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15**Removal of** Cu **(II) and Pb(II) from** wastewater **using** biochar **-clay**

nanocomposite Felycia Edi Soetaredjoa,*, Yi-Hsu Jub, Suryadi Ismadjia, Aning Ayucitraa aDepartment

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31of Chemical Engineering, National Taiwan University of Science and Technology, 43, Sec. 4 Keelung Rd., Taipei 10607, Taiwan Received 2

February 2017; Accepted 24 May 2017 abstract The new nanocomposite material has been synthesized from inexpensive and abundantly available materials. Bentonite and water hyacinth were used as the precursors for the preparation of bentonite – biochar nanocomposite. The nanocomposite was produced at 400°C under a combination of nitro- gen and carbon dioxide environment. The adsorption capability of the nanocomposite

4was tested for the removal of Cu (II) and Pb (II) from aqueous solution.

1Temperature dependent forms of Langmuir and Freundlich equations were employed to correlate the experimental data. Based on the physical meaning assessment of

the parameters, the Langmuir equation with its temperature dependent form can correlate the

39experimental data better than Freundlich. The maximum adsorption capacity for

nanocomposite toward

18Cu(II) and Pb(II) are

78.1 mg/g and 44.7 mg/g, respectively. The adsorption kinetic data of

20Cu(II) and Pb(II) onto bentonite and nanocomposite follow pseudo-first-order

equa- tion, with k1 strongly dependent on temperature. The thermodynamic study reveals that the adsorp- tion

20Cu(II) and Pb(II) was controlled by

physical adsorption and spontaneous. Keywords: Nanocomposite; Biochar; Bentonite; Adsorption isotherm; Adsorption kinetic 1. Introduction Heavy metals are one of the most hazardous contam- inants found in the polluted waterways. The primary sources of these pollutants are from electroplating indus- tries, mining, metal industries, leather tanning, textile and dyeing, fertilizers, etc. The

35contamination of water by heavy metals is a severe problem and need urgent attention because heavy metals are considered as highly life-threat- ening substances toward living organisms. Heavy metals enter the human body via several routes such as inges- tion, skin absorption, and inhalation. Several severe effects caused by heavy metals are reduced mental and central nervous function, damage to vital organs, change in human metabolisms, damage to blood composition, and other seri- ous diseases. Currently, several separation methods are available for the treatment of industrial effluents containing heavy *Corresponding author. metals. Several examples of these conventional methods are chemical precipitation, coagulation, electrodialysis, ion exchange, ultrafiltration, etc. These technologies have their advantages and disadvantages, and industrial applications of these techniques in under developing or developing countries often create other problems such as unsustainable, high operational cost, generation of toxic waste sludge, etc. For removal of heavy metals in low concentration or trace amount from water or wastewater, the adsorption process still the best option due to its simplicity in design and operation, cost-effective, and high removal efficiency [1]. The traditional operation of the adsorption process uses activated carbons or synthetic ion exchange resins as the adsorbents. The use of these kinds of adsorbent will increase the operational cost of the treatments; therefore, special attentions have been focused on the seeking of low- cost adsorbents with high uptake capacity, fast kinetics, abundant availability, renewable, and economically viable [2–4]. As the best candidates for alternative adsorbents are clays and clays minerals. 1944-3994 /

19**1944-3986 © 2017 Desalination Publications. All rights reserved.** F.E. Soetaredjo **et al. / Desalination and Water Treatment** 82 **(2017)**

188–200 189 The utilization of bentonites

1**and its modified forms** Table 1 **for the removal of**

various hazardous pollutants has been Proximate and ultimate analysis of water hyacinth explored by our research group [5–11] and the results indi- cate that these material have very potential application Analysis Water hyacinth for industrial wastewater treatment application. The main problems of using natural bentonites and its chemically Proximate (dry basis) modified forms are low adsorption capacity and create Volatile matter, wt. % 64.14 another problem to the environment due to the excess of Fixed carbon, wt. % 25.01 the chemical as modifying agents. Moisture content, wt. % 6.57 Recent studies indicate that combination of bentonite Ash content, wt. % 4.28 with other natural materials produced composites, which Ultimate (dry basis) have high adsorption capacity [12–14]. A combination between bentonite and biochar from water hyacinth to new Carbon 60.47 nanocomposite is presented in this paper. The composite Hydrogen 9.87 materials called as nanocomposites if the fillers have one Nitrogen 0.74 dimension in nanoscale (clay minerals), two-dimension in Sulphur 0.14 nanoscale (carbon nanotubes, nanofibers, nanowires, etc.), Oxygen (by difference) 28.78 or three dimension in nanoscale (silica nanoparticles, etc.) [15]. This new nanocomposite over several advantages for hazardous substances removal since this material is low- cost and possesses excellent adsorption capability. This new char composite activation, was purchased from Aneka Gas nanocomposite material can be used as the low-cost alter- and obtained as an industrial grade. Nitrogen gas that was native adsorbent for the treatment of water or wastewater used to maintain the system at the inert condition was also containing heavy metals. obtained as an industrial grade from Aneka Gas. 2. Materials and methods 2.2. Cation exchange capacity measurement and surface charge 2.1. Materials The cation exchange capacity (CEC) of the bentonite was measured using methylene blue index. In general, two Bentonite used in this study was obtained from benton- different mechanisms occur during the dye adsorption on ite mining in Pacitan, East Java province, Indonesia. The the bentonite. The first mechanism is the cation exchange initial moisture content of the bentonite was around 52%. between methylene blue cations and exchangeable cations Before using the bentonite was purified using hydrogen from isomorphous substitution in the aluminosilicate lat- peroxide solution to remove the organic impurities. After tice. The second mechanism is the adsorption mechanism, the purification process had completed, the bentonite was which might be either chemisorption (hydrogen bonding)

