

CALCIUM ION ADSORPTION OF *Leucaena leucocephala* WOOD BIOCHAR ACTIVATED WITH COCONUT VINEGAR

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ABSTRACT

A positive correlation has been reported recently among the number of Chronic Kidney Disease of Unknown Etiology (CKDu) patients and the levels of groundwater hardness. Hence, the need for a low cost and a simple domestic process to reduce the hardness of potable water is identified to improve living standards of low-income communities in these disease affected areas. Biochar has emerged as a low cost adsorbent for water treatment, because of its abundance and cost-effectiveness. This study was aimed to evaluate the ability of natural coconut vinegar, in activating *Leucaena leucocephala* wood biochar to be used in calcium ion (Ca^{2+}) removal from potable water. Column tests showed a 1.7 fold increase of Ca^{2+} adsorption capacity and a 7 fold increase of Ca^{2+} retaining capacity upon the vinegar treatment. Batch studies matched with both Langmuir ($R^2 = 0.9761$) and Freundlich ($R^2 = 0.9785$) isotherm models. Ca^{2+} amount in solutions were measured using flame photometry. Ca^{2+} adsorption capacities of raw biochar and activated biochar determined by column tests ranged from 3.10-3.82 mg/g and 5.27-6.68 mg/g respectively while Ca^{2+} retaining capacities ranged from 0.16-0.22 mg/g and 1.28-1.4 mg/g respectively. Fourier transform infrared spectra, suggests hydration of the C-O-C bridges of the biochar surface introducing new -O-H groups and possible introduction of carbonyl/ester/carboxylic functional groups to the biochar surface upon vinegar treatment. According to scanning electron microscopy porosity of the biochar remained stable after the vinegar treatment.

Keywords: Coconut vinegar, Biochar, *Leucaena leucocephala*, Calcium, Adsorption capacity

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INTRODUCTION

Chronic Kidney Disease of Unknown Etiology (CKDu) has currently become one of the most threatening environmentally-related health issues of national concern in Sri Lanka. Geographical distribution of the disease includes villages of North Central, North Western and Uva provinces. People living in disease prevalent areas consume water from shallow wells for their daily needs. One of the striking observations is that these waters have significantly elevated amounts of calcium ions. A positive relationship has been recorded among the number of CKDu patients and the levels of ground water hardness (Paranagama 2013). Although, water hardness alone is not identified as a health concern, when combined with certain other factors higher hardness levels may cause dangerous effects. A hydrogeochemical investigation carried out by Chandrajith et. al. (2019) reveals significantly lower Na/Ca ratios in CKDu prevalent areas with compared to control areas in Sri Lanka. Higher fluoride levels common to all studied areas has been also observed, suggesting that high Ca^{2+} activity aggravates the damage caused by fluoride, resulting in possible lesions on tubular cells of the kidney tissues. A recent study done by using rats, also supports this idea (Perera et. al. 2020). Number of advanced technologies are proposed with a high degree of success to purify water such as ion exchange, reverse osmosis, electrochemical treatment, etc. (Sharma and Bhattacharya 2017, Shannon et. al. 2008). However, complicated procedure and high operational and maintenance cost do not allow rural communities to get the benefit of them. Hence, the need for a simple, low cost domestic water filters which can be regenerated or refilled by users themselves without much technical assistance is crucial.

Over the last few decades biochar has emerged as a popular low cost adsorbent for water treatment, because of its abundance and cost-effectiveness. Number of studies reported in activating biochar, were focused on strong acids such as nitric, sulfuric and

hydrogen peroxide, etc. (Sajjadi et. al. 2018, Peiris et. al. 2019) and mild acids such as phosphoric, citric, acetic, tartaric, etc. (Lonappan et. al. 2019, Xu et. al. 2016, Sun et. al. 2015). However, as these chemicals are expensive, corrosive and difficult to be handled by unskilled personnel, identifying non corrosive and cost effective potential activating agents are important. Also most of these activation processes are based on biochar pyrolyzed at high temperatures, as it improves the porosity of biochar. However, higher temperatures reduce the surface functional groups of biochar which are important in adsorbing potential toxic elements and also diminishes the value of using biochar as a cost effective material as higher temperatures means higher energy consumption (Xu et. al. 2016). Therefore, this study was aimed to evaluate the ability of natural coconut vinegar in activating *Leucaena leucocephala* (Ipil Ipil) wood biochar pyrolyzed at 300 °C, which is easily accessible in a domestic environment.

