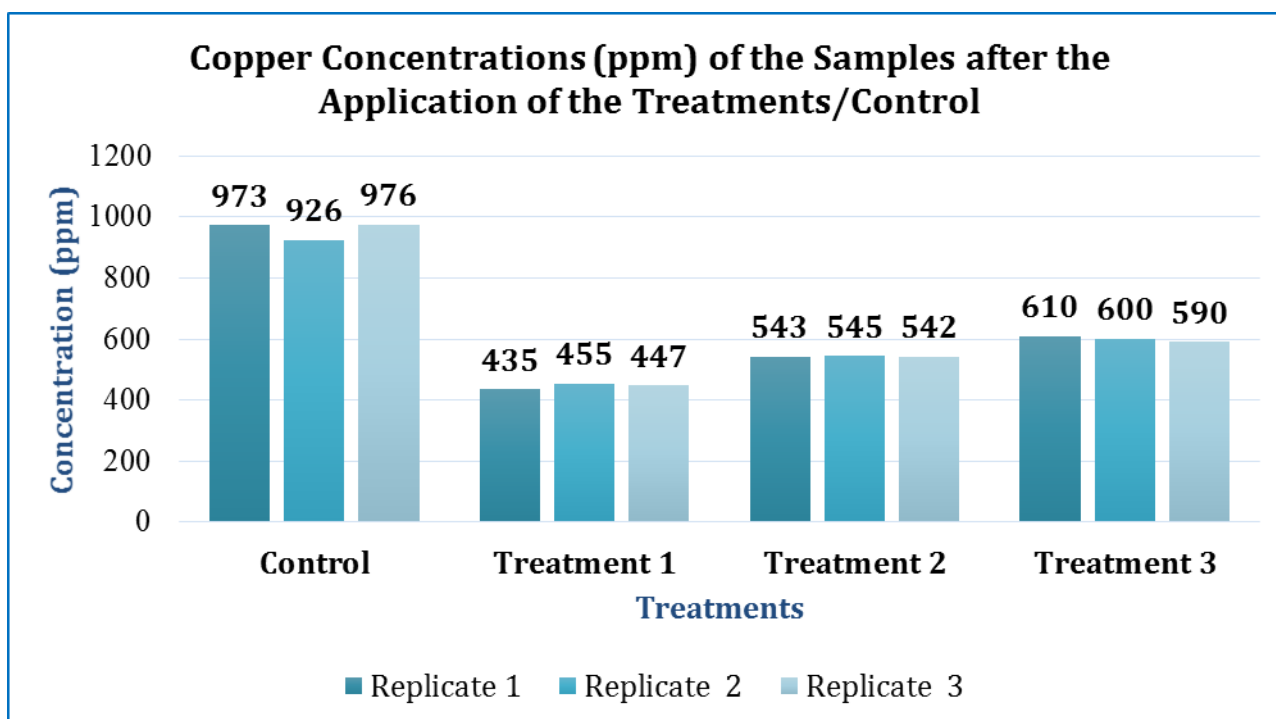

Figure 1. Copper Concentrations (ppm) of the Samples after the Application of the Treatments/Control