11**repeatedly washed with** reverse osmosis **water to remove** with the **surface** SiOH **and**

AlOH of the aluminosilicate lat- excess hydrogen peroxide solution, and subsequently dried tice or physical (Van der Waals) adsorption. The exchange in a forced circulation oven at 110°C until its moisture con- reaction between methylene blue cations and metal cations tent around 10%. The bentonite was pulverized in a Janke & from the aluminosilicate lattice is an irreversible reaction. Kunkel hammer mill until its particle sizes around 180/200 When methylene blue solution is added in a small mesh. The powder bentonite was stored in adesiccat or for amount at a time to the bentonite sample until the cation further use. exchange capacity of the bentonite is reached, the amount Water hyacinth utilized in this study was obtained from of methylene blue adsorbed is equal to the amount of swamp area around Surabaya. Prior to use, the water hya- methylene blue added, and the cation exchange capacity cinth was repeatedly washed using tap water to remove the of the bentonite sample can be calculated by the following impurities such as sands, dirt, etc. Clean water hyacinth equation: was dried in a forced circulation oven at 110°C until its moisture content was around 10%. Dry water hyacinth was 100 pulverized in Janke & Kunkel hammer mill until its particle CEC = Vmb .Nmb (1) mb sizes around 180/200 mesh. Subsequently, the water hya- cinth powder

11**was stored in sealed plastic bags for further**

where CEC is cation exchange capacity (meq/100 g benton- used. The proximate analysis of water hyacinth powder ite), mb is the weight of bentonite (g), Vmb is the volume of was carried out according to the method of ASTM E870-82. methylene blue added (ml), and Nmb is normality of meth- Perkin-Elmer 2400 CHNS/O Elemental Analyzer was used ylene blue solution (meq/ml). The surface charge of ben- for the determination of elemental carbon, hydrogen, nitro- tonite and nanocomposite were determined using a zeta gen, oxygen, and sulfur in water hyacinth. Proximate and potential analyzer (Brookhaven 90Plus). ultimate analyses of water hyacinth are given

27**in Table 1. All** the **chemicals used in this study**

such as hydrogen peroxide, CuSO4, PbCl2, etc. were purchased as an analytical 2.3. Nanocomposite preparation grade

1**from Sigma-Aldrich Singapore and used without any**

The following procedure was used to prepare bentonite further treatment or purification processes. Carbon dioxide, – biochar nanocomposite. Fifty gram of bentonite powder which was used as the activating agent for bentonite – bio- was added into 1 L of reverse osmosis water. The bentonite 190 F.E. Soetaredjo et al. / Desalination and Water Treatment 82 (2017) 188–200 and water mixture was then sonicated until stable benton- ating voltage of 15 kV. Before the analysis, the solid samples ite suspension was obtained. Subsequently, 25 g of water

1**were coated with** a **ultra-thin layer of conductive platinum.**

hyacinth powder was added into the suspension, and the mixture was further sonicated for 120 min. The solid was then separated from the liquid by centrifugation and dried 2.5. Adsorption equilibrium study

11**at 110°C for** 24 **h. The** solid mixture of **bentonite and**

water hyacinth was The

18**adsorption of Cu(II) and Pb(II) from aqueous** solu- thermally treated **at**

400°C under a combination of nitro- tion onto bentonite and nanocomposite were conducted gen and carbon dioxide flow. The thermal treatment was in a static mode at several temperatures (30°C, 40°C and conducted in a tubular furnace (Thermolyne F21130-26). 50°C). A brief description of the adsorption experiments The heat treatment of the solid mixture was performed at are as follow: a known amount of adsorbents (0.1–1.0 g) a heating rate of 10°C. During the heating process of the were introduced to a series of 250 mL Erlenmeyer flask solid mixture to 400°C, the system was under nitrogen envi-

