

Physico-chemical Activation on Rice Husk Biochar for Enhancing of Cadmium Removal from Aqueous Solution

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Abstract: The biochar was prepared from rice husk by pyrolysis at slow pyrolysis at 300, 400, and 500°C. The obtained biochars were activated by combined physico-chemical methods. An alkaline solution of 1.63 M KOH was used for chemical pre-activation and made second pyrolysis at the same condition as first pyrolysis. Adsorption efficiency was studied using the batch static method under laboratory conditions. Cd(II) ion removal efficiency of activated biochars was increased from 13–20% to 95–97% over non-activated biochar. The activated biochar at a pyrolysis temperature of 300°C showed the highest Cd(II) ion removal efficiency of 97% at 180 min of contact time. Cd(II) ion adsorption isotherms of activated biochar were fitted well both in Langmuir and Freundlich model. The maximum Cd(II) ion adsorption capacity of activated biochar pyrolysis at 300°C was 45.87 mg g⁻¹, about six times higher than that of the non-activated biochar (7.76 mg g⁻¹). The activated biochar increased the BET surface area from 7.71 to 11.57 m²g⁻¹. It has been suggested that the simplicity of the physico-chemical activation technique, technically feasible, eco-friendly, and cost effective, can stimulate high Cd(II) ion removal efficiency of rice husk biochar.

Key words: Cadmium removal, rice husk, activated biochar, biosorption, KOH activation.

Introduction

Cadmium (Cd), a toxic and non-essential metal, non-biodegradable, has been used for various industrial processes. The use of Cd in various industrial processes, such as electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium-nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations, refining, causes Cd transport close to the life of humans (Haris et al., 2011; Rao et al., 2010). The increase of

Cd in the environment leads to human health problems, such as organ malfunction, nervous system impairments, and oxidative stress (Gupta et al., 2003).

Adsorption technique is one of the effective methods for removing heavy metals from aqueous solution. It has many advantages, such as, easy availability for adsorbents, utilization to eliminate various wastewater heavy metals contamination, and to remove complex forms of heavy metals (Rao et al., 2010). Although good

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quality adsorbents have been used for high efficiency for removing heavy metal from wastewater, expensive sorbents are needed for treatment to regenerate for new uses (Bailey et al., 1999). Biochar is a carbon rich, produced by pyrolysis process and burning of biomass under limited oxygen with relatively low temperature (Lehmann, 2007). It is stable in nature for more than hundred years due to the function ratio of oxygen to carbon (Spokas, 2010). Biochar has attracted interest over activated carbon because it is cost effective, easy to prepare and high metal removal efficiency. The carbonization of biochar in relative low pyrolysis temperature can preserve many chemical functional groups such as oxygen groups (e.g. carboxylic and lactonic groups) and basic nitrogen groups involved in metal adsorption on the biochar porous surface (Rao et al., 2010; Haris, 2011; Machida et al., 2012). Biochar is generally chemically activated by acids and/or bases to increase oxygen groups or hydroxyl groups which are important for the adsorption of metals. The higher Cd removal efficiency occurs due its higher number of active-binding sites on the surface area after chemical modification, and better ion-exchange properties and formation of new functional groups match metal uptake (Moreno-Castilla et al., 2000; Ngah and Hanafiah, 2008). Physical modification was found when applying high temperature plus stream or inert gas by advance instruments actually call activated carbon which has large surface area and narrow pore size (Carabineiro et al., 2011). Therefore, physico-chemical activation generally makes improvements both increasing the concentration of surface acidic groups and also modify the textural properties of the biochar (Velo-Gala et al., 2014).