The results in Figure 2 are presented in the form of Adsorption Efficiency, it was obtained by the substitution of the values to the equation: **Adsorption efficiency= $(C_i - C_f) / C_i \times 100\%$**, where C_i is the initial concentration and C_f is the final concentration of Copper ions in the contaminated water.
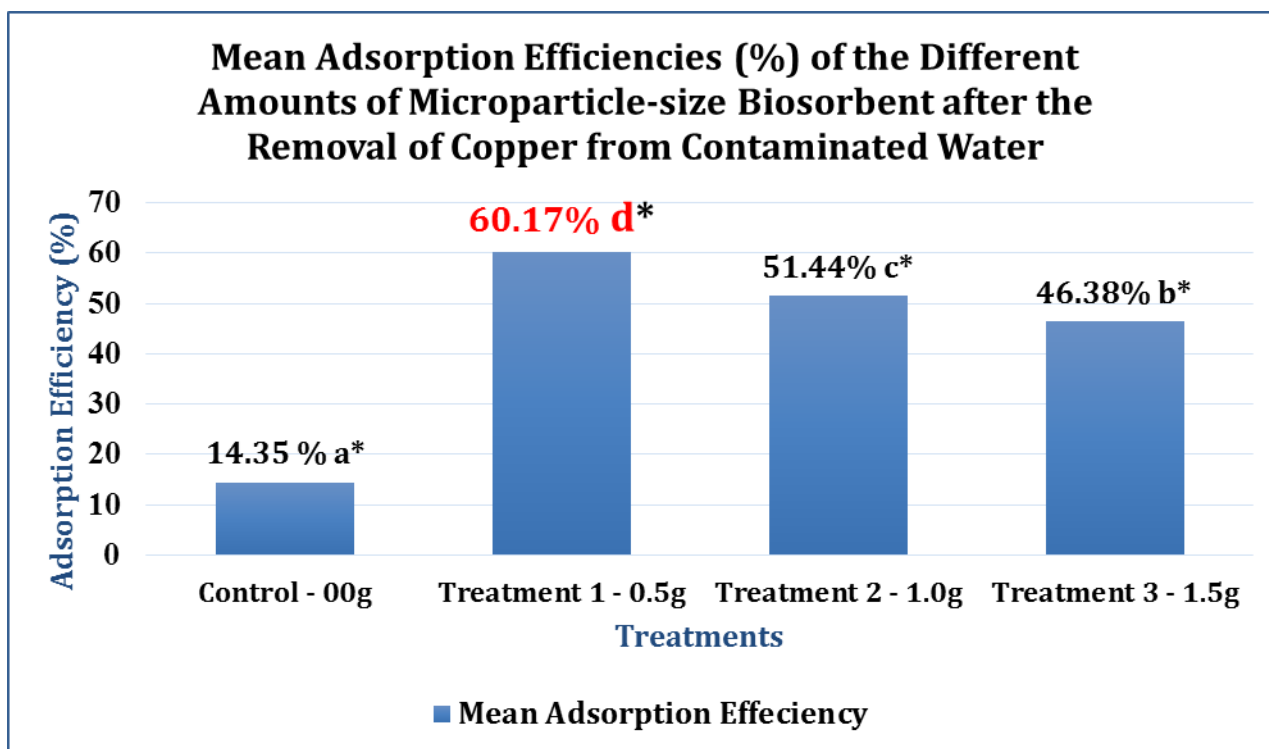

Figure 2. Mean Adsorption Efficiencies (%) of the Different Amounts of Microparticle-size Biosorbent after the Removal of Copper from Contaminated Water

*means with different letters (a, b, & c) are significantly different

For Adsorption Efficiency One way Analysis of Variance (ANOVA) at 0.05 level of significance revealed that there is a significant difference among the means with p value of .000 and Duncan Multiple Range Test as Post Hoc at 0.05 level of significance showed that all means are different from each other. Results in Figure 2 displays that Treatment 1 attained the highest mean adsorption efficiency at 60.17%, followed by Treatment 2 at 51.44%, Treatment 3 at 46.38%, and the Control with 14.35%.

Furthermore, the Treatments 1, 2 and 3 were found to be more efficient in the removal of Copper from the water than the Control group.