29**containing 100 mL of** heavy metal **solution with an initial**

ronment by flowing nitrogen gas

6**at a flow rate of 3** L **/min.** concentration **of**

200 mg/L. Erlenmeyer flasks were placed After the temperature had reached 400°C, the temperature in thermo-controller shaking water bath (Memmert type of the furnace was maintained at constant temperature for WB-14). During the adsorption process, the system was 60 min. During the thermal treatment at 400°C, in the first shaken at 200 RPM and the temperature was controlled at 45 min, the system still under a nitrogen environment, and the desired temperature. for the rest 15 min, the system was under carbon dioxide After the equilibrium condition was reached, the solid environment by switching the nitrogen flow to the carbon was separated from the aqueous solution by centrifugation, dioxide flow. The flow rate of carbon dioxide was 3 L/min. and the remaining heavy metal in the solution was ana- After the thermal process had completed, the resulting lyzed by atomic absorption spectrophotometer (AAS SHI- solid composite was cooled to room temperature under MADZU AA6200). The amount of heavy metal adsorbed by nitrogen flow condition. The bentonite – biochar nano- solid adsorbent was calculated by the following equation: composite was subsequently ground until its particle size 100/120 mesh. The composite was stored in the drying chamber for the subsequent experiment. qe = (Co − Ce) m V (2) where qe is the amount of heavy metal adsorbed by the 2.4. Characterization of bentonite and composite adsorbent at equilibrium condition (mg/g), Co and Ce repre- sent the initial and equilibrium concentration respectively. The bentonite and nanocomposite were characterized by nitrogen sorption analysis, X-ray diffraction (XRD), Fourier The unit of Co and Ce is mg/L. The symbols

27**m and V** repre- sent **the** mass **of adsorbent (g) and the volume of solution**

transform infrared (FTIR), and scanning electron micros- (L), respectively. copy (SEM). The nitrogen sorption analysis was conducted on an automated Micromeritics ASAP 2010. The

11**adsorption and desorption** data **were** collected **at the boiling** point **of**

2.6. Adsorption kinetic study nitrogen gas (–196°C). Before the sorption measurement, the samples were degassed at 200°C for 48 h at a high vacuum The procedure of adsorption kinetic study is similar condition to remove water molecules from the structure of to the equilibrium study. In the adsorption kinetic exper- the samples. The relative pressures used for sorption mea- iment, fixed amount of adsorbent was added to a series surements were 0.0001 to 0.995. The standard BET equation of Erlenmeyer

2**containing 100 mL of** heavy **metal solution**

2**was used to calculate the BET surface area of the**

samples. with initial concentration 200 mg/L. The Erlenmeyer were The BET surface area calculation was conducted at a relative shaken in a temperature controlled water bath at a precise pressure between 0.05–0.25. The total pore volume of the temperature. At certain interval of time, the concentration samples was measured at a relative pressure of 0.995. At this of heavy metal in solution was determined by AAS and the highest relative pressure, all of the pores in the samples were amount of metal adsorbed onto the adsorbent at interval filled with nitrogen gas. The pore size distributions of the time t, called as qt (mg/g), was calculated by the equation samples were determined by the DFT (density functional theory) method using medium regularization. (3)

37**Philips X'pert X-ray diffractometer was used**

to obtain qt = (Co − Ct) V m the XRD patterns of bentonite and composite. The X-ray diffraction measurements were conducted at 40 kV and where Ct (mg/L) is the concentration of metal in solution at 30 mA, and Ni-filtered Cu Kα1 was used as the radiation interval time t. source. The scanning rate of the diffraction was 1°/min. The qualitative analysis of surface functional groups of the solid samples was conducted in FTIR SHIMADZU 8400S. The 3. Results and discussion potassium bromide (KBr) procedure was used to prepare the solid samples. The FTIR spectra were collected at wave 3.1. Characterization of bentonite and nanocomposite number range of 400–4000 cm–1. Surface morphology

