

Activation of Cassava Stem Biochar by Physico-Chemical Method for Stimulating Cadmium Removal Efficiency from Aqueous Solution

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Abstract

Removal of Cadmium (Cd) from aqueous solution using biochar was considered a cost effective sorbent. Biochar quality and specification depend on its carbonization processes. In this study, the cassava stem biochars were produced at temperature of 300, 400 and 500 °C with slow pyrolysis technique. The biochar in each carbonization temperature was activated with physico-chemical treatments, pre-activated by 1.63M KOH solution then activated with second pyrolysis as same as first pyrolysis conditions. Adsorption study by using biochar adsorb Cd ion from Cd(NO₃)₂ solution by batch static method. The results indicated that the removal efficiency of activated biochar produced at pyrolysis temperature 300 °C can be increased from 10.46 to 24.88 mg/g and was selected for adsorption characteristic and biochar properties. Adsorption isotherm of non-activated and activated biochar were fitted both Langmuir and Freundlich isotherm ($r^2 > 0.95$). The BET surface area of activated biochar was increased from 6.8818 to 9.4964 m²/g, while, pore size and chemical properties could be preserved. In summary, our results suggest that KOH pre-activated and second pyrolysis could increase Cd removal efficiency from aqueous solution.

Keywords: cadmium; cassava stem biochar; biosorption

1. Introduction

Cadmium (Cd) is a non-essential heavy metal presents naturally in the earth crust. It occurs to environment by the gradual process of erosion and abrasion of rocks and soils. Therefore, Cd is naturally present everywhere in air, water, soils and foodstuffs. The beneficial use of Cd in the industrial process causes Cd transport close to human surrounding environmental. Contamination of Cd in wastewater from industrial process such as electroplating, alloy manufacturing, pigments, plastics, cadmium-nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining can be accumulated in living tissues, causing various diseases and disorders. Hence, Cd must be removed from the wastewater before discharging to the environment (Haris *et al.*, 2011; Ngah and Hanafiah, 2008; Rao *et al.*, 2010).

Methods to remove Cd from wastewater can be membrane filtration, ion exchange, solvent extraction and adsorption (Haris, 2011; Tangjuank *et al.*, 2009). These conventional techniques have their own

limitations for examples, sensitive operating condition for target efficiency and production of secondary waste for costly disposal. Adsorption technique is one of efficiency method for metal removal from aqueous solution. It has many advantages such as easy available, low cost of operation and utilization in various industrial and domestic wastewaters. Adsorption technique can remove complex forms of heavy metals and can operate in wide range of pH (Rao *et al.*, 2010).

Black carbon or biochar is produced from carbon rich biomass, such as wood manure, some parts of biomaterials in carbonization or pyrolysis process. Biochar stability as a function ratio of oxygen to carbon in the resulting, biochar can be stable in natural environment for more than a hundred year (Spokas, 2010). The use of agricultural plant residue as a precursor material for produced biochar has been used due to its cost effective and makes them as renewable waste (Nuithitikul *et al.*, 2010). The negative charge and chemical functional group on biochar surface provided biochar capability on metal sorption (Pan *et al.*, 2013). The sorption efficiency of biochar depends on the

polarity, surface chemical component, pore size distribution and number of surface area (Kolodynska et al., 2012). The advantage uses of biochar over other biosorbent is the stable form of carbon structure of biochar makes them hard to degrade like other biomaterial. Biochar sorption capacity and enhancement techniques for metals removal have been focused for decade. Activation of biochar for metals adsorption by chemical modification is generally activated by acids or bases. Biochar after activation increases the adsorption efficiency of adsorbents probably due to higher number of active binding sites after modification, better ion-exchange properties or formation of new functional groups that matching metals uptake (Nghah and Hanafiah, 2008).

In this study, cassava stem, large amount of unused agricultural waste those mostly open burning after cultivated, was used as biochar precursor material. The study investigated Cd removal efficiency and enhanced Cd removal efficiency by physico-chemical activation technique. Sorption characteristics of non-activated and activated biochar and biochar properties were compared.

2. Materials and methods

2.1. Preparation of biochar from cassava stem

Cassava stem was used as biochar precursor material. Raw cassava stems were collected and bark was removed, chopped into 5 cm length and oven-dried at 105 °C for overnight. Carbonization of cassava stem was using slow pyrolysis techniques with oxygen limiting condition in laboratory furnace. Pyrolysis conditions were set to temperature rising rate of 15 °C per min until reaching desired setting temperature at 300, 400 and 500 °C, respectively. Each pyrolysis temperature was held for 60 min and biochar was cool down in furnace until reaching room temperature. Prepared biochars at each pyrolysis temperature were divided into two parts; i) a non-activated biochar and ii) an activated biochar. A total of six treatments consist of three treatments of non-activated biochars (C300, C400 and C500) and three treatments of Activated biochars (CA300, CA400 and CA500) were used in the experiments.