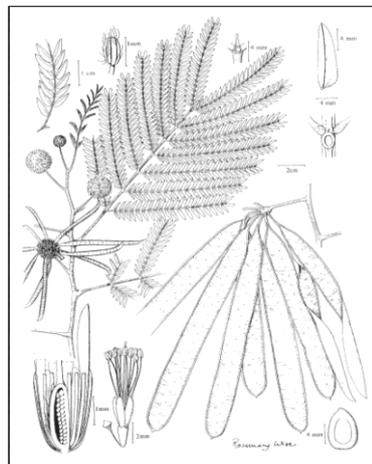


Figure 1: Morphological characteristics of *Leucaena leucocephala* (Walton 2003)

Leucaena leucocephala is a fast-growing shade tree with light wood and soft foliage (Figure 1). It is widely used for fuelwood and green manure consumption. *Leucaena* is said to be originated in Central America and has widely spread to almost all the tropical countries (Nazri et. al. 2012). Coconut vinegar is a common food additive produced from fermentable sap of coconut blossoms, allowing oxidation of ethanol into

acetic acid with no preservatives or chemicals added. This sap turns into vinegar by fermenting for 8-12 months naturally. The fresh coconut vinegar is a ~ 4 % acetic acid solution in water (4 g acetic acid/ 100 mL vinegar) with a pH ~ 2.5.

METHODOLOGY

Preparation of Biochar

Leucaena leucocephala wood was collected from two sites of North Central province, Sri Lanka. A composite sample was made and air dried. These were carbonized (300 °C, 2 h) in a domestic kiln to produce biochar. The carbonized materials (BC) were hand crushed and sieved to select particles of required size for each analysis. For the activation, commercially available natural coconut vinegar was used (Manufactured by C. D. De Fonseka and sons (Pvt) Ltd., Sri Lanka). BC samples were soaked in natural coconut vinegar (biochar: vinegar, 1:2 v/v) for 24 hours. The excess fluid was filtered out and the BC was completely dried in an oven (120 °C, 3 h). It was washed with de-ionized water until washings are clear and dried in oven (80 °C, 12 h). Resulted activated biochar was named as BC-A.

Surface characterization of biochar

For surface characterization, BC and BC-A samples (particle size 2.0-5.6 mm) were carried out using Scanning Electron Microscopy (SEM; Hitachi SU6600, Japan). BC and BC-A samples of <0.5 mm were analyzed using Fourier Transform Infrared Spectroscopy (FTIR; PerkinElmer Spectrum Two L160000A, USA) in the spectral range of 750 cm⁻¹ to 4000 cm⁻¹.

Column breakthrough studies

For column tests both BC and BC-A samples in the size range of 2.0-5.6 mm were used. Laboratory scale filter units were prepared with glass columns (2 cm diameter). Sample materials were packed (10 cm height) into separate columns followed by washing

(200 mL) and soaking in de-ionized water (100 mL, 1 h). Ca^{2+} adsorption was examined by passing a Ca^{2+} solution (350 mg/L, 6.2 ± 0.3 pH), 10.00 mL portions through the column as the influent (0.05 mL/s). Each 10.00 mL effluent was collected and filtered through a 0.45 μm membrane. Filtrates were analyzed for Ca^{2+} using a flame photometer (Jenway PFP7, UK). This process was continued until effluent Ca^{2+} concentration became equal to influent Ca^{2+} concentration (350 mg/L). That was identified as the breakthrough point. Amount of Ca^{2+} adsorbed to the column equals to the difference between total amount of calcium ions eluted and the total amount of Ca^{2+} added to the column until the breakthrough point. After the breakthrough point, 10.00 mL portions of de-ionized water (6.2 ± 0.3 pH, 0.05 mL/s) were added to the column as the influent solution to desorb the adsorbed Ca^{2+} from the column. Effluent was collected in 10.00 mL portions and analyzed for Ca^{2+} using flame photometer until the Ca^{2+} content in the effluent became undetectable (LOD = 1 mg/L). Accordingly, the total amount of calcium ions desorbed was calculated. Retained amount of Ca^{2+} in the column was calculated as the difference between the desorbed and adsorbed Ca^{2+} amounts. Herein, the retained amount of Ca^{2+} was the adsorbed Ca^{2+} which was not washed off with de-ionized water during the desorption process. Above experiments were triplicated for both BC and BC-A samples.

Adsorption isotherm studies

Batch experiments were used to study adsorption isotherms. BC-A samples <0.5 mm (0.10 g) were added to 200 mL Erlenmeyer flasks with a series of Ca^{2+} solutions (20.00 mL) of different concentrations ranging from 35 mg/L to 200 mg/L and allowed to equilibrate in an orbital shaker (120 rpm, 2 hours). Solutions were filtered through a 0.45 μm membrane and analyzed for Ca^{2+} amount using flame photometer.