6**of the** The **cation exchange capacity** of **the bentonite and**

solids was examined using scanning electron microscopy nanocomposite used in this study was determined using technique. SEM images of the samples were obtained by methylene blue titration. The CEC of the bentonite was 65.2 JEOL JSM-6500F. SEM analysis was operated at an acceler- meq/100 g. After thermal treatment, the CEC of bentonite – F.E. Soetaredjo et al. / Desalination and Water Treatment 82 (2017) 188–200 191 biochar nanocomposite was 43.8 meq/100 g. The decrease 350 of CEC after thermal treatment possibly due to the defor- mation of some 2:1 layers of the bentonite structure. With 300 the deformation of 2:1 layers, some of the exchangeable 250 [16] or attach to some surface functional groups of biochar. 200 Therefore, these exchangeable cations did not have the exchange capability anymore with methylene blue cation in Amount adsorbed, cm3/g, STP Bentonite Bentonite - biochar composite cations become associated with anouter tetrahedral sheet 150 the solution. The purpose of zeta potential measurement is to obtain 100 the isoelectric point of bentonite and bentonite biochar nanocomposite. From the measurement of zeta potential, 50 the results indicate

4**that the surface charge of** both adsor- bents **is pH dependent. The isoelectric**

points for benton- ite and nanocomposite are 3.4 and 3.9, respectively. Below 0 0.0 0.2 0.4 0.6 0.8 1.0 these isoelectric points, both of the adsorbents are positively p/po charged while above these points both of the adsorbents are 0.020 negatively charged. Since

42**the adsorption experiments were** (b) **conducted at pH** 5, **the** surface **of**

both bentonite and com- Bentonite Bentonite - biochar composite posite were negatively charged. 0.015 The porosity and surface chemistry of the solid adsor- bents

35**play a significant role** during **the adsorption process.** Therefore, the characterization **of** these properties **in**

solid adsorbents is essential. In this study, the characterization of bentonite and bentonite – biochar nanocomposite was dV(r), cm3/A/g 0.010 conducted using nitrogen sorption analysis, X-ray diffrac- tion (XRD), Fourier transform infrared (FTIR), and scanning 0.005 electron microscopy (SEM). Nitrogen adsorption – desorption measurement is widely used for the characterization of the solid adsorbents. 0.000 The nitrogen sorption isotherms and pore size distribution 20 40 60 80 100 of bentonite and bentonite – biochar nanocomposite is given Pore width, Angstrom in Fig. 1. The BET-nitrogen surface area and cumulative pore volume for bentonite are 147.4 m2/g and 0.23 cm3/g, Fig. 1. (a) Nitrogen adsorption–desorption isotherms of ben- while for bentonite – biochar nanocomposite are 381.9 m2/g tonite and bentonite – biochar nanocomposite, and (b) Density and 0.36 cm3/g. From Fig. 1a it can be seen that both of functional theory pore size distribution of bentonite and ben- these adsorbents possess some amount of micropore struc- tonite – biochar nanocomposite. ture. The addition of biochar to bentonite structure to form composite increased the number of micropores as indicated in Fig. 1a. The microporous structure in the adsorbents port of adsorbates from the bulk liquid into the internal structure is shown by rapid intake of nitrogen gas at a very structure of the adsorbent, while the micropores and small low relative pressure. During the heat treatment, the break- mesopores determine the sorption capability and proper- down of the lignocellulosic structure created some pores in ties of the adsorbent. the structure of the nanocomposite. The addition of carbon X-ray diffraction patterns of bentonite and bentonite – dioxide gas during the heat treatment oxidized some of the biochar composite is given in Fig. 2. The diffractogram of carbon atoms in the biochar structure in composite and gen- bentonite – biochar nanocomposite reveals that the amor- erated new pores and large amounts of reactive sites on the phous structure of the biochar more dominant than ben- biochar basal planes. The combination between type I and tonite structure as indicated in Fig. 2. The heat treatment H3 hysteresis of the nitrogen sorption isotherm is observed at 400°C gave significant effect on the layered structure of for the composite (Fig. 1). H3 hysteresis indicates that com- bentonite, the intensity of several reflection peaks decreased posite has slit-shaped pore characteristic. This evidence due to the release of some structural water molecules from shows that the nanocomposite possesses a combination the bentonite interlayer. The evaporation of this structural between mesoporous and microporous structure. water leaves space in the bentonite interlayer spacing. As The statistical representation of the size of the individ- mentioned before, during the heat treatment at 400°C, lig- ual pore in the bentonite and bentonite – biochar composite nin, hemicellulose, and cellulose molecules decomposed is given as DFT (density functional theory) pore size distri- into smaller molecular weight, and there was a possibility bution (Fig. 1b). This figure clearly shows that the micro- that these low molecular weight organic substances pene- porous structure is more dominant in the nanocomposite, trated and condensed into the space of the bentonite inter- while the bentonite has mesoporous structure. The presence layer spacing leading to a decrease of the reflection peaks of micropores and mesopores in bentonite – biochar nano- of bentonite. composite strongly influences its adsorption capability. Fourier transform infrared spectroscopy (FTIR) was used Large mesopores play a major role in the molecular trans- for the characterization of surface functional groups of ben- 192 F.E. Soetaredjo et al. / Desalination and Water Treatment 82 (2017) 188–200 Bentonite Bentonite - biochar composite Intensity Bentonite Intensity Bentonite - biochar composite 0 10 20 30 40 50 60 70 4000 3000 2000 1000 2θ, o wavenumber, cm-1 Fig. 2. XRD diffraction patterns of bentonite and bentonite – bio- char nanocomposite. Fig. 3.