Non-activated biochar as prepared by suspended each biochar in deionized water pH 6, stirring with orbital shaker at 120 rpm for 2 hr, filtered, and oven-dried overnight at 105 °C.

Activated biochars were done by using physico-chemical activation, chemical pre-activation by KOH and physical activation by second pyrolysis. Each biochars was suspended and shaking in 1.63 M KOH

solution, the ratio of biochar and KOH solution is 1 g of biochar and 100 mL of KOH solution, stirring with orbital shaker at 120 rpm for 2 hr, filtered, and oven-dried overnight at 105 °C (the optimum concentration of KOH and biochar ratio was prepared according to Azargohar and Dalai (2008). After drying, biochars were activated by second pyrolysis in furnace as same as first pyrolysis conditions.

The biochar yields were determined for effective of pyrolysis condition by dry weight basis as in equation (1).

$$\% \text{ Yield} = \frac{\text{Weight of final biochar}}{\text{Weight of parent biomass}} \times 100 \quad \dots\dots\dots (1)$$

All six biochars were ground and sieved to size between 250-500 µm for the further experiments.

2.2. Comparison of cadmium adsorption efficiency

Adsorption study was conducted in laboratory under condition at room temperature (25 + 1 °C). Static equilibrium batch method was used for the adsorption experiments by measured Cd removal efficiency from aqueous solution (Kolodynska et al., 2012). The six treatments of biochars were performed adsorption study in cadmium nitrate (Cd(NO₃)₂) solution. An initial concentration of 10 mg/L Cd(NO₃)₂ in deionized water was used as Cd source. Cd(NO₃)₂ solution was adjusted to pH 6+0.2 by 0.1 M of HCl or 0.1 M of NaOH. A 100 mL of Cd(NO₃)₂ was transferred to 250 mL polyethylene (PE) bottle. A 0.10 g of each biochar was accuracy weighted and packed in PE filter bag before placing in each PE bottle containing Cd(NO₃)₂ solution. Then, all bottles were stirring with orbital shaker at a constant speed 120 rpm at experimental desired time of 30, 60, 90, 180 300 min and 24 hr.

At the end of desired time, biochar bags were removed. The Cd(NO₃)₂ solution were acidified with conc. HNO₃ to pH adjustment to less than 2.0 and Cd in solution were analyzed by Flame Atomic Adsorption Spectrophotometer (FAAS, Perkin Elmer Analyst 800) at the wavelength of 326.1 nm (APHA, AWWA and WEF, 2005). Cd adsorption on PE bag was performed and deducted from total adsorption on biochar as control batch. The amounts of Cd ion adsorbed on biochars were calculated by indirect method from the remaining Cd concentration in solution. The percentage of Cd removal efficiency by biochars (% Cd removal) and adsorption capacity (Q_e) were calculated according to the equation (2) and (3), respectively (Tangjuank et al., 2009).

$$\% \text{ Cd removal} = \frac{C_i - C_e}{C_e} \times 100 \quad \dots\dots\dots (2)$$

$$Q_e = \frac{(C_i - C_e)}{W} \times V \quad \dots\dots\dots (3)$$

Where C_i and C_e are the initial metal concentration (mg/L) and the metal concentration at the experimental time (mg/L), respectively. V is volume of solution (L) and W is dry biochar sorbent weight (mg).

2.3. pH influenced study

The biochar at highest Cd removal efficiency at a pyrolysis temperature were selected to pH influenced study. The effect of initial pH on adsorption efficiency and isotherm study of biochar were done in batch technique. Effect of pH on Cd removal efficiency was determined with initial concentration of 10 mg/L $Cd(NO_3)_2$ solution were adjusted pH in a range of 2 to 9 with 0.1 M HCl or 0.1 M NaOH. In addition, a 0.10 g of biochar was transfer to each 100 mL of $Cd(NO_3)_2$ solution in PE bottle. The batch was stirring at 120 rpm in 60 min contact time, acidified and analyzed Cd in remaining solution.

2.4. Isotherm study

To determine adsorption characteristics, the isotherm study of biochar was done by varied $Cd(NO_3)_2$ concentrations into a range of concentration 10-50 mg/L and adjusted pH to 6+0.2. A 0.10 g of biochar was accuracy transferred to each 100 mL of $Cd(NO_3)_2$ solution in PE bottle. The batch was stirring at 120 rpm in 60 min contact time, acidified and analyzed Cd in remaining solution.

