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by Suryadi Ismadji

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Research paper

1 **Bentonite hydrochar composite for removal of ammonium from Koi fish tank** Suryadi Ismadji a,*, Dong Shen Tong b, Felycia Edi Soetaredjo a, Aning Ayucitra a, Wei Hua Yu b, Chun Hui Zhou a,b,c,** a Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia b Research Group for Advanced Materials & Sustainable Catalysis (AMSC), State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032, China c The Institute for Agriculture and the Environment, University of Southern Queensland, Toowoomba, Queensland 4350, Australia **article**

22 **info Article history: Received 5 February 2015 Received in revised form 21 May 2015 Accepted 10 June 2015 Available online 25 August 2015 Keywords:**

Bentonite Biochar Ammonia Composite Adsorption Koi fish abstract The work is concerned with a bentonite hydrochar composite made from bentonite and cassava peel. Bentonite was obtained from a Ponorogo deposit, Indonesia, and cassava peel was agricultural waste. The preparation of the composite was carried out at 500 °C under a flow of carbon dioxide. The sample was characterized by argon adsorption at 87 K, X-ray diffraction, scanning electron microscope, and Fourier transform infrared spectroscopy methods. The adsorption of ammonium from the solution was conducted in a batch condition at 30 °C. The dynamic

condition was employed in the removal of ammonium from Koi fish tank. Biochar and bentonite hydrochar composite samples had microporous structure whereas the bentonite in the composite possessed mesoporous structure.

8 Langmuir and Freundlich adsorption isotherms were used to correlate the experimental data of adsorption

of ammonium from Koi fish tank. The results indicated that the Langmuir equation described the adsorption experimental data well. Combination between van der Waals force and ion exchange increased the adsorption of ammonia onto the bentonite hydrochar composite. Adsorption of ammonia in a real aquaculture system indicated that the composite could completely remove the ammonia from the Koi fish tank within 60 min. © 2015 Elsevier B.V. All rights reserved. 1. Introduction From the ancient to the modern time, clay minerals have been used in building materials, earthenware, ceramic products, cement, adsorbent, cosmetics, rubber, paper, paints, etc. The application of particular clay minerals depends on their physical and chemical properties and these properties strongly depend on the structure and composition (Murray, 2007). One group of the most important clay minerals is smectite. The smectite group includes sodium montmorillonite (Na-MMt), calcium montmorillonite (Ca-MMt), saponite, hectorite, beidellite, and nontronite (Zhang et al., 2010; Bergaya and Lagaly, 2013). Smectite minerals are composed of

11 two silica tetrahedral sheets with a central octahedral sheet and are designated as 2:1 layer mineral, and water molecules and cations occupying the space between the 2:1 layers

(Murray, 2007; Zhou and Keeling, 2013). Na-MMt and Ca-MMt are most the commonly used clay in smectite group for industrial purposes. * Corresponding author. ** Correspondence to: C.H. Zhou,

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(S. Ismadji), clay@zjut.edu.cn (C.H. Zhou). Since the main clay mineral constituents in bentonite are Ca or Na-MMt (Bergaya and Lagaly, 2013), the term of bentonite is commonly used for these clay minerals (Murray, 2007). Bentonite has been used for the removal of various hazardous substances from water or wastewater by many researchers (Kurniawan

6 et al., 2011; Zhou et al., 2012; Campos et al., 2013; Anggraini et al., 2014; Yao et al., 2014).

High adsorption capacity of bentonite toward heavy metals and some organic substances is due to the high charge on their lattice structure and high cation exchange capacity (CEC). In general, normal cation exchange capacity of bentonite is between 40 and 130 meq/100 g (Murray, 2007). As the main component in the bentonite, MMt is comprised of very small particles and possesses the high swelling capacity. Both of these properties make the MMt have the

2ability to form almost impermeable membranes to the movement of water.

This characteristic **makes**

MMt unsuitable as the adsorbent in fixed bed adsorption for water or waste- water treatment system. Surface modification is required to employ this clay mineral as an adsorbent in the fixed bed system. The inclusion of another porous material to support and host the distribution of MMT is one of the above problem solutions. In the last few years the combination between bentonite with other materials such as metal oxide, polymers, and natural polymers has

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received a great deal of attention (Srinivasan, 2011; Dukic et al., 2015; Ianchis et al., 2015; Rzayev et al., 2015; Vanamudan and Pamidimukkala, 2015). Many of those composites were used as ecofriendly and efficient adsorbent for removal of organic, inorganic, and pathogenic contaminants from water and wastewater (Srinivasan, 2011), however, the main drawback for the application of those composites as adsorbent in real water or wastewater system is in the production cost of the composite. Alternative low cost material that can be used as the precursor for natural clay composite is biochar. Biochar is a porous solid material obtained from the carbonization of biomass. Usually the biochar is used to improve soil functions and biodiversity. Due to its porous structure, biochar helps soils to retain water and some nutrients (Yao et al., 2014). The use of biochar as the raw material for inorganic or metal composite has been studied by many authors (Zhang et al., 2012a, 2012b; Yao et al., 2013; Zhang et al., 2013). In these composites, the biochar acts

27as a good porous structure to support and host the distribution of the nanoparticles within its matrix