42**FTIR spectra of bentonite and bentonite**

– biochar nano- composite. tonite and bentonite – biochar nanocomposite. The main clay mineral in the bentonite is montmorillonite, and the charac- teristic absorption bands of this clay mineral are indicated at wave numbers

9**3620 cm–1 (Al(Mg)–O–H stretching),** 3347 **cm–1**

26**(intermolecular hydrogen-bonded** H **–O–H stretching),** 1634 **cm–1 (H–O–H** deformation vibration **due to adsorbed water),** 1060 **cm–1 (Si–O–** Si **stretching** vibration), 904 **cm–1**

and 621 cm–1 (Al–OH), 841 cm–1 and 790 cm–1 ((Al, Mg)–O), 520 cm–1 and 471 cm–1 (Si–O bending vibration) [5,17]. The FTIR spectra of bentonite – biochar composite (Fig. 3) indicates that several of the characteristic absorption bands of mont- morillonite disappear after heat treatment process, and sev- eral functional groups belong to biochar are present in the nanocomposite such as stretching vibration of C=O (1711

9**cm–1), The** C **–H stretching vibration of** methyl group(2910 **cm–1), C=** C aromatic ring **stretching**

(1580 cm–1), etc. The direct observation of the solid adsorbents morphol- ogy and surface topography was conducted by scanning electron microscopy. Structural information and phase of the solid can be obtained directly through the assessment of the SEM image. The SEM images of bentonite and bentonite – biochar nanocomposite are given in Fig. 4.Totally different surface morphology between bentonite and nanocomposite is observed from this figure. Both of these adsorbents have complex structures. 3.2. Adsorption studies Adsorption process probably is one of the most prac- tical methods for separation and purification of industrial products or by-products. This process is also one of the most widely used methods in the field of environment protection, especially in water and wastewater treatment system. The adsorption capability of bentonite – biochar nanocomposite prepared in this study

21**was tested for the** removal **of** Cu **(II) and Pb(II) from** aqueous solution. **The adsorption** equilibria **of** Cu **(II) and Pb(II)**

onto bentonite and bentonite – biochar nanocomposite were correlated through adsorption isotherm equations. Several adsorption

21**isotherms are** available **to** correlate **the adsorption** experi- mental **data**

[18,19]. Since the adsorption equilibria of these heavy metals were obtained at three different temperatures, therefore, the Langmuir and Freundlich with their tempera- ture

1**dependent forms were used to** correlating **the** adsorp- tion **equilibria data. Langmuir** model originally was developed for the adsorption of gas on a flat surface. Kinetic theory princi- ple was employed to develop this model. The mathematical expression of Langmuir model is as follows qe = qmax KLCe

44**(4) 1** + KLCe **where qe** (mg/g) **is the amount of** solute **adsorbed at equilibrium** condition. Parameter qmax **(mg/g)** represents **adsorption capacity**

of the adsorbent. Parameter KL (L/mg) accounts for the adsorption affinity. Both of parameters qmax and KL are temperature dependent and have the mathe- matic forms as follows q max = qo exp (β (To − T)) (5) KL = KLo exp⎛⎜⎝ ΔRHTL ⎞⎟⎠ (6) In Eq. (5), qo (mg/g) is the adsorption capacity of the adsorbent at reference temperature To (K). The expansion coefficient of the adsorbate is represented by parameter β (1/K). Parameters KLo and ΔHL represent

3**adsorption affinity at** a **reference temperature and** isosteric **heat of adsorption,** respectively. **The**

Freundlich equation is the earliest empirical model to describe the gas phase adsorption data. Since the mathe- matical form of this model is simple, the Freundlich model can also be

1**used for the liquid phase adsorption** by only change **the** term **of**

pressure with equilibrium concentra- tion. Freundlich equation has the form qe = KFCe1/n (7) F.E. Soetaredjo et al. / Desalination and Water Treatment 82 (2017) 188–200 193 (a) (b) Fig. 4. SEM images of (a) bentonite and (b) bentonite – biochar nanocomposite. where KF ((mg/g) (L/mg)–n) and n are Freundlich adsorp- tion capacity and heterogeneity constant for the adsorp- tion system, respectively. Both of these parameters can be extended to temperature dependent forms: KF = KFo exp⎜ − Fo ⎛ αRT ⎞⎟⎠ ⎟ 1 RT n = Fo (8) (9) Here the parameter KFo