Adsorption isotherm models of Cd were calculated by Langmuir (4) and Freundlich (7) adsorption equations as following equations (Kolodynska et al., 2012).

$$\text{Langmuir equation: } q_{eL} = \frac{q_{max}K_L C_e}{1+K_L C_e} \dots\dots\dots (4)$$

Where q_{eL} is the Langmuir adsorption capacity at each equilibrium (mg/g), C_e is the equilibrium concentration of the metal ion (mg/L), q_{max} is maximum adsorption capacity (5) and K_L is the Langmuir adsorption constant of the Langmuir equation and (6) can be determined from the linear Plot of C_e/q_e VS C_e as following equations

$$q_{max} = 1/\text{slope} \dots\dots\dots (5)$$

$$K_L = \frac{1}{(q_0)(intercept)} \dots\dots\dots (6)$$

$$\text{Freundlich equation: } q_{eF} = K_F C_e^{1/n} \dots\dots\dots (7)$$

Where q_{eF} is the Freundlich adsorption capacity at each equilibrium (mg/g), C_e are the equilibrium concentration (mg/L), K_F is Freundlich constant adsorption capacity and $1/n$ is the Freundlich constant relate to the surface heterogeneity. K_F and n can be determined from the linear plot of $\log q_e$ VS $\log C_e$.

2.5. Physical and chemical characteristics of biochar

To know the physical and chemical change of biochars due to activation, surface area and average pore size were detected by Brunauer-Emmett-Teller (BET) Surface Area and Porosity Analyzer (Micromeritics Asap2020); Chemical functional groups were analyzed by FT-IR spectrophotometer (Perkin Elmer Spectrum One) and other elements on biochar surfaces, including carbon (C), magnesium (Mg), phosphorous (P), calcium (Ca) and potassium (K) were detected by Scanning Electron Microscope with Energy Dispersive X-ray spectroscopy (SEM/EDX; JSM-6400).

2.6. Statistical analysis

All sorption experiments were conducted at three replicates were used at each batch study. An initial pH of Cd solution was adjusted at the beginning before experiment. Data of biochar yields at the different pyrolysis temperatures and the percentages of cadmium removal efficiency were analyzed by mean (\bar{x}) and standard error (SE). One-way analysis of variance was used to compare the means of different treatments.

3. Results and Discussion

3.1. Effect of pyrolysis temperature on biochar yields

Pyrolysis process converted raw cassava stem to biochar and made change in weight of about 30-35 % deduction. Fig. 1 shows the effected of pyrolysis temperature on biochar yields (% dry weight). The increases of temperature from 300 to 500^oC were a result of decrease biochar yields by average in both non-activated biochar and activated biochar. However, the biochar yields after activated was not significant different from the yields of non-activated biochar nificance change between three pyrolysis temperatures ($p>0.05$). Linear equations relating the percent of biochar yields and pyrolysis temperature of non-activated biochar and activated biochar were y (\square) = $-2.1849x + 37.003$ and y (\blacktriangle)= $-3.8257x + 38.045$, respectively. Notice from equations, activated biochar equation show greater slope than non-activated biochar which reflected to higher decrease on biochar yields at high pyrolysis temperature. These results indicated that carbonization at low temperature produced high biochar yield same as other studies of Song and Guo (2012), Demirbas (2004), and Hossain et al. (2011). The biochar yields decrease in higher temperature could occur from both high decomposition of organic content of biomaterials at high temperature and the decomposition of biochar residue to ash content

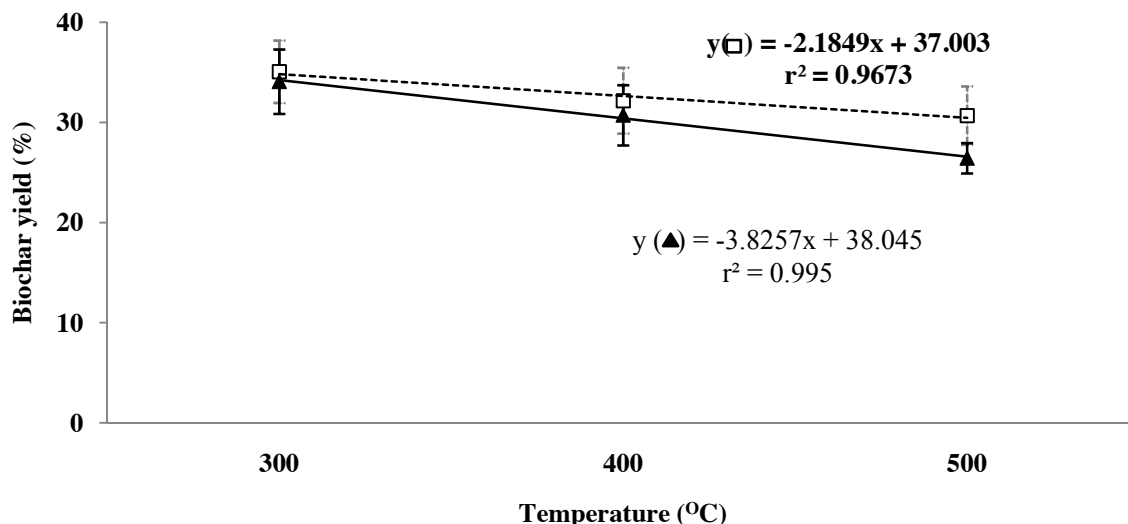


Figure 1. Effects of pyrolysis temperature on yields of non-activated (dot line) and activated biochars (solid line)

(Senoz and Angm, 2008). Moreover, high temperature of pyrolysis could make more dehydration of hydroxyl groups and thermal degradation of ligno-cellulose structures of biochar products cause a result of decreasing of biochar yields (Novak *et al.*, 2009).