The existing data in Figure 3 are presented in the form of Adsorption capacity and it is shown in milligrams per gram. The adsorption capacity is the amount copper in milligrams adsorbed per gram of the Microparticle size biosorbent it can be acquired by substituting the needed data to the equation: **Adsorption capacity = $(C_i - C_f)$ V / W**, where C_i is the initial concentration and C_f is the final concentration of Copper ions in the contaminated water, and V is for the volume of solution in liters and W is the weight of the Biosorbent in grams.
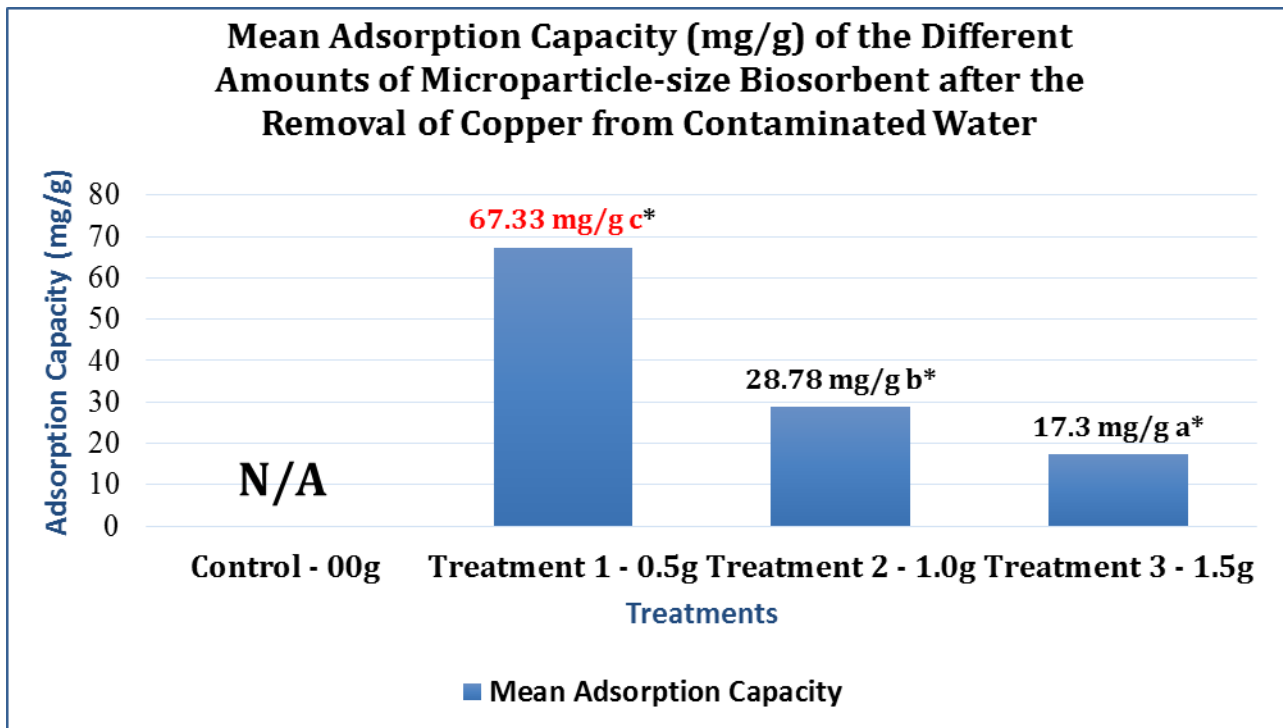
Figure 3. Mean Adsorption Capacity of the Different Amounts of Microparticle-size Biosorbent after the Removal of Copper from Contaminated Water

*means with different letters (a, b, & c) are significantly different

One-way ANOVA and Duncan's Multiple Range Test at alpha value of 0.05 revealed that the means for Adsorption capacity of the Treatments are significantly different from each other.

The figure above shows that Treatment 1 possess the highest Adsorption capacity at 67.33 mg/g (milligrams of copper per gram of Biosorbent), followed by Treatment 2 with 28.78 mg/g and Treatment 3 with 17.30 mg/g. While the control did not give sufficient data for the calculation of the Adsorption capacity.
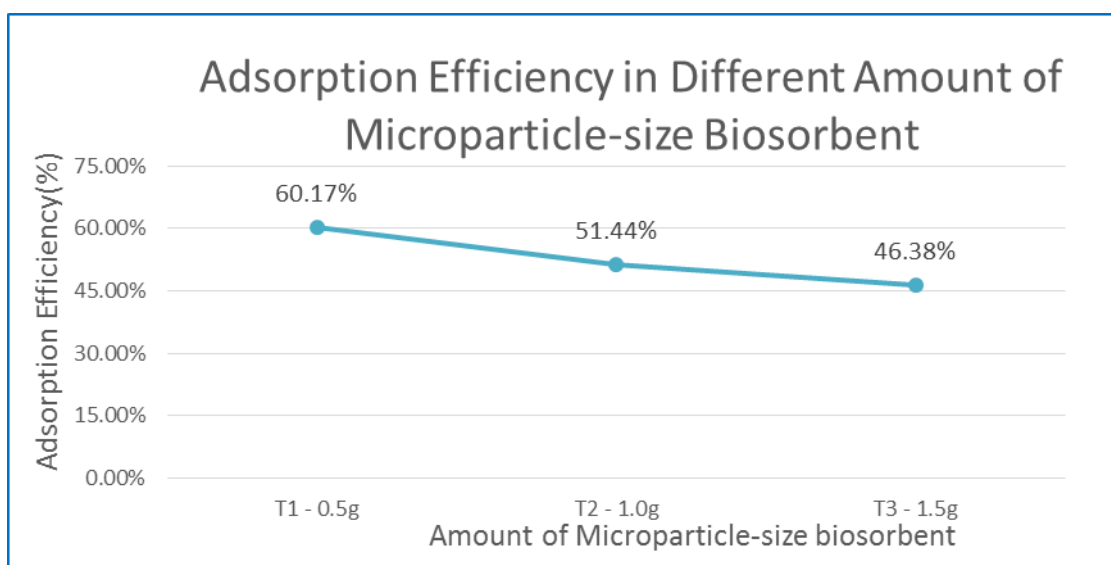