(Yao et al., 2014). A combination between biochar and clay minerals to a new composite will offer several advantages for environmental application since both of these materials are low cost and possess good adsorption capability. To the present, only a few studies have been conducted to combine biochar and bentonite into one composite material (L.M. Wu

26et al., 2014; X. Wu et al., 2014; Yao et al., 2014)

for environmental applications. Yao et al. (2014) prepared clay-biochar composite through slow pyrolysis of biomass pretreated with clay minerals in a N₂

25environment at temperatures of 600 °C for 1 h. One of the

challenges in the synthesis of bentonite hydrochar composite as the adsorbent is to retain the structure (2:1 layer) of the bentonite while increasing the

7specific surface area and pore volume of the composite. To achieve **this** objective, one of **the**

important parameters is to retain the structural water of the bentonite during thermal treatment. The 2:1 layer of bentonite consists of

2two silica tetrahedral sheets with a central octahedral sheet, and

the space between the 2:1 layers is occupied by water molecules (structural water) and cations. The bentonite layers are negatively charged and

39held together by charge-balancing counterions such as Na⁺ and Ca²⁺. The presence of water

and counterions in the 2:1 layers in bentonite makes the clay layers apart (Bray et al., 1998). The water molecules in the space between the layers are structurally oriented

2to form an ice like structure (Bradley, 1959;

Murray, 2007). The

2thickness of these water molecules between the bentonite layers is related to the exchangeable cation present

(Murray, 2007). This structural water molecule controls the properties of the bentonite such as swelling ability, adsorption capability, and cation exchange capacity. The removal of the structural water results in decrease of interlayer space d_{001} . The loss of structural water will make the bentonite become anhydrous, and rehydration of this anhydrous phase becomes impossible when the exchangeable cation itself migrates, either into the crystalline structure, or as it becomes associated with the outer tetrahedral sheets (Bray et al., 1998). In the early study about the structural water removal from smectite structure, Grim (1968) mentioned that this structural water can be removed by heating the smectite at the temperature from 100 °C to 150 °C. Sarikaya

18et al. (2000) studied the effect of thermal treatment on the physicochemical properties of

calcium bentonite. The dehydration of water from the layer structure was observed from 100 to 400 °C, and major change of the structure occurred at temperatures between 300 and 500 °C. The CEC of the calcium bentonite decreased slightly as the temperature increased to 600 °C, and above this temperature the rapid decrease of CEC was observed. The loss of structural water of bentonite occurred above 500 °C. Similar results were also obtained by Zymankowska-Kumon et al. (2012). They found that the structure of the smectite completely collapsed due to the loss of structural water at temperature of 700 °C. In this paper, the preparation of bentonite hydrochar composite was conducted in the presence of carbon dioxide and at moderate temperature. The use of moderate temperature is to avoid the completely loss of the structural water from the bentonite, while the use of carbon dioxide is to activate the biochar in order to develop the pore structure, and increase the adsorption capacity. So far, there is no literature about the preparation of bentonite hydrochar composite in the presence of carbon dioxide, and this is the novelty of the current study. In order to study the adsorption capability, the bentonite hydrochar composite

26 was used to remove ammonia from aqueous solution and

Koi fish tank.

172. Materials and methods 2.1. Materials Bentonite used in this study was obtained from

13a bentonite mining located at Ponorogo, East Java, Indonesia. The pretreatment of bentonite

using hydrogen peroxide solution was conducted in order to remove organic impurities. The pretreatment was conducted at room temperature. The excess hydrogen peroxide was removed by heating the mixture at 100 °C. The pretreated bentonite was repeatedly washed with reverse osmosis

23 water, and dried at 105 °C for 24 h. Dried

bentonite subsequently pulverized using JANKE & KUNKEL microhammer mill until its particle size reach ± 200/300

13 mesh. The cation exchange capacity (CEC) of the bentonite was

measured using methylene blue index following the ASTM C837-99 test method, and the CEC value was 64.5 meq/100 g. The chemical composition of Ca-bentonite

15 was analyzed by a PANalytical MiniPal QC energy dispersive X-ray fluorescence (EDXRF) spectrometer

(Table 1). Agricultural waste residue, cassava peel, was used as the biomass precursor for bentonite hydrochar composite production. Prior to use, the cassava peel

20 was repeatedly washed using tap water to remove organic and inorganic impurities. Subsequently, the clean cassava peel was dried in an oven (Memmert) at 105 °C for 24 h, and then pulverized

until its particle size 80/100 mesh. All chemicals used in this study such as NH₄Cl, HgI₂, KI, NaOH, and sodium salicylate were purchased as analytical grade reagent from Merck GmbH Germany and used without any further purification. Carbon dioxide and nitrogen gases were obtained as industrial grade from PT Aneka Gas, Surabaya, Indonesia. 2.2. Heat treatment test of bentonite The heat treatment test of the bentonite was conducted at temperature of 300, 400, 500, and 600 °C under nitrogen conditions in a tube furnace apparatus (Thermolyne F21130-26 tubular furnace). Ten grams of bentonite was introduced into the tube furnace and then heated under nitrogen flow at a heating rate of 10 °C/min. After the desired temperature was reached, the heating process was continued for 60 min, and subsequently the system

12was cooled to room temperature. 2. 3. Preparation of

bentonite–biochar composite The preparation of bentonite hydrochar composite was conducted according to the following procedure: 25 g of bentonite powder was added into 500 mL of reverse osmosis water. The mixture was then

