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by Aning Ayucitra

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Research paper

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

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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. 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.

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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 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. 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 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 ability 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 wastewater 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.

* Corresponding author at: C.H. Zhou, 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. S. Ismadji, Department of Chemical Engineering, WidyaMandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia.

E-mail addresses: suryadiismadji@yahoo.com (S. Ismadji), clay@zjut.edu.cn (C.H. Zhou).

In the last few years the combination between bentonite with other materials such as metal oxide, polymers, and natural polymers has 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 (Wu et al., 2015; Zhang et al., 2012a, 2012b; Yao et al., 2013; Zhang et al., 2013). In these composites, the biochar acts as 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 et 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 environment 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 specific 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 two 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 held 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 to form an ice like structure (Bradley, 1959; Murray, 2007). The thickness 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 et 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 was used to remove ammonia from aqueous solution and Koi fish tank.

2. Materials and methods

2.1. Materials

Bentonite used in this study was obtained from a 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 water, and dried at 105 °C for 24 h. Dried bentonite subsequently pulverized using JANKE & KUHEL microhammer mill until its particle size reach ± 200/300 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 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 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 was cooled to room temperature.

Table 1
Chemical composition of Ca-bentonite.

Metal oxide	Composition, %
SiO ₂	63.14
Al ₂ O ₃	19.77
Na ₂ O	1.56
K ₂ O	1.08
MgO	2.41
CaO	3.05
MnO	0.31
Fe ₂ O ₃	2.49
TiO ₂	0.09

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 sonicated for 60 min using 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 then 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 heating rate of 10 °C/min. During the heating process to the desired temperature (500 °C), the nitrogen with the flow rate of 3 L/min (STP) was also introduced into the tube furnace. After the desired 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 powder 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 d_{001} was calculated based on the Bragg's law

$$d = \frac{n\lambda}{2\sin\theta} \quad (1)$$

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 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 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 sample was mixed with the KBr powder with the ratio of 10% and finely grinded in a mortar. The mixed 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 range of 4000–500 cm^{-1} .

Table 2

Ultimate and proximate analysis of cassava peels.

Proximate analysis	Wt, %	Ultimate analysis	Wt, %
Moisture	12.05	Carbon	60.74
Volatile matter	54.84	Nitrogen	2.01
Fixed carbon	30.71	Hydrogen	10.48
Ash	2.40	Oxygen	26.74
		Sulfur	0.03

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.

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

$$q_e = \frac{C_0 - C_e}{m} V$$

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. 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). Reson 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:

- 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

Table 3
The characteristic of tap water used for fish Koi.

Parameter	Value
pH	6.5
Total alkalinity, mg/L as CaCO ₃	56
Total hardness, mg/L as CaCO ₃	74
Fe, mg/L	0.03
Mn, mg/L	0.01
F, mg/L	–
Cl, mg/L	82
SO ₄ , mg/L	77
NO ₃ , mg/L	–
Total ammonia, mg/L	–
PO ₄ , mg/L	–

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 5 min, and the measurement was stopped after the concentration of ammonium was not detected.

4 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 to 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 that 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 (d_{001}) 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; Zymankowska-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

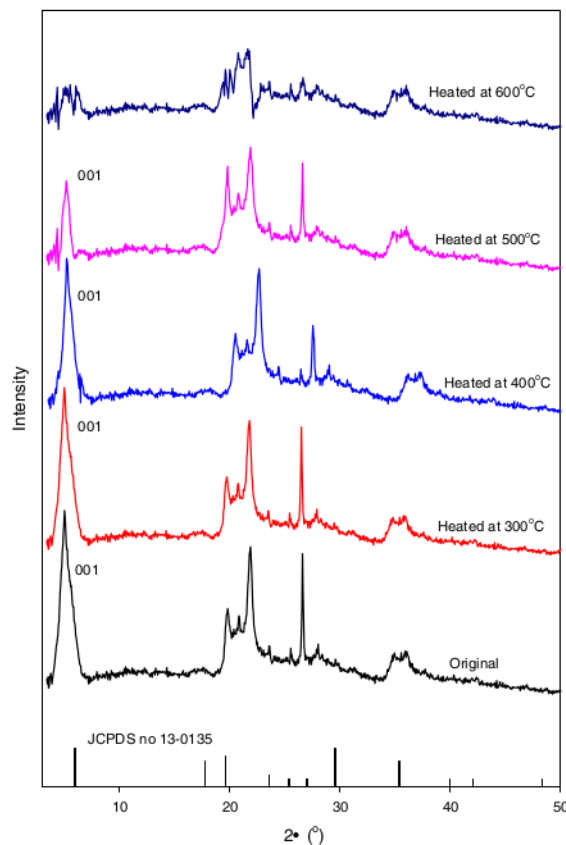


Fig. 1. X-ray diffractograms of calcium-bentonite.