Rice husk is an agricultural by-product and some of them leave to be a waste. There are some studies for an activating rice husk pitcher in high temperature and some chemicals were used to increase the adsorption capacity of heavy metals, but lack of information on generating rice husk biochar at a low pyrolysis temperature plus activation by physico-chemical method. The physico-chemical activated method with a common alkaline solution and second pyrolysis at low temperature can be done by common instruments for local applications. This study was to investigate the Cd(II) ion removal efficiency of physico-chemical activated rice husk biochar in aqueous solution. Cd(II) ion removal efficiency, adsorption characteristics and biochar properties were reported in this study.

Materials and Methods

Preparation of Biochar

Raw rice husk was collected from rice mill and dried at 105°C for overnight. Carbonization process was done in the absence of air in laboratory furnace. Pyrolysis temperature was set at the increasing heat rate of 15°C per min until reaching desired setting temperatures of 300, 400 and 500°C. The carbonization process was maintained for 60 min and made cool in furnace to reach the room temperature. The biochar from each pyrolysis temperature was divided into two parts: as (i) non-activated biochar and (ii) activated biochar.

The non-activated biochars (RH300, RH400 and RH500) were prepared by suspending biochar in deionized water at the pH 6, stirred with orbital shaker at 120 rpm for 2 h for cleanup block pore, filtered and dried overnight at 105°C. The activated biochars (RHA300, RHA400 and RHA500) were activated by physico-chemical method. The biochars were pre-activated with 1.63 M KOH solution (Molar of deionized water). The ratio of biochar and 1.63 M KOH was 1 g of biochar to 100 mL of KOH solution according to the optimum conditions reported by Azargohar and Dalai (2008). The biochar was suspended in KOH solution and stirred with orbital shaker at 120 rpm for 2 h, filtered and dried overnight at 105°C and made second pyrolysis as same as the first pyrolysis condition. Both activated and non-activated biochars were grounded and sieved to size in the range of 250-500 μm , washed with deionized water until pH 7 (± 0.5), filtered and dried overnight at 105°C to use in the experiments.

Adsorption Study on Cd Removal Efficiency

The series of adsorption experiments were conducted to determine the effect of the pyrolysis temperatures for Cd(II) ion removal from aqueous solution. The experiments were conducted in the laboratory at room temperature of $25 \pm 1^\circ\text{C}$. The equilibrium batch static method was used to study removal efficiency of biochar by removing Cd(II) ion from cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$) solution. An initial concentration of 10 mg L^{-1} Cd (NO_3)₂ solution was used as a Cd(II) ion source. For each batch experimental run, 0.10 g of biochar was weighed and flaccidly packed in a PE filter bag to avoid effect of hindrance before placing in each 250 mL-polyethylene (PE) bottle. 100 mL of $\text{Cd}(\text{NO}_3)_2$ was transferred to each PE bottle. An initial pH of $\text{Cd}(\text{NO}_3)_2$ solution was adjusted to pH 6 with 0.1 M of NaOH. Then, all bottles were shaken with orbital shaker at a constant shaking speed of 120 rpm until adsorption

desired time at 30, 60, 90, 180, 300 and 24 h. At the end of desired time, the PE filter bags were removed. The remaining solutions were acidified by conc. HNO_3 to pH less than 2.0 and an amount of Cd(II) ion in solution were analyzed using Flame Atomic Adsorption Spectrophotometer at the wavelength of 326.1 nm (APHA, AWWA and WEF, 2005). The amount of Cd(II) ion adsorbed by biochar was calculated indirectly from the remaining Cd concentration in solution. Cd(II) ion adsorbed PE filter bags were studied as a control batch to deduct from total adsorption on biochars. The experiment was run in triplicate for each batch. The removal efficiency of Cd(II) ion (% Cd(II) ion removal) and adsorption capacity (Q_e) were calculated according to the equations (1) and (2), respectively (Tangjuank et al., 2009).

$$\% \text{ Cd removal} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$Q_e = \frac{(C_i - C_e)}{W} \times V \quad (2)$$

where C_i and C_e are the initial metal concentration (mg L^{-1}) and the metal concentration at the experimental time (mg L^{-1}), respectively, V is the volume of solution (L) and W is dry of biochar (mg).