RESULTS AND DISCUSSION

Ca^{2+} adsorption capacities of BC and BC-A determined by laboratory scale column tests ranged from 3.10-3.82 mg/g and 5.27-6.68 mg/g respectively while Ca^{2+} retaining capacities of the same ranged from 0.16-0.22 mg/g and 1.28-1.4 mg/g respectively. BC packed column reached the breakthrough point after passing 80 mL of the influent Ca^{2+} solution while BC-A reached the same with 170 mL of water. According to the results, *Leucaena leucocephala* biochar shows a 1.7 fold increase of Ca^{2+} adsorption capacity and a 7 fold increase of Ca^{2+} retaining capacity after the vinegar treatment.

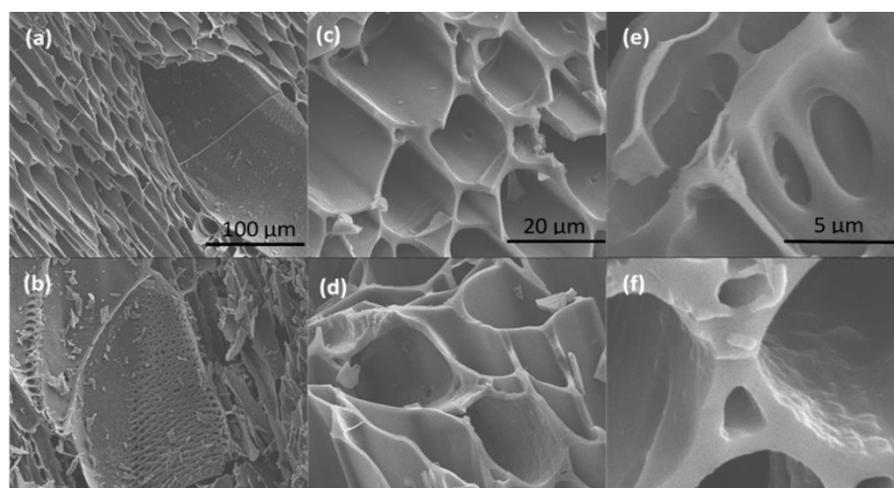


Figure 2: SEM images of (a) BC at magnification x400 (b) BC-A at magnification x400 (c) BC at magnification x2000 (d) BC-A at magnification x2000 (e) BC at magnification x10000 (f) BC-A at magnification x10000

SEM images of BC and BC-A (Figure 2) exhibit the porous nature of biochar. The mild activation process used in this study utilizing vinegar (a mild acid) at low temperatures has not induced significant changes in porosity of biochar. Most of the harsh activation processes which utilize high temperatures and strong acids lead to partial destruction of the porous structure causing significant reduction of reactive surface area (Khandaker et. al. 2017, Sun et. al. 2015).