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 the specific surface area of the bentonite (Table 5). The BET surface area of the thermal 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 basal spacing of 1.529 nm. Comparing the basal spacing of bentonite structure in

Table 4
Typical reflections and basal spacing of heat treated bentonite.

Temperature, °C	2θ , °	d_{001} , nm
30	5.012	1.762
300	5.150	1.714
400	5.220	1.691
500	5.300	1.665
600	–	–

Table 5

The physical characteristic of heat treated bentonite.

Temperature, °C	CEC, meq/100 g	BET, m ² /g	Pore volume, cm ³ /g
30	64.5	152.3	0.23
300	61.3	141.8	0.22
400	58.2	134.5	0.19
500	52.4	128.2	0.17
600	5.3	22.4	0.04

composite with the heat treated at 500 °C, d_{001} 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 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 d_{001} .

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 moment of nitrogen gas that can interact with the hydroxyl or other polar groups in solid samples, and this phenomenon can change the cross sectional area of the adsorbed molecule. The reason of using argon as the probe molecule is the fact that argon 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 BET 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 (Kumiawan 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

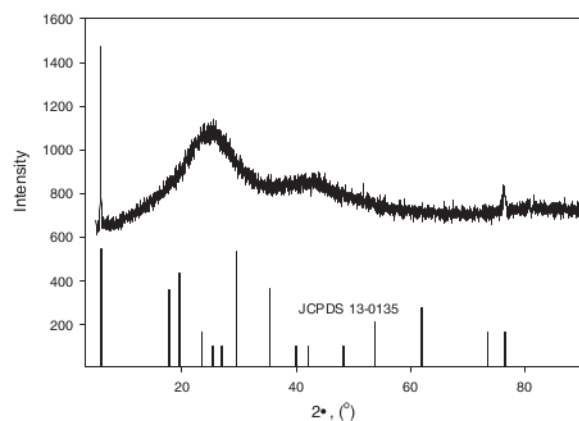


Fig. 2. XRD diffraction pattern of bentonite-hydrochar composite.

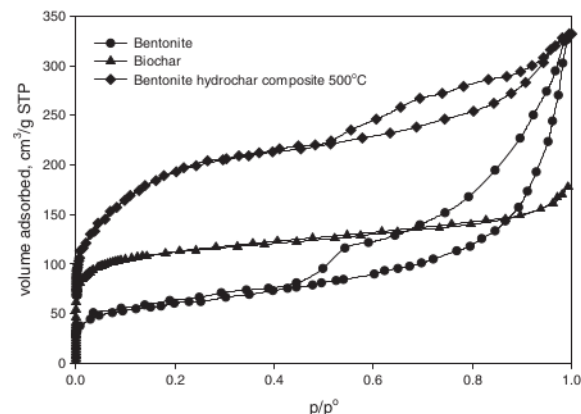


Fig. 3. Argon sorption isotherm of raw materials and composite.

(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 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 is the most widely used technique for characterization of clay minerals since it provides informative information on the mineralogy and crystal-chemistry of a clay mineral sample. The infrared 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 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 (Prahast et al., 2008). A relatively low intensity peak at wavenumber around

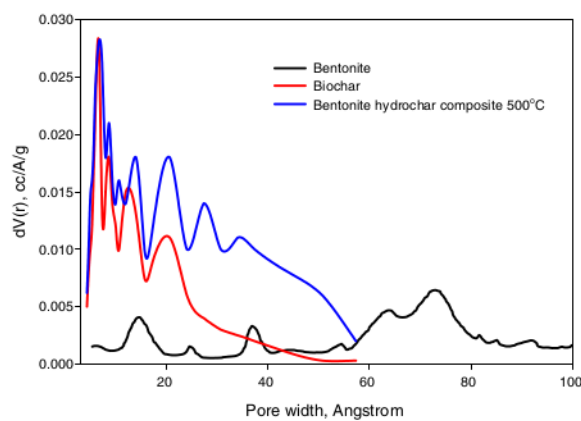


Fig. 4. Density functional theory (DFT) pore size distribution of raw materials and composite.