Figure 4. Line graph of the Relationship of the Amount of the Biosorbent to the Adsorption Efficiency.
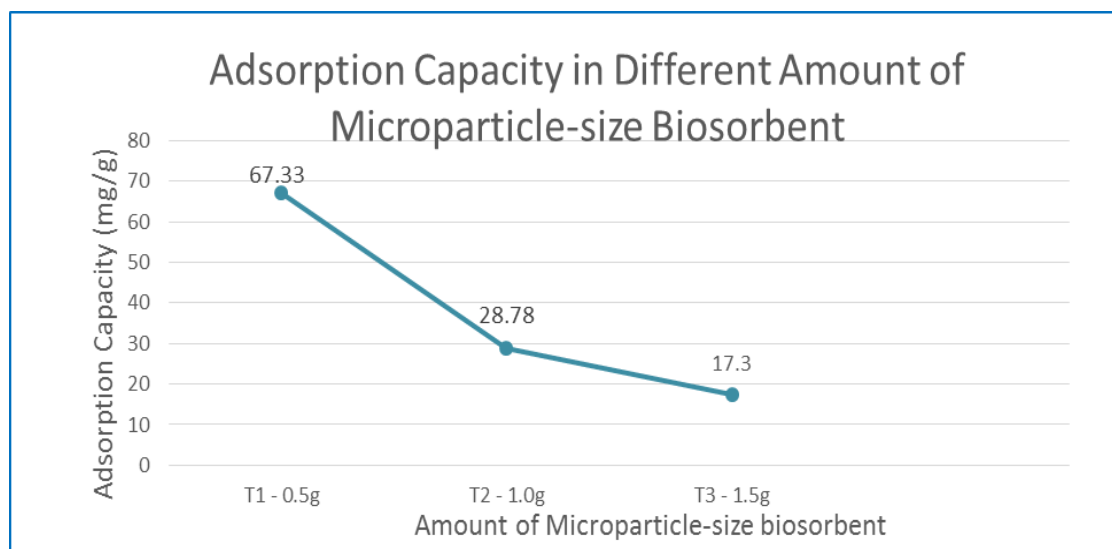
Figure 5. Line graph of the Relationship of the Amount of the Biosorbent to the Adsorption Capacity.

Figure 4 and 5 showed that the relationship between the amount of Microparticle-size Biosorbent and the resulting Adsorption Efficiency and Capacity is Linear and is inversely proportional to each other, and it was supported by the results of the Pearson's Correlation Bivariate at 0.01 level of significance with Pearson's r of -.983 and -.954 for Adsorption Efficiency and Adsorption Capacity respectively. The previous values of the Pearson's r shows negative values which indicates negative or inverse relationship between the two variables.

Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy for the Determination of Functional groups

Table 1. IR peaks of the Calamansi Peels Biosorbent and their assigned functional groups