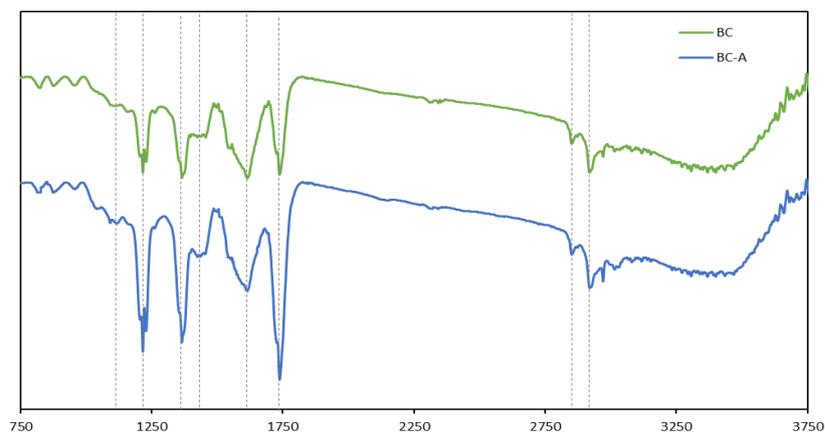


Figure 3: FTIR-ATR spectra of BC and BC-A

The FTIR-ATR spectra (Figure 3) evidence to suggest the available functional groups on the biochar surface. The intensities of the bands at 1230, 1375 and 1737 cm^{-1} were significantly increased in BC-A spectrum with compared to the BC spectrum. These bands can be assigned to phenolic C-O stretch, aromatic C-O stretch/aliphatic CH_3 deformation and C=O stretch vibrations of carbonyl/esters/carboxylic/lactone groups respectively (Parikh et. al. 2014, Nanda et. al. 2012). Moreover, the broad band at about 3400 cm^{-1} represents the stretching vibrations of -O-H groups of water/carboxylic acids/phenols/alcohols. These bands may reflect the possible modification of the BC-A surface with carbonyl/esters/carboxylic/lactone groups and hydroxyl groups by the vinegar treatment. Other absorption peaks are almost similar in both spectra. Weak band at 1111 cm^{-1} was identified as stretching vibrations of C-O-C bonds in the cellulose ring skeletal (Moran et. al. 2008). Nanda et. al. (2012) outlined that, the bands at 1434, 1609, 2852 and 2930 cm^{-1} can be aliphatic C-H stretching/ alkane C-H scissoring and bending, aromatic C=C ring stretching, aliphatic C-H stretching in CH_2 groups and CH_3 groups respectively. According to the FTIR spectral analysis of BC and BC-A samples authors suggest a possible acid catalyzed hydration of the C-O-C bridges of the cellulose and hemicellulose,

introducing new O-H groups and carbonyl/ester/carboxylic/lactone groups to the biochar surface by the vinegar treatment.

Langmuir isotherm model is described based on the two major assumptions; adsorbent surface is homogenous with uniformly distributed active sites and the adsorption process continues only to form a monolayer. In this study, following derivative of the Langmuir model was used to plot a graph,

$$1/q_e = 1/q_m + 1/bq_m C_e \quad (1)$$

where q_e is the adsorbate adsorbed at equilibrium per unit mass of the adsorbent (mg/g), q_m is the maximum adsorption per unit mass of the adsorbent (mg/g), b is the Langmuir constant, C_e is the concentration of the adsorbate in the solution at equilibrium (mg/L) (Kuang et. al. 2012). Freundlich isotherm model is an empirical expression explaining the isothermal variation of adsorption of a liquid or gas onto the surface of a solid, assuming heterogeneous and multilayer adsorption. In this study, following equation was used to plot a graph, where K_F is Freundlich equilibrium constant, n is an empirical constant (Kuang et. al. 2012).

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

Batch experiments revealed that the amount of Ca^{2+} adsorbed at equilibrium (q_e) has increased with increasing initial Ca^{2+} concentrations (C_o) (Figure 4). The R^2 values for Langmuir and Freundlich isotherm models were nearly similar, 0.9761 and 0.9785 respectively (Figure 5).

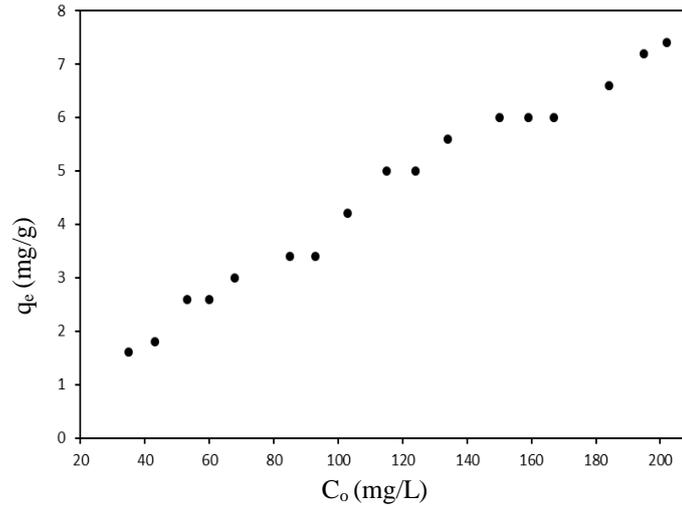


Figure 4: The plot of Ca^{2+} amount adsorbed at equilibrium against initial Ca^{2+} concentration