The activated biochar with the highest Cd(II) ion removal efficiency and non-activated biochar maintained under the same pyrolysis temperature were selected to study the effects of pH, sorption characteristic by isotherm model and adsorbent characterization.

Initial pH on Cd(II) Ion Removal Study

To study the initial effect of pH on Cd(II) ion removal efficiency, the earlier selected biochars were studied by the batch equilibrium method. A 10 mg L^{-1} of $\text{Cd}(\text{NO}_3)_2$ solution was adjusted to the pH in the range of 2 to 9 by 0.1 M HCl or 0.1 M NaOH. The biochar was weighed an amount 0.10 g in PE bag and 100 mL of $\text{Cd}(\text{NO}_3)_2$ was transferred to each PE bottle. The batches were stirred at 120 rpm until 60 min of contact time. The condition for analyzed Cd(II) ion remaining in solution was used as same as adsorption study in preceding subsection. The results were interpreted for Cd(II) ion removal efficiency.

Isotherm Study of Selected Biochars

In order to investigate adsorption characteristics, batch static experiments were carried out at pH 6. The earlier selected biochars were accurately weighed (0.10 g)

and filled in PE bag, and 100 mL of $\text{Cd}(\text{NO}_3)_2$ was transferred to each PE bottle. The initial concentration of $\text{Cd}(\text{NO}_3)_2$ were varied into a range of 10-50 mg L^{-1} . The batches were stirred at 120 rpm until 60 min of contact time. The condition for analyzed Cd(II) ion remaining in solution was used as same as adsorption studied earlier. The Cd(II) ion sorption capacities were calculated in each final concentration. Adsorption data were interpreted by Langmuir (3) and Freundlich (4) adsorption equations (Kolodynska et al., 2012).

$$\text{Langmuir equation: } q_{eL} = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (3)$$

where q_{eL} is the Langmuir adsorption capacity at equilibrium (mg/g), C_e is the equilibrium concentration of the metal ion (mg/L), when C_e/Q_e was plotted against C_e and q_{\max} is the maximum sorption capacity obtained from (1/slope). K_L , the Langmuir adsorption constant, was obtained from equation (4).

$$K_L = \frac{1}{(q_{\max})(y - \text{intercept})} \quad (4)$$

$$\text{Freundlich equation: } q_{eF} = K_F C_e^{1/n} \quad (5)$$

where q_{eF} is the Freundlich adsorption capacity of Cd ion adsorbed (mg/g), C_e is the equilibrium concentration (mg/L), when $\log Q_e$ was plotted against $\log C_e$, n is the Freundlich constant related to the surface heterogeneity of adsorbing sites was obtained from (1/slope). K_F , Freundlich constant adsorption capacity, was obtained from equation (6).

$$y\text{-Intercept} = \log K_F \quad (6)$$

Adsorbent Characterization Studies

The physical properties of the biochar relating to specific surface area and total pore volume were obtained by Brunauer–Emmett–Teller (BET) Surface Area and Porosity Analyzer (Micromeritics Asap2020). Biochar surface characteristics of chemical functional groups were determined by FT-IR spectrophotometer (Perkin Elmer Spectrum One). The addition of elements on biochar surface including carbon (C), magnesium (Mg), phosphorous (P), calcium (Ca), potassium (K) and silica (Si) were randomly detected by Scanning Electron Microscope with Energy Dispersive X-ray spectroscopy (SEM/EDX; JSM-6400) which provides a comprehensive picture of the organic and inorganic chemistry on a biochar (Chia et al., 2012). All experimental data were done in three replications.