| FTIR Absorbance Peak	Functional Group
3286 cm^{-1}, 3256 cm^{-1} & 2924 cm^{-1}	**O-H** bond (Carboxylic acids)
2361 cm^{-1}	**CO$_2$** (Carbon dioxide)
1728 cm^{-1}	**C=O** (Carboxylic acid)
1612 cm^{-1}	**COO$^-$** (Carboxylic acid salts)
1404 cm^{-1}	**OH** in-plane bending (Carboxylic acid)
1366 cm^{-1} & 1319 cm^{-1}	**COO-** symmetric stretch (Carboxylic acid salts)
1234 cm^{-1}	**C-O-C** stretch (Esters)
1018 cm^{-1}	**C-O stretch** (Cyclic alcohols)
918 cm^{-1}	**Lower Fingerprint Region** (*Not Assigned*)
602 cm^{-1}	**Lower Fingerprint Region** (*Not Assigned*)
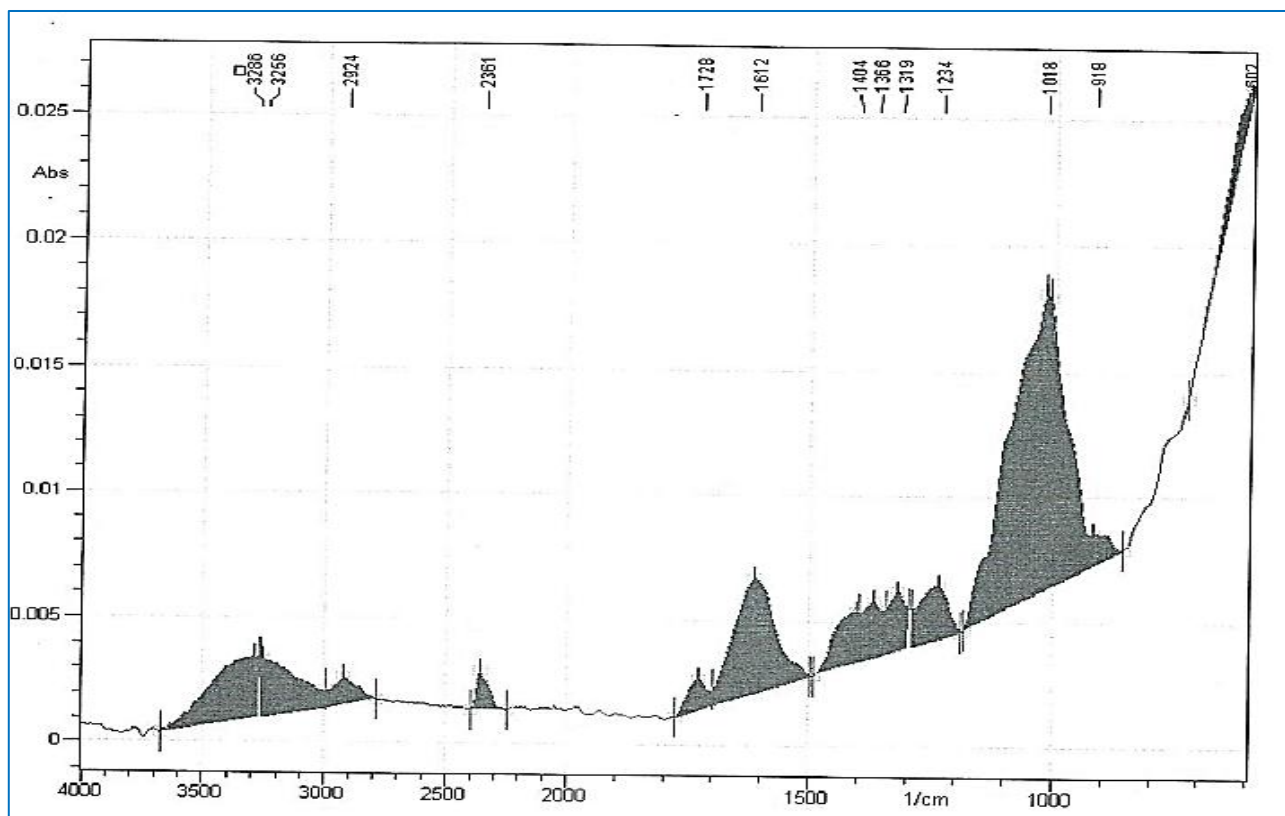
Figure 6. Attenuated Total Reflectance - Fourier Transform Infrared Spectra of Microparticle-size Biosorbent from Calamansi Peel Wastes

Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy was used to determine the functional groups present in the Microparticle-size Biosorbent which could have caused the removal of Copper from the aqueous solution. The peaks at 3286 cm^{-1}, 3256 cm^{-1}, and 2924 cm^{-1} may be assigned for O-H bond in carboxylic acids while the peak at 2361 cm^{-1} is for CO_2 (Carbon dioxide). And the peak at 1728 cm^{-1} represents the C=O also of carboxylic acid. 1612 cm^{-1} peak is assigned to the COO$^-$ in carboxylic acid salts and peak at 1404 cm^{-1} is for in-plane OH bending of carboxylic acid, also the peaks at 1366 cm^{-1} and 1319 cm^{-1} are assigned to the symmetric stretch COO$^-$ of carboxylic acid salts. Peak at 1234 cm^{-1} is assigned for C-O-C stretch of esters. The strong peak at 1018 cm^{-1} is assigned to the C-O stretch of cyclic alcohols. However, peaks at 919 and 602 cm^{-1} are difficult to assign because they are in the fingerprint region (Lambert, J. B., 1987).ATR-FTIR Spectroscopy revealed that the biomaterial is mainly composed of the functional groups of carboxylic acids, carboxylates, cyclic alcohols, ester, hydrocarbon and the remaining belongs to the fingerprint region which was not assigned based on their peak area as shown in Table 1 and Figure 6. The detected peak for Carbon dioxide was probably adsorbed by the material.
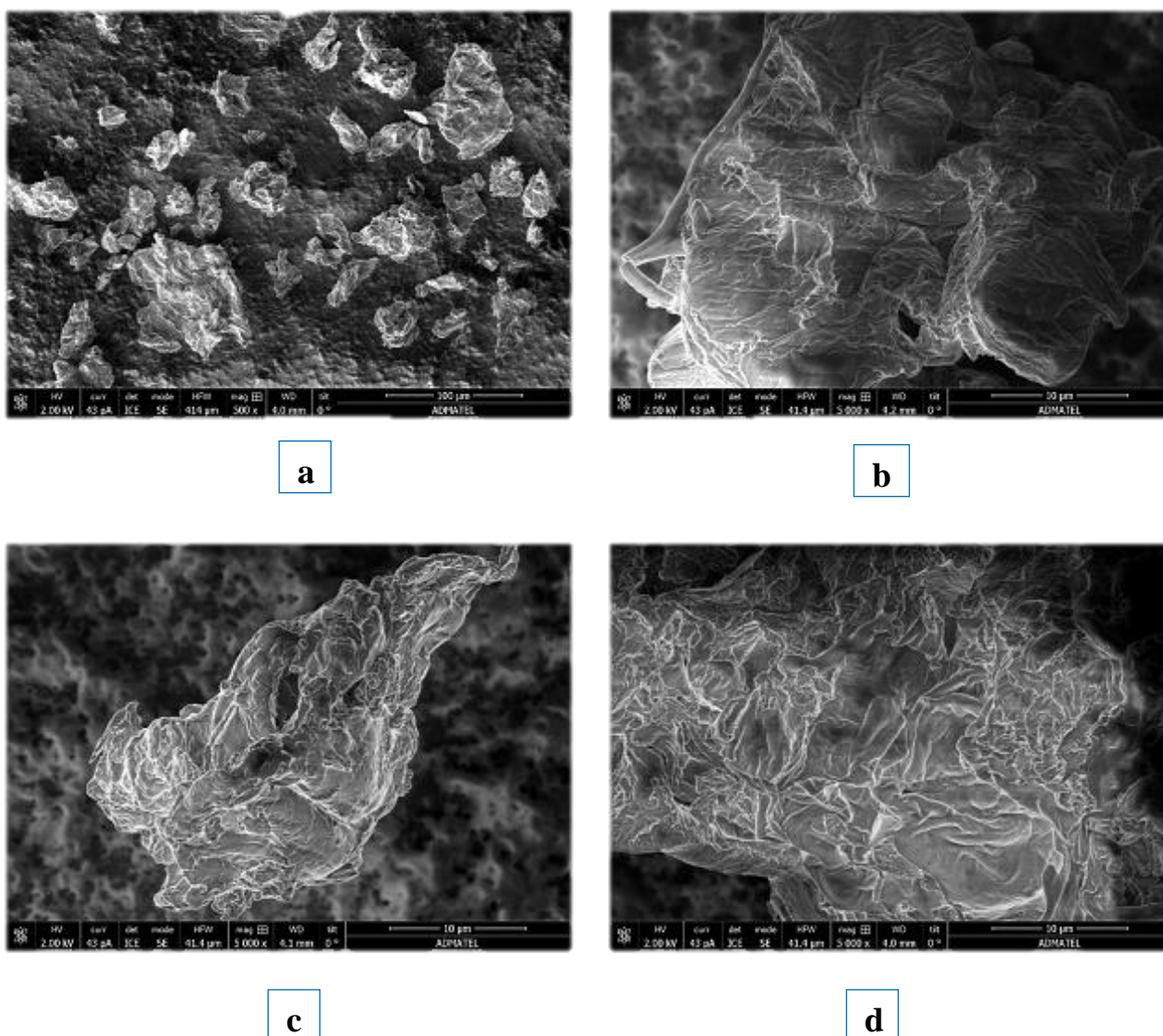
Field Emission Scanning Electron Microscopy for the Determination of Morphology and Particle size