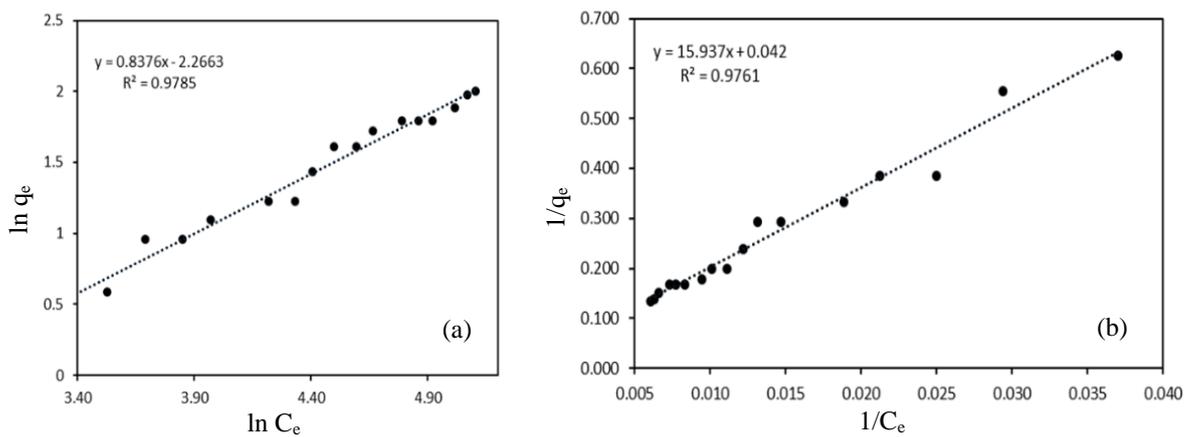


Figure 5: (a) Freundlich isotherm model (b) Langmuir isotherm model

It could be due to the fact that surface adsorption does not form a monolayer with single site adsorption, but with two nearby sites, to compensate the $+2$ charge of Ca^{2+} . At higher concentrations, abandoned single active sites dispersed over the adsorbent could also be weakly occupied with hanging metal ions by compensating only $+1$ charge (Parangi et. al. 2014). Maximum adsorption q_m and Langmuir constant b were determined from the intercept and slope of the plot of $1/q_e$ vs $1/C_e$ respectively. Maximum adsorption q_m was calculated as 23.8 mg/g . The Langmuir constant b was calculated as 0.0026 L/mg . It indicates a favorable adsorption. Equilibrium constant of the adsorption K_{eq} and Gibbs

free energy change of the adsorption ΔG were calculated using following equations. M_A is the molar mass of the adsorbate (Ghosal and Gupta 2016).

$$K_{eq} = b M_A \quad (3)$$

$$\Delta G = -RT \ln K_{eq} \quad (4)$$

ΔG of the adsorption is -11.5 kJ/mol. Negative value of the ΔG confirms the feasibility and the spontaneous nature of adsorption. Freundlich constants K_F and n , correspond to the adsorption capacity and adsorption intensity, were calculated as 0.10 mg/g and 1.19 L/mg respectively. Freundlich constant, n , between 1 and 10 indicates a favorable adsorption.

Table 1. Calcium Isotherm Parameters for BC-A

	Langmuir			Freundlich		
	ΔG	q_m	R^2	K_F	n	R^2
BC-A	-11.5 kJ/mol	23.8 mg/g	0.9761	0.10 mg/g	1.19 L/mg	0.9785

The maximum monolayer Ca^{2+} adsorption capacities (q_m) of several modified adsorbents, according to literature are, sugarcane bagasse modified with tartaric acid with a q_m of 14.72 mg/g (Soliman et. al. 2011), elephant foot yam (*Amorphophallus campanulatus*) skin modified with hydrochloric acid with a q_m of 27.64 mg/g (Lestari et. al. 2018) and mercerized cellulose modified with ethylene diamine tetra acetic dianhydride (EDTAD) with a q_m of 15.6 mg/g (Jinior et. al. 2010). The activation methods used in above studies were expensive and used corrosive chemicals that are not accessible by rural communities. In contrast, the activating agent, natural coconut vinegar used in the present study, which is an abundant and easy to handle weak acid, exhibits a remarkable q_m of 23.8 mg/g.

CONCLUSION

Leucaena leucocephala wood biochar surface was successfully modified with natural coconut vinegar with a simple activation process to increase its Ca^{2+} adsorption and retaining capacities. Ca^{2+} adsorption capacities of BC and BC-A determined by laboratory scale column tests ranged from 3.10-3.82 mg/g and 5.27-6.68 mg/g respectively while Ca^{2+} retaining capacities of the same ranged from 0.16-0.22 mg/g and 1.28-1.4 mg/g respectively. Activation with vinegar resulted in a 1.7 fold increase of Ca^{2+} adsorption capacity and a 7 fold increase of Ca^{2+} retaining capacity. According to SEM, porous surface structure of the biochar remained unchanged after the activation. The FTIR analysis revealed the rise of oxygenated functional groups on the biochar surface after the activation. Theoretical analysis using thermodynamic parameter ΔG of the adsorption (-11.5 kJ/mol) confirms the spontaneous nature of the adsorption process. This study concludes that *Leucaena leucocephala* biochar can be activated using natural coconut vinegar and used as a safe and cost-effective adsorbent for Ca^{2+} removal under laboratory conditions.

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