3.2. Cadmium removal efficiency

The physical and chemical properties of biochar vary significantly depending on the biomaterial sources, pyrolysis conditions, post and pre-treatments (Song and Guo, 2012). Adsorption efficiency of non-activated biochars (C300, C400 and C500) and activated biochars (CA300, CA400 and CA500) were compared for Cd removal efficiency by batch equilibrium method.

The results indicated that biochar produced from all pyrolysis temperatures can act as effective sorbent with different sorption efficiencies (Fig. 2). The results of Cd removal efficiency were clearly presented into two data groups; i) low removal efficiency of non-activated biochar and ii) high removal efficiency of activated biochar. The biochar produced from pyrolysis at temperature 300 °C (C300 and CA300) gave the highest Cd removal efficiency of each biochar. The high adsorption efficiency of biochar produced at low pyrolysis temperature (300 °C) probably occurred from present of complex chemistry on biochar surface. Low pyrolysis temperature could preserve organic carbon content and aromatic carbon on biochar surface which importance for surface composition of metal

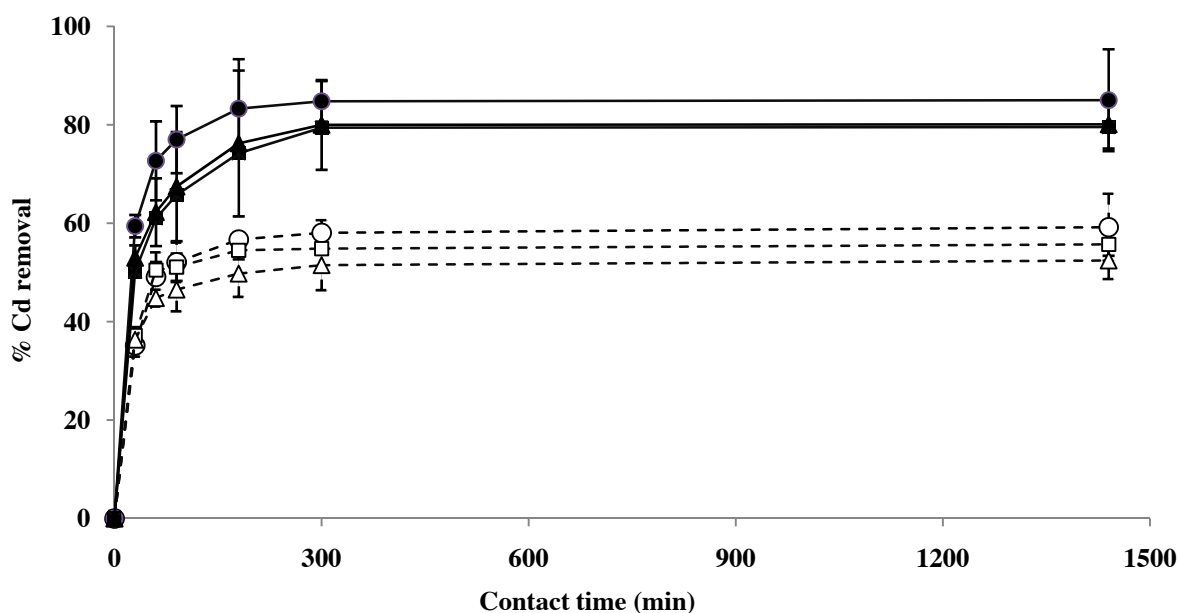


Figure 2. Comparison of the Cd removal efficiency of non-activated (dot line with clear bullet) and activated (solid line with solid bullet) biochars treated at 300 (●), 400 (■) and 500 °C (▲)

adsorption, while the high pyrolysis temperature could leach surface chemistry such as aromatic carbon composition. (Song and Guo, 2012; Regmi *et al.*, 2012).

In addition, the rapid removal rates of Cd from aqueous solution were found in all adsorbents within 60 min of contact time (Fig. 2). These results obviously showed that the large number of free surface sites was available during initial stage of time. The adsorption of Cd remains almost constant after 300 min upto 24 hr showed the occupied binding sites on biochar surface. The Cd removal efficiency of CA300 was increased up to 1.5 times after activation process compared to non-activated (C300) (increased from 59% to 84%). Hence, C300 and CA300 were selected to study of adsorption characteristics and biochar properties.