Figure 7. Microscopic images of the Microparticle-Size Biosorbent from Calamansi Peel Wastes sample taken at (a) 500x and (b, c, d) 5,000x magnifications.
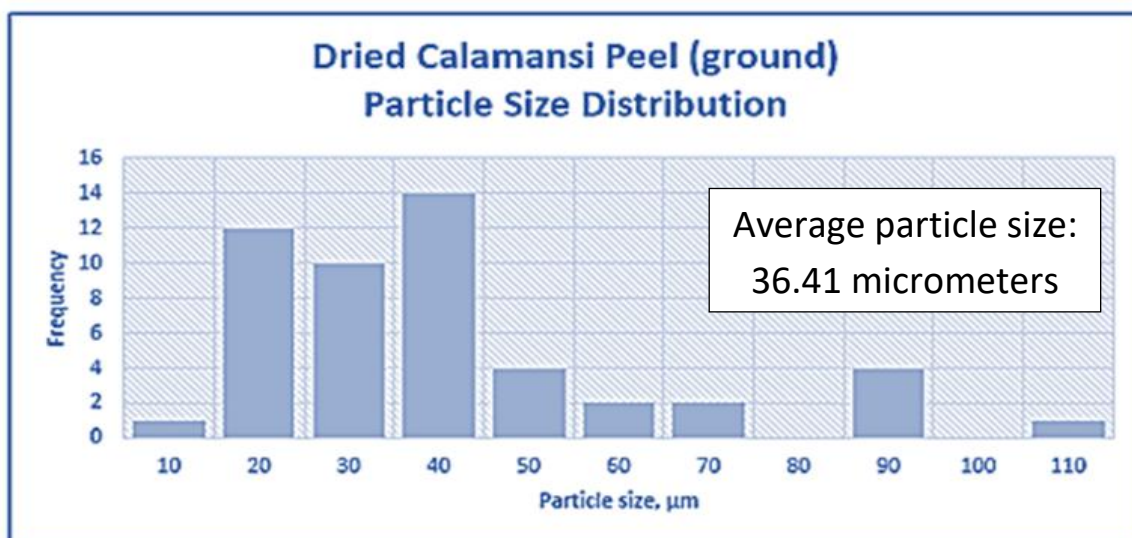
Figure 8. Particle Size Distribution of the Microparticle size Biosorbent from Calamansi Peel Wastes

The Field Emission - Scanning Electron Microscopy with particle size measurement revealed that the Calamansi Microparticle size biosorbent as shown in Figure 7 has rough, irregular surfaced and irregular shaped particles similar to rock aggregates. Moreover, the particles shows folded surfaces which gave unevenness to its exterior area resulting to elevated surfaces in some parts of the particles.

The particle size and morphology of a material may significantly affect its properties therefor they were identified in this study. The material has an unequal size distribution with 10 μm as the lowest and 110 μm as the highest particle size and is frequent in the 20, 30, & 40 μm, with an average particle size of 36.41 μm as shown in Figure 8.

DISCUSSION

The high values of Adsorption Efficiency and Capacity that were obtained from the screening of the Microparticle size Biosorbent from Calamansi peel wastes indicates that the material was good in removing Copper from the water. The positive removal of Copper from water may have been caused by various reasons. The potential mechanism of the biosorption may include diffusion, adsorption, chelation, complexation, coordination or micro-precipitation (Chopra & Pathak, 2010).

The results of the Pearson's Bivariate Correlation Analysis indicates that as the amount of the Microparticle size Biosorbent decreases, the Adsorption efficiency and Capacity increases or the removal of Copper from the water increases. Though, commonly in most studies directly proportional relationship of the dosage of the adsorbent and the removal of the metal ions are established, meanwhile this study showed the inverse, this behavior may have happened because of the interference and competition between the available binding sites at higher material densities causing a decrease in the biosorption capability of the material (Volesky & Holan, 1995) As sated by Abdel-Ghani and El-Chaghaby (2014), the adsorbent dosage influences the density of reactive groups available for metal binding on the external surface area of the sorbent. The proposed mechanism in biosorption processes include ion exchange between hydrogen ion (H+) and metal ions at the surface of the biomass hence saturation of the available binding sites on the biosorbent is most likely to happen, this is according to Babarinde, Babalola and Adebisi, (n.d.)

There have been numerous studies about the usage of plant materials especially fruit peels as biosorbent materials. Various peels of fruits such as Dalandan, Pineapple, Santol (Solidum, 2013), Pomelo (Saikaew, Kaewsarn, & Saikaew, 2009), and Mango (Ashraf, Maah, & Yusoff, 2010) have been proven to possess the ability to remove metal ions from aqueous solution.