37Table 1 Chemical composition of Ca -bentonite. Metal oxide Composition, %
SiO₂ 63.14 Al₂O₃

19.77 Na₂O 1.56 K₂O 1.08 MgO 2.41 CaO 3.05 MnO 0.31 Fe₂O₃ 2.49 TiO₂ 0.09 sonicated for 60 min in a Branson 3510 sonicator. After stable clay dispersion obtained, 50 g of cassava peel powder was added to the mixture and stirred for another 60 min. The solid was

25then separated from the liquid and dried at 105 °C for 24 h. The

mixture of bentonite and cassava peel was placed in a quartz container and inserted into a tube furnace (Thermolyne F21130-26 tubular furnace). The carbonization of the sample to produce the composite was conducted at 500 °C at a

19heating rate of 10 °C/min. During the heating process to the desired temperature (500 °C), the

nitrogen

32with the flow rate of 3 L/min (STP) was

also introduced into the tube furnace. After the

19desired temperature was reached, the temperature of the furnace was kept constant at

500 °C for 60 min. For the first 45 min, the system was under nitrogen environment, and for the rest of 15 min, the nitrogen flow was switched to the carbon dioxide gas at the flow rate of 3 L/min (STP). After the process completed, the carbon dioxide flow was switched back to the nitrogen flow and the system was cooled to the room temperature. 2.4. Characterization The characterization of bentonite, biochar, and bentonite hydrochar composite was conducted using X-ray diffraction, argon adsorption and desorption isotherms, Scanning Electron Microscopy (SEM), and FTIR methods. The

12powder X-ray diffraction patterns were obtained by a Philips X'pert X-ray diffractometer. The

XRD patterns were acquired at 40 kV and 30 mA using Ni-filtered Cu K α 1 as the source of radiation with the scanning rate of 1°/min. The value of d₀₀₁ was calculated based on the Bragg's law $n\lambda = d \sin \theta$

3 $n \sin \theta = d \sin \theta$ where n is the order of diffraction, λ is the wavelength of the

X-ray ($\lambda = 0.15405$ nm), d is the basal spacing and θ is diffraction angle. In most cases, the value of n is taken to be 1. The argon adsorption and desorption measurements were conducted on an automated Micromeritics ASAP 2010 adsorption analyzer

9 at the boiling point of argon gas (-185.8 °C). Prior to the analysis, the samples were degassed at 150 °C for **24** h at

high vacuum condition. Bentonite is hydrophilic material, the choice of the degassing temperature is important. In the degassing process, all of the free moisture content should be removed from the structure bentonite, while the structural water molecules must not be affected by the process. The argon adsorption and desorption

4 isotherms were measured at a relative pressure (P/P_0) range from approximately 10^{-4} to **0.995**. The BET surface area

was calculated by the standard BET equation at a relative pressure between 0.05 and 0.25. The total pore volume was determined at a relative pressure of 0.995. At the highest relative pressure, all of the available pores were completely filled with the argon gas. The pore size distribution of the samples was determined using the density functional theory (DFT) with medium regularization. SEM images of the raw materials and composite were obtained with a JEOL JSM-6500F. Prior to SEM analysis, the samples were coated with thin layer platinum. The sputter coater was operated in an argon atmosphere for 90 s. The SEM analysis was conducted at 15 kV and 20 kV with 9.6 mm working distance. The FTIR analysis was conducted in FTIR SHIMADZU 8400S using the KBr method. In this method, the

3 sample was mixed with the KBr powder with the ratio of **10%** and

finely grinded in a mortar. The mixed

3 powder was mounted to the instrument and the sample measurement was conducted in the transmittance % T mode.

The analysis was carried out in the wavenumber

9 range of $4000-500$ cm^{-1} . The proximate analysis of cassava peel was conducted according to the

ASTM E870-82 method, while the ultimate analysis was performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. High carbon content in the proximate and ultimate analysis (Table 2) indicated that cassava peel was a suitable precursor for biochar preparation. Table 2 Ultimate and proximate analysis of cassava peels. Proximate analysis Wt, % Ultimate analysis Wt, % Moisture Volatile matter Fixed carbon Ash 12.05 Carbon 54.84 Nitrogen 30.71 Hydrogen 2.40 Oxygen Sulfur 60.74 2.01 10.48 26.74 0.03 2.5. Batch adsorption experiments The adsorption of ammonium from aqueous solution using bentonite, biochar, and

bentonite hydrochar composite was conducted in batch process at 30 °C and pH 6. Ammonium solutions with initial concentration of 200 mg/L were prepared by adding the appropriate amount of ammonium chloride into reverse osmosis water. Known amounts of adsorbent (0.1 to 1 g) were added into

10 a series of 250 mL stoppered conical flasks containing 100 mL of solution. The flasks, then were transferred into a

temperature controlled shaking water bath and shaken at 100 rpm for 6 h. After the equilibrium condition was reached, the solution

8 was separated from the adsorbent by centrifugation at 3000 rpm for 10 min. The

10 initial and equilibrium concentration of the ammonium were determined by a

Nesslerization method (Golterman, 1991) using a Shimadzu UV/VIS-1700 Pharmaspec spectrophotometer. The amount of ammonium adsorbed by the adsorbent at equilibrium condition (q_e) was calculated by the following equation: $q_e = \frac{C_0 - C_e}{V} \cdot m$

4 where C_0 and C_e are the initial and equilibrium concentrations, respectively, V is the volume of solution, and m is the mass of adsorbent.