1**is the** Freundlich **adsorption capacity at reference temperature** To, and **α/** Fo **is**

the charac- teristic of the adsorption potential. The temperature dependent parameters of the Lang- muir and Freundlich

1**were obtained by non-linear least** square methods. **The fitting** process **was conducted for all the data at various temperatures simultaneously**

by mini- mizing Sum Square of Error (SSE) as the objective function SSE = ⎡⎢⎢(∑( )2)⎤⎥⎥ 1/2 qe(exp) − qe(cal) ⎢ N ⎥ (10) ⎣ ⎦ ⎥ Here the experimental amount of heavy metal adsorbed indicated by symbol qe(exp), while the calculated amount of heavy metal adsorbed by the adsorbent is qe(cal). The temperature dependent parameters of the Lang- muir and Freundlich obtained from the fitting process are summarized in Table 2.

14**The adsorption** isotherms **of Cu(II) and Pb(II) onto**

bentonite and bentonite – biochar nano- composite are depicted in Figs. 5 and 6.

43**In these figures, the** adsorption **experimental data are indicated** as **symbols, while the solid lines represent the**

theoretical data from the models. Visually, both of Langmuir and Freundlich equations can represent the adsorption experimental data pretty well as seen in Figs. 5 and 6. However, the correct procedure to determine the applicability of adsorption model to repre- sent the experimental data is not just only depend on the visual representation of the model and the values of R2, but we must examine the values of fitted parameters. The fitted value of each parameter should be reasonable and consis- tent with its physical meaning. The parameter qo (Langmuir) and KFo (Freundlich) rep- resent the adsorption capacity of the adsorbent. Based on the adsorption experimental data depicted in Figs. 5, 6, at high equilibrium concentration, the adsorption isotherm of Cu(II) onto bentonite become flat at adsorption capac- ity around 31 mg/g (30°C) and for the composite around 75 mg/g (30°C). For adsorption of Pb(II), the experimen- tal adsorption capacities are around 24

36**mg/g for bentonite and** 42 **mg/g for** composite. By comparing **the**

experimental adsorption capacity with the parameter qo and KFo, it is clear that the values of parameter qo for all systems are similar to experimental results. The failure of Freundlich model and

1**its temperature dependent forms** to **represent the** adsorp- tion experimental **data** due to **the**

absence of saturation capacity in the equation. Every adsorbent has a certain limit to accommodate adsorbate molecules, and the Freundlich equation does not capture this phenomenon. Since the parameter KFo in Freundlich equation cannot describe the experimental data correctly, therefore we will not discuss another parameter further. Parameter βin Eq. (5) is a parameter relates to expan- sion coefficient of adsorbate.

1**This parameter is specific for** each adsorbate **and independent** of the **type of adsorbent**

[20]. The values of parameter β

1**obtained from the fitting of experimental data** listed **in Table**

2 are substantially independent of the adsorbent, reasonable, and consistent. Parameter KLo measures how strong the attraction and attachment of

3**adsorbate molecules** onto **the surface of the adsorbent. The** high value **of**

this parameter indicates that the attraction force is strong and the surface of the adsor- bate is covered with more adsorbate molecules. The value of this parameter for composite is greater than natural bentonite. The surface of nanocomposite contains various functional groups from either bentonite or biochar, and the presence of these functional groups gives a positive con- 194 F.E. Soetaredjo et al. / Desalination and Water Treatment 82 (2017) 188–200

2**Table 2 The fitted temperature** dependent **parameters of isotherm models for**

14**Cu(II)and Pb (II) adsorption onto**

bentonite and bentonite – biochar nanocomposite Isotherm model Bentonite Bentonite – biochar nanocomposite Parameter Value R2 Parameter Value R2 Cu(II) adsorption Langmuir Freundlich Pb(II) adsorption Langmuir Freundlich qo (mg/g) β (1/K) KLo (L/mg) ∆HL (kJ/mol) KFo (mg/g)(mg/L)1/n α/Fo(mol/J) 32.5 0.0042 1.88 × 10–6 30.7 39.31 7.584 0.998 0.993 qo (mg/g) β (1/K) KLo (L/mg) ∆HL (kJ/mol) KFo (mg/g)(mg/L)1/n α/Fo (mol/J) 78.1 0.0043 2.14 × 10–6 33.2 1107.62 217.7 qo (mg/g) β (1/K) KLo (L/mg) ∆HL (kJ/mol) KFo (mg/g)(mg/L)1/n α/Fo (mol/J) 27.2 0.0053 1.29 × 10–6 27.8 5.49 2.52 0.998 0.923 qo (mg/g) β (1/K) KLo (L/mg) ∆HL (kJ/mol) KFo