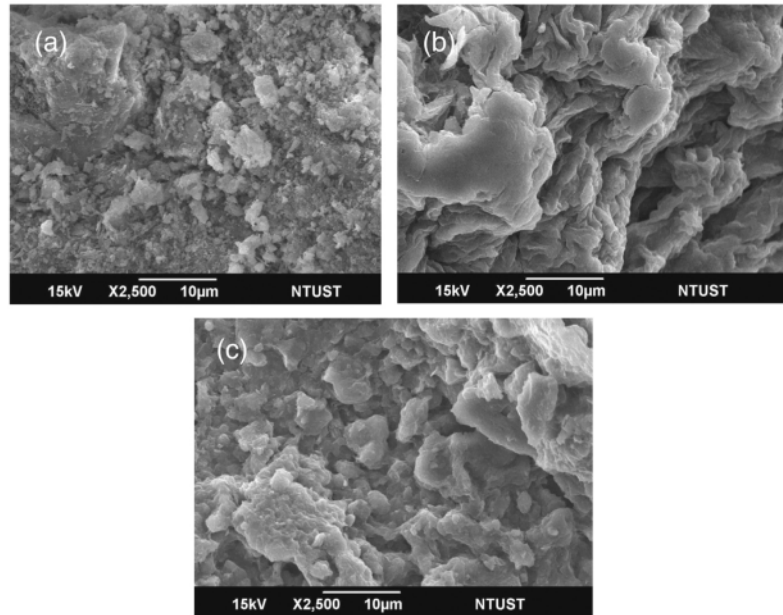


Fig. 5. SEM micrographs of (a) bentonite, (b) biochar, and (c) bentonite-hydrochar composite.

3108 cm^{-1} represents O–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 composite, however, for several absorption bands such as 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 Langmuir and Freundlich adsorption equations. The Langmuir isotherm has the form as follows:

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_{\max} 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 to correlate liquid phase adsorption data.

Freundlich isotherm is an empirical equation which was developed for the adsorption on heterogeneous surface. This model has the form as follows:

$$q_e = K_F C_e^{1/n} \quad (3)$$

The parameter K_F is Freundlich constant, usually associated with 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 heterogeneous 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 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 used 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

Table 6
FTIR spectra data of bentonite, biochar, and bentonite-hydrochar composite.

Assignment	Wavenumber, cm^{-1}		
	Bentonite	Biochar	Composite
Al(Mg)–O–H stretching	3620	–	3598
H–O–H stretching	3347	–	–
O–H stretching vibration	–	3108	3101
C–H stretching	–	2906	2925
C=O stretching vibration	–	1705	1714
H–O–H bending (H_2O)	1634	–	–
aromatic ring stretching	–	1588	1591
Si–O–Si stretching	1060	–	1065
Al–OH	904 and 621	–	907 and 619
(Al, Mg)–O	841 and 790	–	829 and 784
Si–O bending vibration	520 and 471	–	521 and 475