2.6.

37 Removal of ammonium from Koi tank

The adsorption of ammonium from the real aquaculture system was conducted in continuous and circulation mode. The fiberglass fish tank used in the study has the capacity of 750 L and filled with 500 L of tap water. The fish tank contains 30 Japanese Koi fishes with the average length of 30 cm and the average mass of 1.1 kg. The initial pH of the water was 6.5, and the tap water also contained other minerals (Table 3). Resun submerged water pump with the capacity of 4000 L/h was used to circulate the water within the fish tank. Fish food used in this study was produced by Central Protein Prima Pty. Ltd., Sidoarjo, East Java, Indonesia. The nutritional contents of the fish food were as follows: •

35 Crude protein: min 35% • Crude fat: min 3% • Crude fiber: Max 5% • Crude ash: Max 13% • Moisture: Max 12%.

Fish feeding was conducted three times daily, with a total food intake around 1% of the fish body mass. Prior the adsorption experiment, the pH and total concentration of ammonium in the tank were measured and monitored every 60 min. Measurement of ammonium in water after 60 min the first time feeding on fish. During the monitoring of ammonia or ammonium concentration in the fish tank, the oxygen was continuously bubbled into the fish tank to maintain the level of dissolved oxygen in the desired value (10–11 mg/L). The adsorption experiment was conducted after 24 h of the first fish feeding, the water in the fish tank was circulated into the filtering system containing 5 kg of bentonite–biochar composite using Resun submerged

water pump. The concentration of ammonium in the fish tank was measured every Table 3 The characteristic of tap water used for fish Koi. Parameter Value pH Total alkalinity,

16mg/L as CaCO₃ Total hardness, mg/L as CaCO₃ Fe, mg/L Mn, mg/L F, mg/L Cl, mg/L SO₄, mg/L NO₃, mg/L Total ammonia, mg/L PO₄, mg/L

6.5 56 74 0.03 0.01 – 82 77 – – – 5 min, and the measurement was stopped after the concentration of ammonium was not detected. 3. Results and discussion 3.1. Influence of temperature on the change of the bentonite structure Thermally stable porous materials are required for many kinds of applications such as adsorbent, catalyst, and catalyst support. In clay minerals, the porosity is closely linked to their water content, and during the heating process the release of water from a clay interior can alter the porosity and interlayer structure (Heller-Kallai, 2006). Since the preparation of bentonite hydrochar composite was conducted at high temperature, it is necessary

28to study the behavior of the bentonite structure as the function of

temperature. XRD diffractograms of calcium bentonite and its heat treated forms (Fig. 1) clearly show

7that the temperature has a significant effect on the layered structure of bentonite. The

001 reflection decreases in intensity with the increase of temperature of the thermal treatment. At 600 °C, the disappearance of the 001 reflection was observed. The basal spacing (d₀₀₁) of bentonite and heat treated forms as the function of temperature (Table 4) indicates that the temperature slightly alters the basal spacing of the bentonite, however, if the temperature further increases to 600 °C, the bentonite structure disappears. As mentioned in the previous section, the temperature has a significant effect on the structural water of the bentonite, the evaporation of structural water will alter the basal spacing of bentonite (Sarikaya et al., 2000; Zybankowska-Kumon et al., 2012). Completely lost of the structural water will destroy the MMt characteristic. XRD diffractograms reveal that bentonite from Ponorogo, East Java, Indonesia also contains quartz, calcite, and feldspar. The thermal treatment of bentonite at high temperature decreases the value of CEC (Table 5). At 500 °C, the ability of bentonite to exchange the cation has reduced around 18.8%. At higher temperature, the ability of bentonite to exchange the cation almost completely lost. The decrease in the CEC is an indication of the deformation of 2:1 layers of the bentonite or MMt. The lost of structural water of bentonite is an irreversible process, the CEC of bentonite was determined based on the adsorption of methylene blue solution (a cationic dye), with the collapse of interlayer structure, some the exchangeable cation itself migrates, either in the crystalline structure, or as it becomes associated with the outer tetrahedral sheets (Bray et al., 1998), and these migrate exchangeable cations that are no longer have the exchange capability with methylene blue cation in the solution. The specific surface area of the bentonite is one of the most important properties to control the surface phenomena. For swelling clay minerals such as bentonite, the specific surface area also depends on the nature of the exchangeable cation. Since the evaporation of the structural water also affects the exchange capability of exchangeable cations as mentioned earlier, therefore, it also affects

7the specific surface area of the

bentonite (Table 5).