3.3. Effect of pH on Cd removal efficiency by activated biochar

The pH in aqueous solution affects the sorption process via changing in surface charges and ionic strength in aqueous medium (Illes and Tombacz, 2004). The results indicated that trend of removal efficiency between C300 and CA300 were similar (Fig. 3). At pH 2.0, Cd adsorption efficiency was very low due to the high potential of H^+ to compete with the metal cations for the adsorption sites on the sorbent surface, meanwhile, the heavy metal cations are released under acidic conditions (Forstner and Wittmann, 1981). The highest percentages of Cd removal by both non-activated and activated biochars was found at pH 5.0 to 6.0 and then the percentages of Cd removal slightly decreased from pH 7.0 to 9.0. Hence, the activated biochar by alkaline pre-activated could not

change on biochar pH property. KOH might leach out by second pyrolysis. This study gave similar results to the others study of Regmi *et al.* (2012) and Kolodynska *et al.* (2012), at pH 5-6 are the best working solution for Cd removal from aqueous solution.

3.4. Adsorption isotherms

Adsorption isotherm was studied for understanding sorption efficiency and sorption characteristics of Cd on biochar surface. The results showed that, at equilibrium conditions, the Cd removal rate increased with increasing the initial concentration of $Cd(NO_3)_2$. Fig. 4 and Fig. 5 show the linear isotherm plot of non-activated and activated biochar (C300 and CA300). To determine adsorption characteristic, on the basis of coefficient of correlation (r^2), r^2 was determined affinity between biosorbent and metal ion. The non-activated biochar, the linear plot of Langmuir and Freundlich isotherm show r^2 equal to 0.98. It was meaning that the sorption characteristics of non-activated biochar were fitted to both isotherm models at study equilibrium concentration. The sorption mechanism of Cd on biochar surface not only strict mono layer with limited binding site adsorption, but also have some complex mechanism with physical interactions on biochar surface and lead to involved multilayer adsorption (Liu, 2012). The isotherm study of biochar after activation, the r^2 of isotherm plots were higher than 0.95 both Langmuir and Freundlich, but Langmuir r^2 was provided better fitted over the Freundlich isotherm at r^2 value of 0.98. It was probably means that adsorption characteristics of Cd on biochar surface after activation was trended to be monolayer adsorption with chemical adsorption.

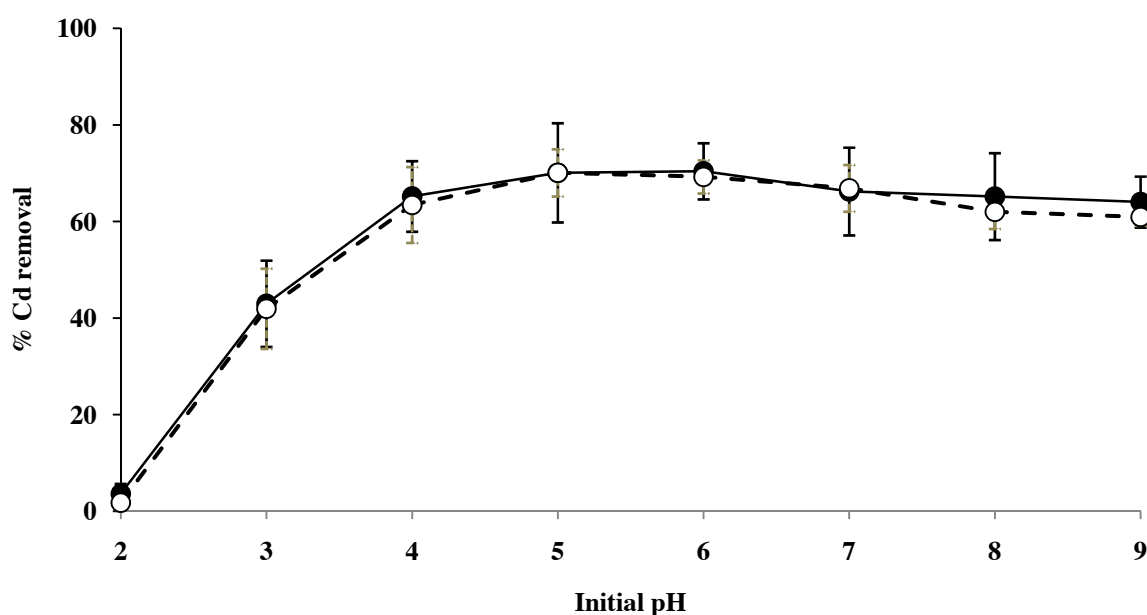


Figure 3. Effects of pH on Cd removal efficiency by non-activated; C300 (dot line) and activated; CA300 (solid line) biochars