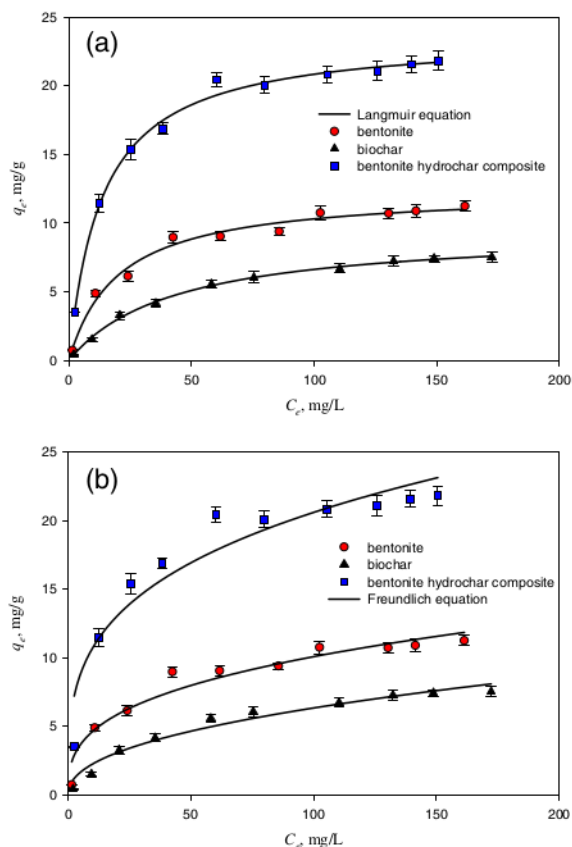


Fig. 6. Adsorption isotherms of ammonium ion on different adsorbents and plots of (a) Langmuir equation, and (b) Freundlich equation.

composite structure, leading to the opening of the existing pore and creating new pores 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 in the interlayer of bentonite in composite structure also enhanced the adsorption process through the cation exchange mechanism.

The adsorption affinity (K_L) measures the type of interaction between adsorbate and adsorbent. The higher the value of K_L , the interaction between adsorbate and adsorbent also becomes stronger and more adsorbates attach to the surface of adsorbent. The fitted value of parameter K_L is in the order of bentonite-hydrochar composite > bentonite > biochar (Table 7). For bentonite-hydrochar composite, the adsorption of ammonium ions occurred in two different adsorption

Table 7
Langmuir and Freundlich parameters on the adsorption of ammonium on bentonite, biochar, and bentonite-hydrochar composite.

Parameter	Bentonite	Biochar	Bentonite-hydrochar composite
<i>Langmuir equation</i>			
q_{max} , mg/g	12.37	9.49	23.67
K_L , L/mg	0.0501	0.0232	0.0738
R^2	0.9834	0.9976	0.9941
<i>Freundlich model</i>			
K_F , (mg/g) (L/mg) ^{1/n}	2.13	0.80	5.58
n	2.96	2.23	3.53
R^2	0.9406	0.9674	0.9095

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 K_L for this system is higher than other adsorbents. For biochar, the interaction between ammonium ions and the surface of the adsorbent is mainly 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 (<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

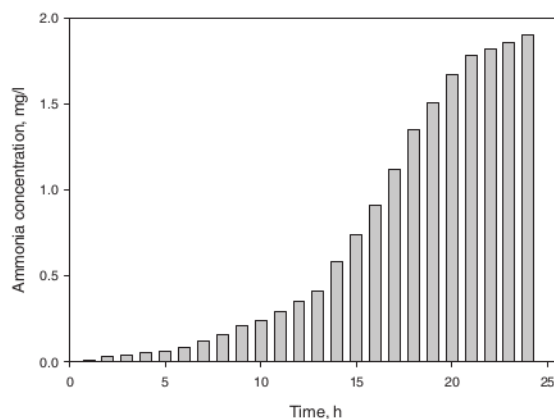
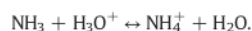
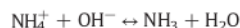


Fig. 7. Ammonia concentration in fish water as function of time.

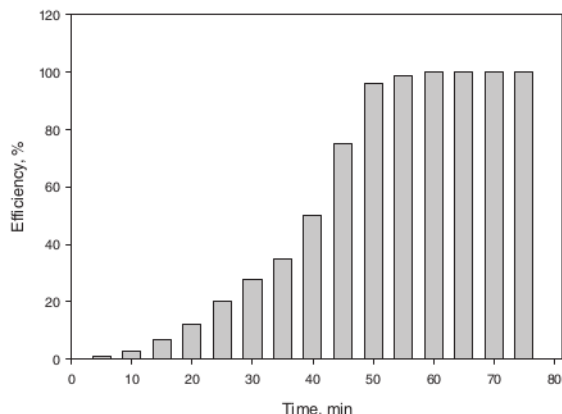
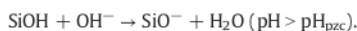


Fig. 8. The removal efficiency of ammonia from the fish water using bentonite-hydrochar composite.

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 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



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 (d_{001}) 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 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.

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