7 The BET surface area of the

thermal Fig. 1. X-ray diffractograms of calcium-bentonite. treated bentonite decreases with the increase of the temperature. The complete evaporation of structural water at 600 °C significantly decrease the BET surface area and pore volume of the heat treated bentonite. 3.2. Bentonite hydrochar composite The X-ray diffraction pattern of bentonite hydrochar composite (Fig. 2) shows that the amorphous structure of the biochar more dominant than the bentonite structure. However, the main characteristic of basal spacing of bentonite still remains in the composite structure and observed at $2\theta = 5.778^\circ$, and this value corresponds to

12 basal spacing of 1.529 nm. Comparing the basal spacing of

bentonite structure in composite with the heat treated at 500 °C, d001 of bentonite in the composite is smaller than heat treated form. During the heating process of the composite, some of the structural water molecules evaporated and leave empty space in the interlayer space of the bentonite, meanwhile, at high temperature some parts of the interior structure of biochar Table 4 Typical reflections and basal spacing of heat treated bentonite. Temperature, °C 2θ , ° d001, nm 30 5.012 300 5.150 400 5.220 500 5.300 600 – 1.762 1.714 1.691 1.665 – Table 5 The physical characteristic of heat treated bentonite. Temperature, °C CEC, meq/100 g BET, m²/g Pore volume, cm³/g 30 64.5 300 61.3 400 58.2 500 52.4 600 5.3 152.3 0.23 141.8 0.22 134.5 0.19 128.2 0.17 22.4 0.04 were thermally decomposed into gas or organic compounds with low molar mass. Some of these low molar masses of organic compounds penetrated and condensed in the interlayer space of the bentonite leading to decrease of the value d001. The use of nitrogen as the gas probe for the characterization of the pore structure of clay minerals is not recommended due to the quadrupole

5 moment of nitrogen gas that can interact with the hydroxyl or other polar groups

in solid samples, and this phenomenon can change the

5 cross sectional area of the adsorbed molecule.

The reason of using argon as the probe molecule is the fact that argon

5 is a symmetrical non-polar atom which should be less subject to specific interactions affected by changes in the chemical nature of surfaces

(Aylmore, 1973). The adsorption and desorption isotherms of all the samples indicate that both of bentonite and biochar possess micropore structure (Fig. 3), indicated by rapid intake of argon gas at low relative pressure. The biochar is type 1 isotherm, and according to IUPAC classification, this type of isotherm belongs to microporous material. The argon adsorption and desorption isotherms of bentonite from Ponorogo, East Java, Indonesia possess type H3 hysteresis, the material with type H3 hysteresis has slit-shaped pore characteristic. A combination between microporous and mesoporous structure is observed for bentonite hydrochar composite. The

34BET surface area and pore volume of bentonite hydrochar composite **were** 402 m²/g and 0.34 cm³/g, respectively. During the

pyrolysis process, the carbon dioxide acted as the activating agent, the partial oxidation of the biochar with carbon dioxide occurred resulting in the extension of biochar surface area and the generation of new pores and large amounts of reactive sites on the biochar basal planes which have electron rich oxygen free-radical character (Kurniawan and Ismadji, 2011). The pore size distribution is a statistical representation of the size property of individual pores and closely related to both the equilibrium and kinetic features of adsorption in these mesoporous materials (Ismadji and Bhatia, 2001). The density functional theory was employed to calculate the pore size distribution of bentonite, biochar, and bentonite hydrochar composite (Fig. 4). The dominant microporous structure is obvious for biochar and the composite, while the bentonite possesses mesoporous structure. The SEM images of the surface morphology of all Fig. 2. XRD diffraction pattern of bentonite hydrochar composite. Fig. 3. Argon sorption isotherm of raw materials and composite. samples (Fig. 5) clearly reveal the heterogeneity structures of all samples. Fourier transform infrared spectroscopy (FTIR) is a technique for characterization of materials based on the vibrations of atoms within the molecules. The FTIR method

28 is the most widely used technique for characterization of clay minerals

since it provides informative information on the

14 mineralogy and crystal-chemistry of a clay mineral sample.

The infrared

14 spectrum of clay mineral is sensitive to its chemical composition, isomorphous substitution and layer stacking order

(Petit, 2006). The characteristic absorption bands of MMT as structural indicated by Al(Mg)-O-H stretching (3620 cm⁻¹), intra or intermolecular hydrogen bonded H-O-H stretching (3347 cm⁻¹), H-O-H deformation vibration due to adsorbed water (1634 cm⁻¹), Si-O-Si stretching vibration at 1060 cm⁻¹, Al-OH (904 and 621 cm⁻¹), (Al, Mg)-O (841 and 790

17 cm⁻¹) and Si-O bending vibration (520 and 471 cm⁻¹)

(Koswojo et al., 2010; Unlu et al., 2012). The FTIR spectra data of biochar prepared from cassava peel indicate that several functional groups are present in the surface of biochar. A peak around 1705 cm⁻¹ is the stretching vibration of C=O which indicates the presence of carboxylic group in the surface of biochar (Prahas et al., 2008). A relatively low intensity peak at wavenumber around 3108 cm⁻¹ represents O

23 -H stretching vibration in phenol. The C-H stretching vibration of methyl group

indicated by a peak at wavenumber 2906 cm^{-1} , while a strong band at wavenumber 1588 cm^{-1} is C-C aromatic ring stretching. Most of the surface functional groups and structural characteristic of the raw materials are available in the Fig. 4. Density functional theory (DFT) pore size distribution of raw materials and composite. Fig. 5. SEM micrographs of (a) bentonite, (b) biochar, and (c) bentonite hydrochar composite. composite, however, for several absorption bands such as

30 Si-O-Si stretching, Al-OH, (Al, Mg)-O, and Si-O,

relative low intensity peaks are observed (Table 6). 3.3. Adsorption of ammonium from aqueous solution The adsorption experimental data of ammonium onto bentonite, biochar, and bentonite hydrochar composite are represented by

8 Langmuir and Freundlich adsorption equations. The Langmuir isotherm has the form

as follows: $q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$ where q_{\max}

18 is the adsorption capacity of adsorbent toward specific solute and K_L is adsorption

affinity, this parameter measures how strong the adsorbate attach to the adsorbent. One of the advantages of using the Langmuir equation for representing the adsorption equilibria data is it reduces to Henry's law at a very low concentration and it possesses the limit saturation capacity. Langmuir model is one of the widely used isotherm models

10 to correlate liquid phase adsorption data.