Results and Discussion

Effect of Pyrolysis Temperatures on Biochar Yield

The dry weight of biochar was determined in each pyrolysis condition compared to dry weight of precursor biomass. As expected, the biochar yield was significantly decreased when pyrolysis temperature was increased ($p < 0.05$). At a pyrolysis temperature of 300°C, the biochar yield was higher than 400°C and 500°C for both non-activated and activated biochar. Biochar yields after activation was not significantly different from first pyrolysis ($p > 0.05$). Biochar yields are expected to increase as the pyrolysis temperature becomes lower (Song and Guo, 2012; Hossain et al., 2011; Sukiran et al., 2011; Demirbas, 2004). The decrease of biochar yields at higher temperature could be occurred by both high decomposition of organic content of biomaterials and the decomposition of the biochar residue to ash content (Sensoz and Angin, 2008).

Cd(II) Ion Removal Efficiency of Biochars

Figure 1 shows a comparison between different biochar treatments for Cd removal efficiency at equilibrium time. It is clear that all activated biochars (RHA300, RHA400 and RHA500) had much higher Cd(II) ion removal efficiency than those of non-activated biochars (RH300, RH400 and RH500). The Cd(II) ion removal efficiencies of all activated biochars were higher than those of non-activated biochar about 8-9 times at 180 min; hence, RHA300 gave the highest Cd(II) ion removal efficiency of 97%. The low pyrolysis temperature preserves higher organic carbon contents and aromatic carbon that are important for metal binding on the biochar surface, while the higher pyrolysis temperature can leach aromatic carbon compound from its surface (Song and Guo, 2012; Regmi et al., 2012).

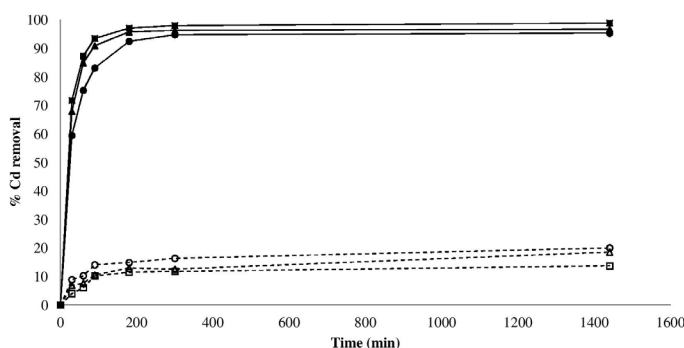


Figure 1: Effect of contact time on removal efficiency of non-activated (clear bullet) and activated (dull bullet) biochars treated at 300 (■), 400 (▲) and 500 (●) °C.

The highest Cd(II) ion removal efficiency of RHA300 and RH300 were selected for comparison study.

Effect of pH on Cd(II) Ion Removal Efficiency

The results of initial pH on Cd adsorption of selected RH300 and RHA300 are shown in Figure 2. At pH 2, Cd removal efficiency was extremely low due to the acidic condition with high potential of H^+ ion (Forstner and Wittmann, 1981). At pH 2 to 4, Cd removal efficiency was significantly increased. At pH 5-8, the result shows an increase in Cd adsorption with high removal efficiency and at pH 8-9, the percentages of Cd removal efficiency slightly decreased. The negative charge on the biochar surface was the major adsorption method through electrostatic attraction and the adsorption efficiency was increased due to a possible association from the anions of oxygen-containing functional groups that can form surface complexes with Cd ion on the biochar surface (Pan et al., 2013). These results support other metal adsorption investigations on other biochar surface (Kolodynska et al., 2012; Regmi et al., 2012; Srivastava and Thakur, 2006; Low et al., 2000). They reported that working pH solution for metal removal from aqueous solution should be slightly acidic.