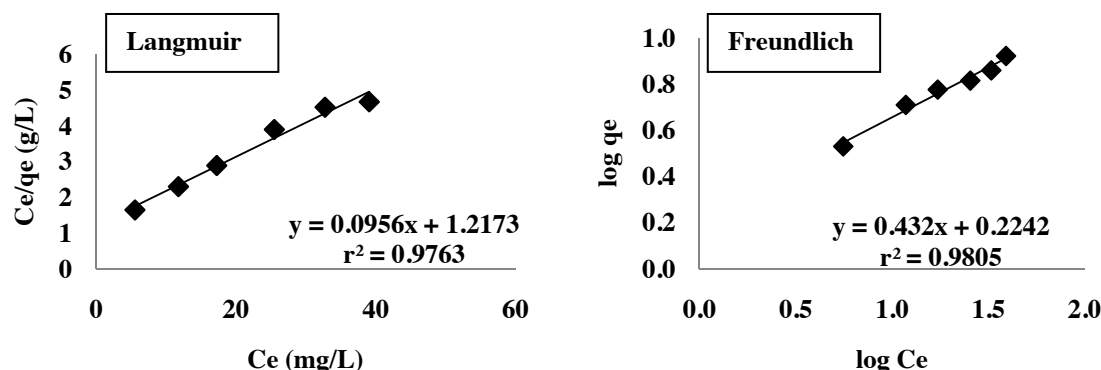


Figure 4. Adsorption isotherms of Cd on non-activated biochar

However, adsorption characteristics of multilayer can be occurred on a heterogeneous surface by others physical forces. As similar to the study of Kolodynska *et al.* (2012), studied of Cd removal by manure biochar which presented r^2 values above 0.9 both Langmuir and Freundlich isotherm.

Adsorption isotherm parameters are shown in Table 1. Langmuir equation, the value of q_{\max} and K_L were determined from the slope and intercepts of the straight-line plots by equation (5) and (6). It can be compared sorption capacity from the values of slope, non-activated biochar showed greater slope than activated biochar about 2.4 times which corresponded to maximum adsorption capacity of activated biochar from calculation. Hence, maximum adsorption capacity of non-activated biochar and activated biochar illustrated from Langmuir equation were 10.46 and 24.88 mg/g, respectively. For Freundlich's constant, the values of $0.1 < 1/n < 1$ showed favorable adsorption of Cd ions onto adsorbents. The greater of sorption for activated biochar was approximately three times that of non-activated biochar as inferred from the values of K_F , 4.88 and 1.67, respectively. From the presented factors, it can be concluded that the sorption of Cd on surface of activated biochar is known to be a homogenous surface by monolayer adsorption which had some interaction of multilayer adsorption by complexities of biomaterials surface.

3.5. Adsorbent characterization

Biochar structure is not a homogeneous material, but it is carbon rich, porous, various functional group

and relatively pollution-free material which can be used as a favorable non-biodegradable adsorbent for industrial wastewater treatment (Liu *et al.*, 2012). Surface area, element composition and functional groups on surface area of non-activated (C300) and activated (CA300) biochars were presented as follows:

3.5.1. Surface area

The surface area of C300 and CA300 were analyzed by BET method. The results in Table 2 showed that CA300 exhibited higher surface area than C300 about 1.3 times (6.8818 to 9.4964 m^2/g), while CA300 was maintained pore volume and average pore size. It can be seen that the activation can increased surface area due to the KOH adsorbed to biochar surface, burn out by second pyrolysis and leaved micro-pore on biochar surface (Azargohar, 2008). Fig. 6 show SEM images compared non-activated and activated biochar. Activation did not make change on major structure morphology. It can be observed micro-pores occurred on activated biochar surface. These micro-pores occurred from KOH burn out by second pyrolysis and result in connected between meso-pores and made accessibility to the inner closed macro-pores to exhibited larger surface area.

3.5.2. Element composition

Proximate analysis by random spot of SEM/EDX showed similar element compositions of biochar surface both non-activated and activated. The carbon and oxygen contents were not significance change, $p > 0.05$ after activation (Table 3). Hence, Carbon and oxygen were major elements for carbonyl/carboxyl

Table 1. Isotherm parameters of Cd adsorption by non-activated (C300) and activated biochars (CA300)

Biochar	Langmuir isotherm			Freundlich isotherm		
	K_L (L/mg)	q_{\max} (mg/g)	r^2	K_F (L/g)	$1/n$	r^2
C300	0.078	10.46	0.98	1.67	0.43	0.98
CA300	0.014	24.88	0.98	4.88	0.44	0.95

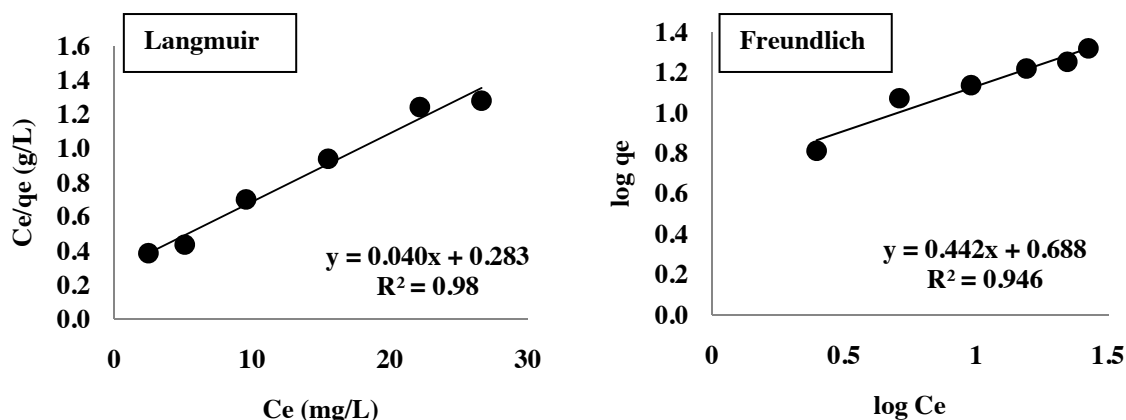


Figure 5. Adsorption isotherms of Cd on activated biochars

Table 2. Physical characteristics of cassava stem biochar under non-activated and activated conditions