Table 6 FTIR spectra data of bentonite, biochar, and bentonite hydrochar composite. Assignment Wavenumber, cm^{-1} Bentonite Biochar Composite Al(Mg

40) O-H stretching H-O-H stretching O-H stretching vibration C-H stretching C-O stretching vibration H-O-H bending (H_2O) C-

C aromatic ring stretching

30 Si-O-Si stretching Al-OH (Al, Mg)-O Si-O

bending vibration 3620 3347 --- 1634 - 1060 904 and 621 841 and 790 520 and 471 -- 3108 2906 1705 - 1588 --- 3598 - 3101 2925 1714 - 1591 1065 907 and 619 829 and 784 521 and 475 Freundlich isotherm

24 is an empirical equation which was developed for the adsorption on heterogeneous surface.

This model has the form as follows: $q_e = \frac{K_F C_e^n}{1 + K_F C_e^n}$ The parameter K_F is Freundlich constant, usually associated with

13 the adsorption capacity of the adsorbent. The

system heterogeneity is represented by parameter n . The value of parameter n usually higher than 1, the higher value of parameter n , the more heterogenous of the adsorbent. The adsorption isotherms of ammonium on bentonite, biochar, and bentonite hydrochar composite and the plots of Langmuir and Freundlich equations indicate that the Langmuir equation can represent the experimental data better than Freundlich, especially at very low concentration (Fig. 6). As mentioned before, Langmuir possesses the

15 Henry's law at low concentration and limit saturation capacity at high concentration,

therefore the Langmuir model is more superior than the Freundlich equation. The parameter q_{max} of the Langmuir equation represents the adsorption capacity of the adsorbent. The adsorption capacity of the adsorbents use in this study is in the order of bentonite hydrochar $>$ bentonite $>$ biochar (Table 7). The adsorption mechanism of ammonium on the biochar is mainly due to physical adsorption (van der Waals interaction), since the surface area of the biochar is also lower compared with bentonite and composite, therefore, the amount uptake of ammonium is lower than other adsorbents. Bentonite hydrochar composite has the highest adsorption capacity possibly due to its highest BET surface area and a more developed porous structure. During the thermal process in the preparation of the composite, the carbon dioxide gas has the role as an activating agent for the biochar, at high temperature, CO_2 becomes reactive gas, it oxidized some part of biochar in composite structure, leading to the opening of the existing pore and creating new micropores in the composite structure as indicated in Figs. 3 and 4. With the increase of surface area and pore volume, the capability of composite to attach more ammonium ions from the solution through van der Waals force also increased. Furthermore, the presence of cations Fig. 6. Adsorption isotherms of ammonium ion on different adsorbents and plots of (a) Langmuir equation, and (b) Freundlich equation.

31 ions and the surface of the adsorbent

is mainly

31 due to the van der Waals force, therefore it has the lowest value of

parameter K_L . 3.4. Removal total ammoniacal nitrogen from Koi tank In the intensive aquaculture system, one of the important water quality parameters after the oxygen is ammonia content. In healthy aquaculture system, the level of ammonia content should always be in a very low concentration (below 0.1 ppm). It means that the ammonia primarily produced from the gills of the fish directly converted into less harmful nitrate by nitrifying bacteria in biological filtration system. The next step is the denitrification and dissimilation process that converts nitrate to nitrogen gas. However, to bring this process into an in-house aquarium tank system often is not practical due to the need of a constant carbon source. The concentration of ammonia in the fish tank as the function of time is reported as the total ammonia (both unionized ammonia and ammonium ion) (Fig. 7). The tolerance of the Koi fish with ammonia concentration becomes less with increasing the pH of the water. Based on the preliminary experiments, in good aeration system, at pH 6, the Koi fish can tolerate the ammonia concentration up to 10 mg/L, at pH 7, the level decreases to around 1.5 mg/L, and at pH 9, the concentration of ammonia at a level of 0.1 mg/L becomes lethal to the Koi fish. In the first 6 h, the

concentration of ammonia in the tank still below 0.1 mg/L, and slowly increased in the next 6 h to level 0.4 mg/L, and the pH of water in the fish tank was still constant around 6.5. In the subsequent hours, the increased of ammonia level was quite significant and at the end of 24 h, the ammonia concentration was 1.9 mg/L and the pH of the water was 6.6. In the beginning of the experiment, the source of ammonia in the water was mainly from fish excretion through the gills, while the decomposition of fecal solid excreted by fish still did not occur in the early hours of the experiment. In water, ammonia exists in two different forms according to the following reversible reactions $\text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_3 + \text{H}_2\text{O}$ in the interlayer of bentonite in composite structure also enhanced the adsorption process through the cation exchange mechanism. The adsorption affinity (KL) measures the type of