Adsorption Characteristic by Isotherm Study

The isotherm parameters of RH300 and RHA300 are listed in Table 1. The adsorption data of RH300 was fitted to Langmuir and Freundlich isotherm with correlation coefficient value (r^2) greater than 0.90 (0.94 and 0.93). For RHA300, after activation, r^2 was shifted higher and fitted well to both Langmuir and Freundlich with the value of 0.98 and 0.99, respectively. Activated biochar exhibited a higher adsorption capacity (Q_{max} , 45.87 mg g⁻¹) more than six times over non-activated biochar (7.76 mg g⁻¹). The Freundlich constant, K_F

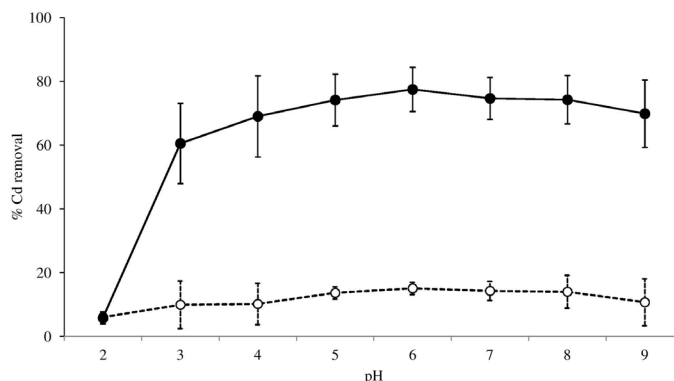


Figure 2: Effects of pH on Cd removal efficiency at 60 min contact time by non-activated (RH300) (□) and activated (RHA300) (■) biochars.

Table 1: Isotherm parameters of Cd adsorption by non-activated (RH300) and activated (RHA300) biochars

<i>Biochar</i>	<i>Langmuir isotherm</i>			<i>Freundlich isotherm</i>		
	K_L (Lmg^{-1})	Q_{max} (mg/g)	r^2	K_F (L/g)	$1/n$	r^2
RH300	0.047	7.76	0.94	0.69	0.549	0.93
RHA300	0.040	45.87	0.98	2.40	0.717	0.99

value of activated biochar showed greater value than non-activated biochar about 3.5 times which presents higher adsorption capacity after activation. Hence, Q_{max} and K_F were used as the adsorption factors for grading the adsorption efficiency of adsorbents (Okeola and Odebunmi, 2010). It can be concluded that adsorption characteristic of Cd(II) ion on activated biochar surface is not restricted to mono layer adsorption with the finite binding site, but have characteristic of multi layer adsorption with non-uniform distribution of chemical and physical forces (Gulipalli et al., 2011). Kumar (2006) reported on the Cd(II) ion adsorption capacity of the alkaline-treated raw rice husk for Cd(II) ion was 8.58 mg g^{-1} to 20.24 mg g^{-1} . While El-Shafey (2007) reported that acid treated raw rice husk had the Cd(II) ion adsorption capacity between 32.05 and 41.15 mg g^{-1} . This study found that the higher adsorption capacities of activated rice husk biochar occurred from a high porous surface area which could provide more binding sites for Cd(II) ion adsorption.

Physical and Chemical Characteristics of Biochar

Surface Area

The surface area and porosity of RH300 and RHA300 are shown in Table 2. The physico-chemical activation increased the RHA300 surface area 1.5 times higher than RH300 (7.71 to $11.57 \text{ m}^2 \text{ g}^{-1}$). This larger surface area of activated biochar was affected to higher Cd(II) ion removal efficiency. Furthermore, the activation could decrease about 0.5 times pore volume and 2.5 times average pore size which are the important factors for increasing surface area.

Martinez-Escandell and Castro (2013) reported the interesting mechanism of KOH activated to

carbon material. The KOH attached to carbon surface and reacted with biochar carbon released hydrogen originates from KOH and formed potassium carbonate (K_2CO_3) as reaction (1). The pyrolysis process with limited oxygen also evolved CO and CO_2 described in reactions (2 and 3). The decomposition of K_2CO_3 was carbon consumption, which is associated with the further development of porosity by the decomposition of carbon as described in reaction (5).



Figure 3 shows the scanning electron micrographs of biochar surface structure between RH300 (Figure 3a) and RHA300 (Figure 3b). Activation made a change in biochar surface structure. These can clearly be observed from the images of activated biochar, which show a high porosity correlation to a BET surface area.