Biochar	BET(m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
C300	6.8818	0.002373	1.379
CA300	9.4964	0.002468	1.395

group (C=O) which was in agreement with the study of FT-IR part (Fig. 7).

3.5.3. Functional groups on biochar surface

The present of functional groups involve interact of pollution by various of chemical force such as electrostatic interaction, ion-exchange, chelation/complexion, hydrogen bonding and weak force of van der Waal forces, are importance for bio-sorption process (Crini and Badot, 2009). The adsorption efficiency of biochar is mainly influence by chemical structure on surface of biochar. The low pyrolysis temperature could preserve surface functional group and lead to combined chemical and physical adsorption (Trakal et al., 2014).

Biochar surface functional group was analyzed by FT-IR technique. Fig. 7 shows the functional groups on surface of non-activated (C300) and activated (CA300) biochars in range of spectra between 4000 cm⁻¹ to 400 cm⁻¹. The peaks of functional groups of C300 and CA300 were quite similar but CA300 showed slightly larger area than that of C300. The larger functional groups are at band of hydroxyl group, methylene group and aromatic C-H components. The band at about 3434 cm⁻¹ showed vibration of hydroxyl a group (OH) present all of the fiber sources and was mainly functional group of metal adsorption form aqueous solution (Rao et al., 2010; Haris, 2011). The bands locate between

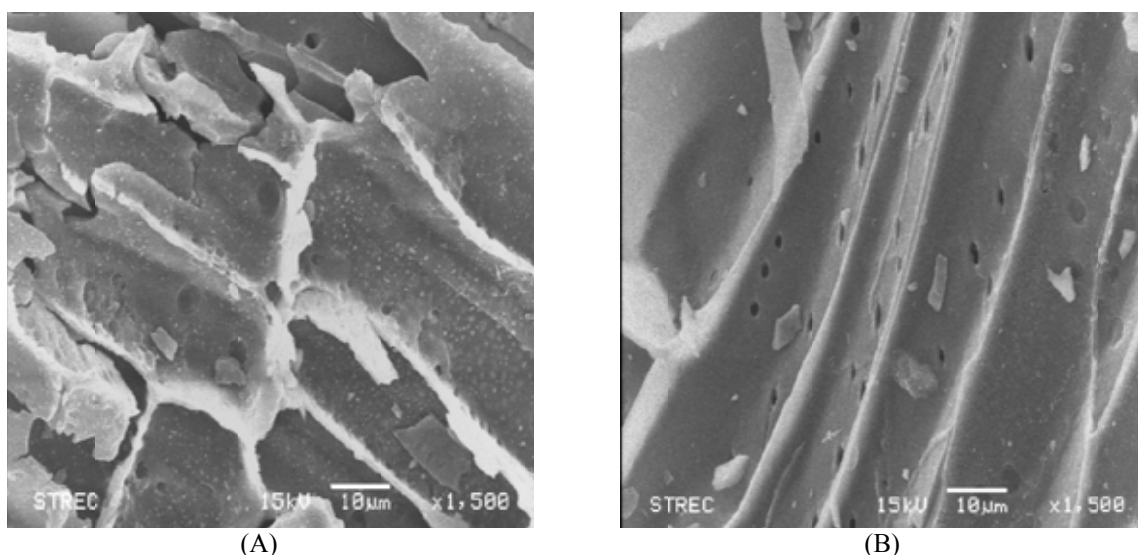


Figure 6. SEM images of (A) non-activated and (B) activated biochars

Table 3. Element compositions of non-activated (C300) and activated (CA300) biochars

Biochar	C (%)	O (%)	Mg (%)	P (%)	Ca (%)	K (%)
C300	70.64±4.56	28.12±3.82	0.31±0.12	0.35±0.37	0.01±0.06	0.55±0.31
CA300	73.78±3.69	24.66±2.84	0.11±0.54	0.17±0.16	0.15±0.15	0.11±0.67

2960-2924 cm^{-1} corresponded to vibration of methyl and methylene groups (C-H) (Tangjuank *et al.*, 2009). The peak at 1696 cm^{-1} indicates aromatic carbonyl/carboxyl group (C=O) (Regmi *et al.*, 2012; Yungbin, 2013) and the peak at 1595 cm^{-1} is present aromatic rings vibration (C=C) (Regmi *et al.*, 2012). Broad peaks between 1439 cm^{-1} to 1233 cm^{-1} present methylene group (CH_2) (Bardakçi and Bahçeli, 2010; Regmi *et al.*, 2012). The peaks at 874-780 cm^{-1} and 572 cm^{-1} are assigned to the aromatic C-H components (Haberhauer *et al.*, 1998; Chen *et al.*, 2011).