According to Abdel-Ghani and El-Chaghaby (2014) the main reason for the removal of metal ions from water using agro-waste like fruit peels is because of the passive transport mechanisms and various functional groups existing on the cell wall of biosorbents. So it is conclusive to state that the ability of the microparticle-size biosorbent from calamansi peels was predominantly because of its functional groups which serves as the active reacting sites for the copper ions. Also, it was supported by the results of the Fourier Transform Infrared Spectroscopy, it suggest that the Microparticle-size Biosorbent from Calamansi peels contains the functional groups mainly of Carboxylic acid (Carbonyl & Hydroxyl).

The Carboxylic acid (RCOOH) and the Carboxylates functional groups may have been of the organic compound from the peels of calamansi called pectin. Pectic substances are high molecular weight polysaccharides widely spread in plants. They can be found as an essential part of the primary cell wall and middle lamella of higher plants (Normah & Ku Hasnah, 2000). Citrus pectin and Citrus peels were found to be possessing similar surface functional groups especially Carboxylic acid groups, and this confirms that pectin is an important component in the biosorption of Lead (Pb) as elucidated in the study of Balaria (2006). In addition, Normah and Ku Hasnah (2000) were able to extract high amounts of pectin ranging from 2.99 to 4.08% from calamansi peels.

Furthermore, the microparticle-size biosorbent from peel wastes of calamansi has the advantage compared to bulk biosorbents and synthetic adsorbents that have low surface to volume ratio which affects its efficiency and capacity in the elimination of metal contaminants from the water. The Microparticle-size Biosorbent has an average particle size of 36.41μm giving it a high surface area which gives it an advantage in terms of the reactivity of binding sites to Copper ions. Particularly, materials in the micrometer range behave in a different manner compared to the ones in the higher meter scale. Also, the roughness of their folded-like surfaces could play a crucial role in the biosoption process.

For these reasons the potential mechanisms for the biosorptive capability of the Calamansi peels microparticle-size biosorbent are through ***ion exchange and complexation/chelation***, whereas the carboxylic and carboxylates functional groups present reacts with the Copper ions to form complexes or chelates. Also the removal associated to the physical characteristics of the material could be considered. The viable reaction would be:

$$2RCOOH + Cu^{2+}(aq) + SO_4^{2-}(aq) \rightarrow (RCOO)_2Cu + H_2SO_4$$
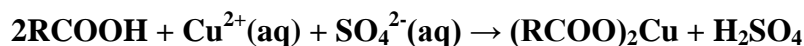
Where Two (2) carboxylic acid functional group releases hydrogen, which reacts with the sulfate ion, as it binds the divalent copper cation to form a complex and sulfuric acid.

Likewise, compared to the traditional techniques in the treatment of Copper contaminated water biosorbents in general, which comprises the product of this study, are available, simple, feasible, natural, biodegradable, sustainable and eco-friendly.

Therefore the calamansi peels microparticle-size biosorbent can be utilized for the treatment of Copper contaminated wastewater especially the waters from mining industries and other processing plants. Also it can be added to water filtration systems as substitute to synthetic

ion exchange resins, and further modifications of the material could be done for its in situ and ex situ remediation of Copper polluted bodies of water. In addition, because of the presence of functional groups in the material it can be possibly used for the removal of other heavy metals in water, and desorption potentials of the material can also be explored. Likewise, compared to the traditional techniques in the treatment of Copper contaminated water biosorbents in general, which comprises the product of this study, are available, simple, feasible, natural, biodegradable, sustainable and eco-friendly.

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CONCLUSIONS

Based on the results of the screening and on the calculated efficiency and capacity, the researcher concludes that the microparticle-size biosorbent from the peel wastes of calamansi is a good and a promising biomaterial for the removal of copper from contaminated water. The 0.5 g of Microparticle-size biosorbent was found to be the most efficient and has the highest capacity in terms of the detoxification of the contaminated water and, it was dosage dependent in an inversely proportional manner. Using ATR-FTIR the material was found to be containing mostly of the functional groups of Carboxylic acids, the highly probable binding sites, and FE-SEM showed that the particles have rough and irregular surfaces and irregular shapes similar to rock aggregates with an average particle size of 36.41μm. The rough morphology along with the micro-size of the biosorbent may have provided high surface area resulting to high reactivity.

RECOMMENDATIONS

The promising results of the experiment may lead to the usage of the biosorbent in water treatment and remediation, also this may lead to desorption of Copper from the biosorbent which will give the biosorbent its role in the recovery of copper from aqueous solution. The screening for the ability of the biosorbent in detoxifying water contaminated by other metals such as Lead, Cadmium, Chromium, Zinc, Mercury and others is recommended.

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