32 **interaction between adsorbate and adsorbent. The higher the value of**

KL, the interaction between adsorbate and adsorbent also becomes stronger and more adsorbates attach to the surface of adsorbent. The fitted value of parameter KL is in the order of bentonite hydrochar composite > N bentonite > N biochar (Table 7). For bentonite hydrochar composite, the adsorption of ammonium ions occurred in two different adsorption pathways, one through the ion exchange mechanism, and the other is the van der Waals mechanism. The ion exchange process has the much stronger interaction force compared with the van der Waals force, therefore the value of fitted parameter KL for this system is higher than other adsorbents. For biochar, the interaction between ammonium Table 7 Langmuir and Freundlich parameters on the adsorption of ammonium on bentonite, biochar, and bentonite hydrochar composite. Parameter Bentonite Biochar Bentonite hydrochar composite Langmuir equation

29 **q_{max}, mg/g KL, L/mg R² Freundlich model KF, (mg/g) (L/mg)^{1/n} n R²**

12.37 9.49 0.0501 0.0232 0.9834 0.9976 2.13 0.80 2.96 2.23 0.9406 0.9674 23.67 0.0738 0.9941 5.58 3.53 0.9095 $\text{NH}_3 + \text{H}_3\text{O}^+ \leftrightarrow \text{NH}_4^+ + \text{H}_2\text{O}$. The toxic form of ammonia for aquatic biota is NH_3 . In good aeration system, the presence of air bubbles in the water accelerates the diffusion of NH_3 from water into the air and subsequently release to the environment. Therefore, a low concentration of ammonia in water during the first and second 6 h is observed. With the increased of time, due to Fig. 7. Ammonia concentration in fish water as function of time. Fig. 8. The removal efficiency of ammonia from the fish water using bentonite hydrochar composite. microbial activity, the fecal solid excreted by fish begins to decompose and produces ammonia, thus it significantly increased the concentration of ammonia in water. The rate of water circulation in the fish tank was 4000 L/h, and during the adsorption experiment the aeration process and fish feeding were stopped. The removal efficiency of the adsorption column as a function of time (Fig. 8) shows that the composite could completely remove the ammonia from the fish tank system which contains 500 L of water and 30 Japanese Koi fishes within 60 min. As mentioned in the previous section, the adsorption mechanism between composite and ammonia or ammonium ion from the solution occurred through physical (van der Waals force) and chemical (ion exchange) adsorption process. The combination of both these mechanisms enhances the adsorption capability of the composite. The pH has strong effect on the surface charge of the composite. Depending on the silica structure on the composite and the pH of the solution, the net surface charge can be either positive or negative. At pH less than pH_{pzc} , the bentonite hydrochar composite would have an anion exchange capacity, while at pH higher than pH_{pzc} , the composite would have a cation exchange capacity. The pH_{pzc} of the composite was 5.4, since the pH of the water was 6.6, the composite has a negative surface charge, and silanol group in the composite was hydrolyzed according to the following reaction $\text{SiOH} + \text{OH}^- \rightarrow \text{SiO}^- + \text{H}_2\text{O}$ (pH > pH_{pzc}). With negative surface charge, the composite would have a cation exchange capacity. In water, the ammonia exists in the forms of NH_3 and NH_4^+ , therefore, the adsorption of ammonium ion from the water onto composite occurred through ion exchange mechanism, while the existence of micropore structure on the composite (Figs. 3 and 4) enhanced the adsorption or removal of ammonia through physical or van der Waals mechanism. 4. Conclusion A bentonite hydrochar composite was prepared by thermal treatment of bentonite and cassava peel at 500 °C under a flow of

carbon dioxide. During thermal treatment, the temperature has a significant effect on the 2:1 layer structure of bentonite. The biochar and the composite had micropore structure whereas the bentonite in the composite possessed mesoporous structure. The characteristic of interlayer space (d001) of bentonite still remained in the composite and observed at $2\theta = 5.778^\circ$, and this value corresponds to basal spacing of 1.529 nm. Langmuir equation can represent the adsorption experimental data of adsorption of ammonium onto bentonite, biochar, and bentonite hydrochar composite. The maximum adsorption capacity of ammonia onto bentonite, biochar, and composite were 12.37

24 mg/g, 9.49 mg/g, and 23.67 mg/g,

respectively. Since the pH of the water was higher than the pH_{pzc} of the composite, it enhanced the adsorption capacity of the composite through ion exchange mechanism. The composite could completely remove the ammonia from the fish tank system which contains 500 L of water and 30 Japanese Koi fishes within 60 min. Acknowledgment The authors would like to acknowledge financial support for this work provided by Directorate of Higher Education, Indonesia Ministry of Research, Technology, and Higher Education through Competency Research Grant with project number 003/SP2H/P/K7/KM/2015, the Distinguished Young Scholar Grants from the Natural Scientific Foundation of Zhejiang Province (R4100436), and the

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by organo-bentonite from Pacitan. *Appl. Clay Sci.* 48, 81–86. Kurniawan, A., Ismadji, S., 2011. Potential utilization of *Jatropha curcas* L. press-cake residue as new precursor for activated carbon preparation: application in methylene blue removal from aqueous solution. *J. Taiwan Inst. Chem. Eng.* 42, 826–836.