34**(mg/g)(mg/L)1/n**

α/Fo (mol/J) 44.7 0.0051 1.76 × 10–6 30.9 32.88 30.18 35

34**(a) 35 30 (b) 30** Amount adsorbed **(qe), mg/g 25 20 15 10 5**

0 0 T = 30oC T = 40oC T = 50oC Langmuir 20 40 60 80 100 120 140 160 Equilibrium concentration (Ce), mg/L Amount adsorbed (qe), mg/g 180 25 20 15 10 5 0 0 T = 30oC T = 40oC T = 50oC Freundlich 20 40 60 80 100 120 140 160 Equilibrium concentration (Ce), mg/L 180 80 (c) 80 (d) Amount adsorbed (qe), mg/g 60 40 20

12**T = 30oC T = 40oC T = 50oC**

Langmuir Amount adsorbed (qe), mg/g 60 40 20

12**T = 30oC T = 40oC T = 50oC** Freundlich **0** 0 **0**

20 40 60 80 100 120 140 160 180 0 20 40 60 80 100 120 140 160 180 Equilibrium concentration (Ce), mg/L Equilibrium concentration (Ce), mg/L 0.998 0.989 0.997 0.988 Fig. 5. Equilibrium data of Cu(II) adsorption onto bentonite and fitting of (a) Langmuir, (b) Freundlich, and equilibrium data of Cu(II) adsorption onto bentonite – biochar nanocomposite and fitting of (c) Langmuir, and (d) Freundlich. F.E. Soetaredjo et al. / Desalination and Water Treatment 82 (2017) 188–200 195 30 30 (a) (b) 25

22**25 Amount adsorbed (qe), mg/g 20 15 10 5 0 0**

50 (c) T = 30oC T = 40oC T = 50oC Langmuir 20 40 60 80 100 120 140 Equilibrium concentration (Ce), mg/L 160

22**Amount adsorbed (qe), mg/g 20 15 10 5 0 0**

50 (d) T = 30oC T = 40oC T = 50oC Freundlich 20 40 60 80 100 120 140 160 Equilibrium concentration (Ce), mg/L Amount adsorbed (qe), mg/g 40 30 20 10

12**T = 30oC T = 40oC T = 50oC**

Langmuir Amount adsorbed (qe), mg/g 40 30 20 10

12**T = 30oC T = 40oC T = 50oC** Freundlich **0** 0 **0**

20 40 60 80 100 120 140 160 0 20 40 60 80 100 120 140 160 Equilibrium concentration (Ce), mg/L Equilibrium concentration (Ce), mg/L Fig. 6. Equilibrium data of Pb(II) adsorption onto bentonite and fitting of (a) Langmuir, (b) Freundlich, and

28**equilibrium data of Pb(II)** adsorption **onto** bentonite – biochar nanocomposite **and**

fitting of (c) Langmuir, and (d) Freundlich. tribution to the attraction force of the adsorbent. Since the bentonite – biochar composite has higher attraction force so that it can adsorb more adsorbate molecules than ben- tonite. The values of parameter KLo are reasonable and con- sistent with all systems. Figs. 5, 6 show that temperature gives

3**an adverse effect on the amount** of heavy metal **adsorbed** by **the** adsorbent. The uptake **of**

heavy metal decrease with the increase of tem- perature as seen in Figs. 5–6. This phenomenon is belonging to physical adsorption. The isosteric heat of adsorption of physical adsorption is less than 40 kJ/mol. The increase of temperature weakens the interaction between heavy metals

18**(Cu(II) and Pb(II)) and the** adsorbents. Therefore **the**

3**uptake of heavy metals by the adsorbents** decreased **with** increas- ing temperature. **The** values **of** isosteric heat **of**

adsorption (ΔHL)

1**obtained from the fitting of the experimental data are**

consistent with the physical meaning for physical adsorp- tion. Isosteric heat of adsorption of both metals on nano- composite is higher than on bentonite. This phenomenon indicates that other bonding mechanisms between surface functional groups in the nanocomposite and heavy metals possibly took place during the adsorption process. Based on the assessment of the physical meaning of the value of fitted parameters of Langmuir and Freundlich, it is evident that Langmuir equation with

1**its temperature dependent forms** can **represent the** adsorption **data better than**

Freundlich equation. 3.3. Kinetic studies

3**In the design of** the **adsorption system,** it **is** necessary **to**

have information about the rate at which the adsorbate removal takes place in a given solid/solution system [21]. There is some adsorption kinetic models are available. Some of the models were developed based on fundamen- tal approach, while others are purely empirical with two or more adjustable parameters.