Elements Composition on Biochar Surface

The element compositions on the biochar surface were randomly spot analyzed by SEM/EDX technique. Table 3 shows different elements compositions on the biochar surface of RH300 and RHA300. After activation, the element contents were not significantly changed ($p > 0.05$) due to the element contents of biochar being preserved by low temperature pyrolysis (Uchimiya, 2010). The activated biochar found K a residual of KOH pre-activation. The result founded mean carbon was slightly increased due to the increases of surface area after activation.

Surface Functional Group Study

FT-IR technique was used to study the chemical functional group of biochar surface before and after activation. Figure 4 shows the vibration frequency of functional groups on RH300 and RHA300 surfaces. The spectra were in a range between 4000 cm^{-1} and 400 cm^{-1} . The peaks of functional groups of RH300 and RHA300 were similar dominant spectra, but RHA300 showed a larger area of two major peaks, 3411 cm^{-1}

Table 2: Characteristics of rice husks surface area under non-activated (RH300) and activated (RHA300) biochars

<i>Biochar</i>	<i>BET</i> ($\text{m}^2 \text{ g}^{-1}$)	<i>Pore volume</i> ($\text{cm}^3 \text{ g}^{-1}$)	<i>Average pore size</i> (nm)
RH300	7.71	0.009046	46.9181
RHA300	11.57	0.005484	18.9573

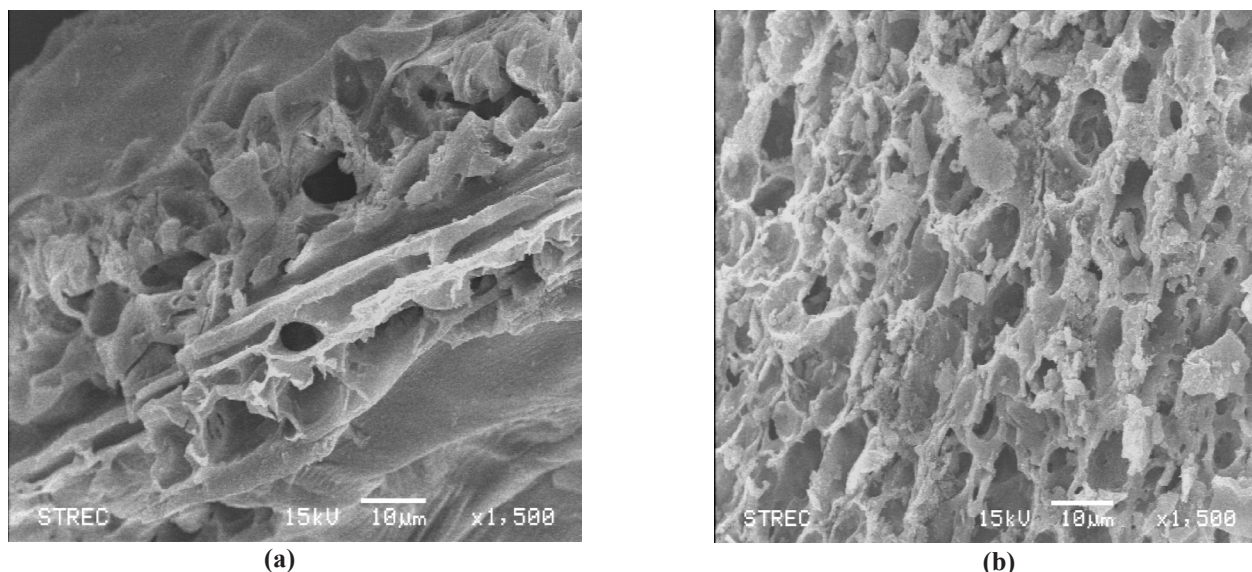


Figure 3: SEM images of (a) non-activated (RH300) and (b) activated (RHA300) biochars.