Kurniawan, A., Sutiono, H., Ju, Y.H., Soetaredjo, F.E., Ayucitra, A., Yudha, A., Ismadji, S., 2011. Utilization of rarasaponin natural surfactant for organo-bentonite preparation: application for methylene blue removal from aqueous effluent. *Microporous Mesoporous Mater.* 142, 184–193.

Murray, H.H., 2007. *Applied Clay Mineralogy: Occurrences, Processing and Application of Kaolins, Bentonites, Palygorskite–Sepiolite, and Common Clays*. First ed. Elsevier, Amsterdam.

Petit, S., 2006. Fourier transform infrared spectroscopy. In: Bergaya, F., Theng, B.K., Lagaly, G. (Eds.), *Development in Clay Science* vol. 1. Elsevier Ltd, Amsterdam, pp. 909–918.

Prahas, D., Kartika, Y., Indraswati, N., Ismadji, S., 2008. Activated carbon from jackfruit peel waste by H₃PO₄ chemical activation: pore structure and surface chemistry characterization. *Chem. Eng. J.* 140, 32–42.

Rzayev, Z.M.O., Uzgoren-Baran, A., Bunyatova, U., 2015. Functional organo-Mt/copolymer nanoarchitectures: microwave-assisted rapid synthesis and characterisation of ODA–Mt/poly[NIPAm-co-(MA-alt-2,3-2H-DHP)] nanocomposites. *Appl. Clay Sci.* 105–106, 1–13.

Sarikaya, Y., Onal, M., Baran, B., Alemdaroglu, T., 2000. The effect of thermal treatment on some of the physicochemical properties of a bentonite. *Clay Clay Miner.* 48, 557–562.

Srinivasan, R., 2011. Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. *Adv. Mater. Sci. Eng.* <http://dx.doi.org/10.1155/2011/872531> (Article ID 872531).

Unlu, C.H., Gunister, E., Atici, O., 2012. Effect of acidity on xylan–montmorillonite bionanocomposites. *Mater. Chem. Phys.* 136, 653–660.

Vanamudan, A., Pamidimukkala, P., 2015. Chitosan, nanoclay and chitosan–nanoclay composite as adsorbents for Rhodamine-6G and the resulting optical properties. *Int. J. Biol. Macromol.* 74, 127–135.

Wu, L.M., Zhou, C.H., Tong, D.S., Yu, W.H., Wang, H., 2014a. Novel hydrothermal carbonization of cellulose catalyzed by montmorillonite to produce kerogen-like hydrochar. *Cellulose* 21, 2845–2857.

Wu, X., Gao, P., Zhang, X., Jin, G., Xu, Y., Wu, Y., 2014b. Synthesis of clay/carbon adsorbent through hydrothermal carbonization of cellulose on palygorskite. *Appl. Clay Sci.* 95, 60–66.

Yao, Y., Gao, B., Chen, J., Zhang, M., Inyang, M., Li, Y., Alva, A., Yang, L., 2013. Engineered carbon (biochar) prepared by direct pyrolysis of mg-accumulated tomato tissues: characterization and phosphate removal potential. *Bioresour. Technol.* 138, 8–13.

Yao, Y., Gao, B., Fang, J., Zhang, M., Chen, H., Zhou, Y., Creamer, A.E., Sun, Y., Yang, L., 2014. Characterization and environmental applications of clay–biochar composites. *Chem. Eng. J.* 242, 136–143.

Zhang, D., Zhou, C.H., Lin, C.X., Tong, D.S., Yu, W.H., 2010. Synthesis of clay minerals. *Appl. Clay Sci.* 50, 1–11.

Zhang, M., Gao, B., Yao, Y., Xue, Y.W., Inyang, M., 2012a. Synthesis of porous MgO–biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions. *Chem. Eng. J.* 210, 26–32.

Zhang, M., Gao, B., Yao, Y., Inyang, M., 2012b. Phosphate removal ability of biochar/MgAl–LDH ultra-fine composites prepared by liquid-phase deposition. *Chemosphere* 92, 1042–1047.

Zhou, C.H., Keeling, J., 2013. Fundamental and applied research on clay minerals: from climate and environment to nanotechnology. *Appl. Clay Sci.* 74, 3–9.

Zhou, C.H., Zhang, D., Tong, D.S., Wu, L.M., Yu, W.H., Ismadji, S., 2012. Paper-like composites of cellulose acetate–organo-montmorillonite for removal of hazardous anionic dye in water. *Chem. Eng. J.* 209, 223–234.

Zymankowska-Kumon, S., Holtzer, M., Olejnik, E., Bobrowski, A., 2012. Influence of the changes of the structure of foundry bentonites on their binding properties. *Mater. Sci.* 18, 57–61.

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S. Ismadji et al. / *Applied Clay Science* 119 (2016) 146–154

S. Ismadji et al. / *Applied Clay Science* 119 (2016) 146–154

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S. Ismadji et al. / *Applied Clay Science* 119 (2016) 146–154

S. Ismadji et al. / *Applied Clay Science* 119 (2016) 146–154

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S. Ismadji et al. / *Applied Clay Science* 119 (2016) 146–154

S. Ismadji et al. / *Applied Clay Science* 119 (2016) 146–154

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S. Ismadji et al. / *Applied Clay Science* 119 (2016) 146–154