This study had complied with the study of Regmi *et al.* (2012) and Kumar *et al.* (2011) that confirmed the presence of several oxygen functional groups (carboxylic, hydroxyl/phenolic, carbonyl) on the surface of the biochars. Functional groups, such as (C=O) demonstrated high coordination with heavy metals. These findings suggested that both non-activated and activated biochar have similar functional groups which mostly remained intact during activation with KOH and the second pyrolysis at 300 $^{\circ}\text{C}$.

4. Conclusions

The pyrolysis temperatures were the major factor affected to adsorption efficiency of Cd on biochar surface. Cassava stem biochar which was produced from the pyrolysis temperature at 300 $^{\circ}\text{C}$ had higher Cd removal efficiency than pyrolysis at 400 and 500 $^{\circ}\text{C}$. Activation of biochar with physico-chemical method could increase Cd removal efficiency for all pyrolysis temperatures. The highest Cd removal efficiencies were found at initial pH in range of 5-6 and trended to be decreased when pH solutions was decreased. The activation could increase BET surface area as a result of increased Cd removal efficiency from 59 to 84%. Nevertheless, FT-IR results showed the results of unchanged surface functional group by second pyrolysis. The adsorption isotherms of both non-activated and activated biochars were fitted well to Langmuir and Freundlich isotherms ($r^2 > 0.95$) and indicated that adsorption characteristics occurred with mono layer adsorption and have some complex of multilayer adsorption behavior. The major conclusion

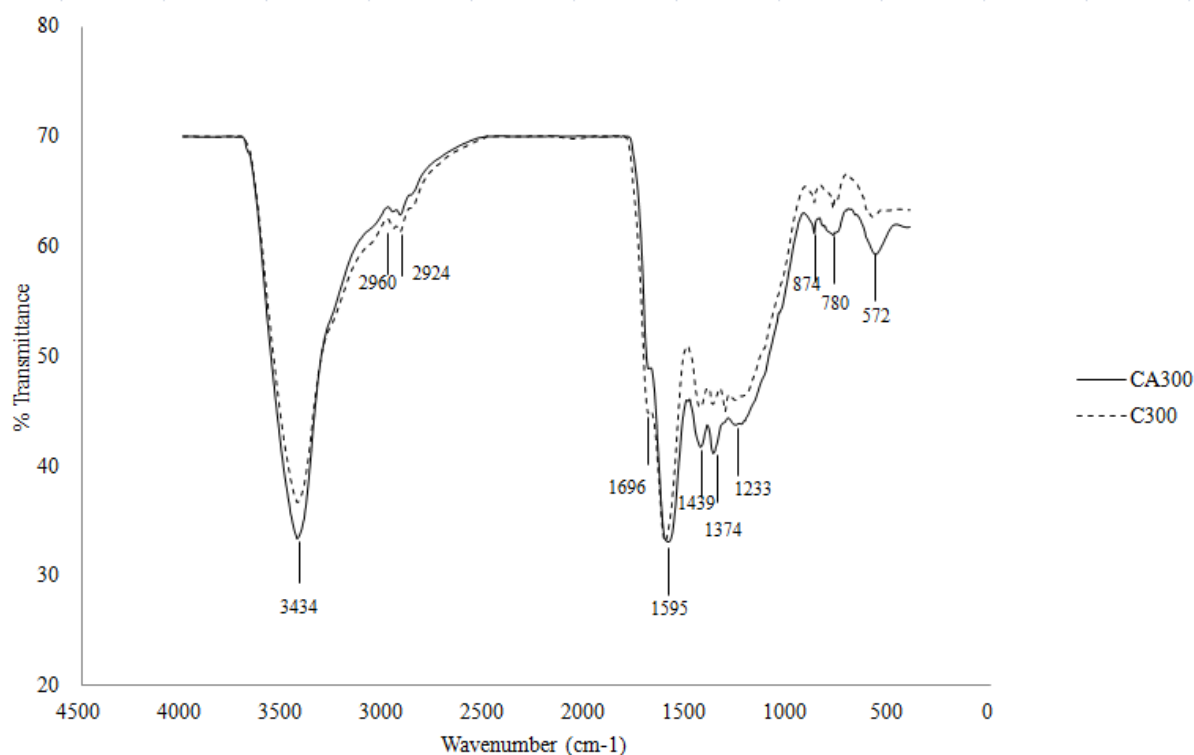


Figure 7. FT-IR spectra of non-activated biochar (C300) (dash line) and KOH-activated biochar (CA300) (solid line)

of this study is that activated cassava stem biochar have to be consideration as cost efficiency adsorbent for Cd removal from wastewater.

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