Table 3: Element compositions of non-activated (RH300) and activated (RHA300) biochars

Biochar	C (%)	O (%)	Mg (%)	P (%)	Ca (%)	K (%)	Si (%)
RH300	39.61±6.27	44.42±1.21 ^a	0.14±0.05	0.14±0.08	0.14±0.09	-	14.28±2.64
RHA300	46.00±0.94	50.86±2.21 ^b	0.17±0.05	0.13±0.15	0.13±0.01	0.21±0.20	12.56±4.93

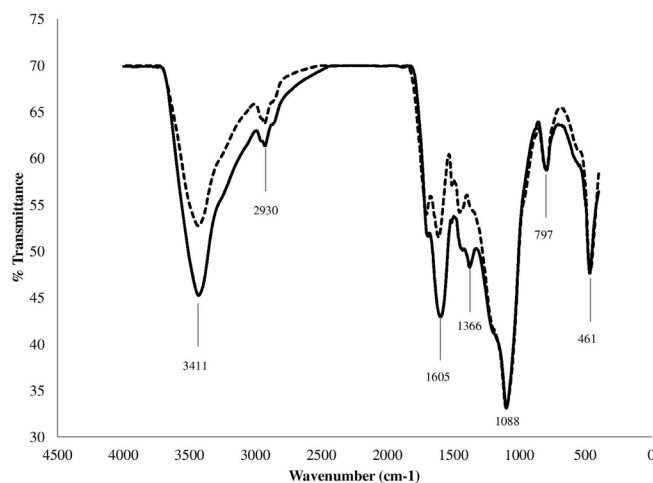


Figure 4: FTIR spectra of non-activated (RH300) (dot line) and activated (RHA300) (solid line) biochars.

and 1605 cm^{-1} . The broad band at about 3411 cm^{-1} showed vibration of a hydroxyl group (OH). The peak at 2930 cm^{-1} corresponded to the vibration of methyl and methylene groups (C-H) (Tangjuank et al., 2009), peak at 1605 cm^{-1} indicated aromatic carbonyl/carboxyl group (C=O) (Regmi et al., 2012; Yungbin, 2013), peak at 1088 cm^{-1} showed the silica function group of Si-O-Si, (Daffalla et al., 2010) and the sharp peak at 461 cm^{-1}

showed metal-halogen bond (Daifullah et al., 2003). The weak peaks at 1366 cm^{-1} appeared after activation might bealkyne or isopropyl group and the peak at 797 cm^{-1} assigned to Si-H (Daifullah et al., 2003).

FT-IR results showed the difference of intensity peak of two groups, a hydroxyl group and carbonyl/carboxyl group. The activation makes change to enhance the quantity of these two groups that are mainly a functional group of metal adsorption from aqueous solution (Haris, 2011; Rao et al., 2010). However, the activation was not made to silica groups, which are the major functional groups of rice husk biochar same as the study of Daifullah et al. (2003). These findings indicated that the activation of rice husk biochar could increase Cd adsorption capacity by increasing functional group as Cd binding sites on the biochar surface.

Conclusions

Rice husk biochar, a low cost adsorbent biomaterial and economical, could be attractive alternative sorbent for Cd(II) ion removal from aqueous solution. The simplicity of the physico-chemical activation technique—technically feasible, eco-friendly and cost effective—can stimulate Cd(II) ion removal efficiency

of rice husk biochar for 8-9 times. The use of KOH, a common chemical reagent, could be better for pre-activated biochar before making second time pyrolysis. The activation made changes on rice husk biochar in both physical and chemical properties. The increase of the BET surface area and specific chemical functional groups could be synergism for enhanced Cd(II) ion removal efficiency. Therefore, advantages of easy availability of adsorbent and technically feasible perform an efficient alternative biosorbent for Cd(II) ion removal from aqueous solution.

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