3**Pseudo-first and pseudo-second order** probably **the most widely used** models **to** correlate **the** adsorption **kinetic data**

due to its simplicity. Both of these models were devel- 196 F.E. Soetaredjo et al. / Desalination and Water Treatment 82 (2017) 188–200 oped based on fundamental of inter facial kinetic approach The boundary conditions used to solve Eq. (13) are: [21]. The pseudo-first order was initially developed in late of the ninetieth century by Lagergren [22]. The differential

16**t = 0 → qt = 0, and t = t → qt = qt,** and give **the** result as follows **form of** the **pseudo-first order**

is: ddqtt = k1 (qe − qt) (11) qt = qe $\left(1 +qeqke2kt2t \right)$ (14) The integration of Eq. (11) with the boundary conditions Here k2 is a time constant of pseudo-second order model.

16**t = 0 → qt = 0, and t = t → qt = qt** give **the**

following result Figs. 7a and 7b depict the adsorption experimental kinetic data (as symbols) of Cu(II) onto bentonite and qt = qe (1 − exp(−k1t)) (12) badensotornpittieon– obfioPcbh(IaIr), nthaneokcionmetpicosdiateta, raersepgecivtievneliyn. FFiogrs.th7ec where qt (mg/g) is the amount of adsorbate adsorbed and 7d. The solid lines are the theoretical values of pseu- at time t, and k1 is a time constant of pseudo-first-order do-first order while the dash lines are theoretical values model. of pseudo-second-order equation. The parameters of the The pseudo-second order kinetic model was first devel-

20**pseudo-first and pseudo-second order** obtained from **the**

oped by Blanchard et al. [23]. Usually, this kinetic model is

1**fitting of the experimental data are summarized in Table 3.** associated with **the**

rate of adsorption/desorption directly Both of these models can represent the adsorption kinetic

3**controls the overall sorption kinetics** [21]. **The** differential data well with the value of R2 > 0.99. However, if we com-

3**form of pseudo-second order is as follows:**

pare the values of qe

1**obtained from the fitting** with the **experimental** results, **the pseudo-first order** gives **smaller**

ddqtt = k2 (qe − qt)2 (13) deviation than pseudo-second order. This evidence indi- cates that physical adsorption is the primary controlling (a) (b) (c) (d) Fig. 7. Adsorption kinetic and plots of pseudo-first and pseudo-second order models(a) Cu(II) onto bentonite, (b) Cu(II) onto benton- ite – biochar composite, (c) Pb(II) onto bentonite, and (d) Pb(II) onto bentonite – biochar nanocomposite. F.E. Soetaredjo

19**et al. / Desalination and Water Treatment** 82 **(2017)** 188–200 197 **Table**

3 kinetic parameters

40**for pseudo-first and pseudo-second order** models Temperature (°C) **Pseudo-first order Pseudo-second order k1 (min–** 1) qe (mg **/g)**

R2 Kinetic adsorption of Cu(II) onto bentonite 30 0.0172 40 0.0121 50 0.0094 30.71 0.998 28.86 0.995 27.25 0.997 Kinetic adsorption of Cu(II) onto bentonite – biochar nanocomposite 30 0.0208 75.18 0.997 40 0.0179 71.65 0.996 50 0.0138 66.62 0.994 Kinetic adsorption of Pb(II) onto bentonite 30 0.0125 22.28 0.994 40 0.0091 18.84 0.993 50 0.0074 16.91 0.995 Kinetic adsorption of Pb(II) onto bentonite – biochar nanocomposite 30 0.0160 41.61 0.999 40 0.0126 38.77 0.998 50 0.0089 35.56 0.995 k2

38**(g/mg·min) 0.** 0005 **0.** 0003 **0.** 0002 **0.** 0002 **0.** 0002 **0.** 0002 **0.** 0004 **0.** 0003 **0.** 0003 **0.** 0003 **0.** 0003 **0.** 0002 qe **(mg/g)**

36.57 36.86 37.32 88.21 85.82 82.78 28.19 25.95 23.31 50.30 48.69 47.57 R2 0.992 0.994 0.993 0.990 0.991 0.991 0.994 0.992 0.994 0.994 0.995 0.994 mechanism for the

29**removal of Cu(II) and Pb(II) from aque- ous solution**

using bentonite and bentonite – biochar com- posite as the adsorbents. Both parameters k1 and k2

1**are time scaling factor for pseudo-first and pseudo second order, respectively**

[21]. These parameters strongly depend on the applied operat- ing conditions

33**such as** temperature, **initial** condition, **pH of the solution, and** agitation rate. The value of parameter k1 strongly dependent on the temperature of adsorption as indicated in Table 3. It decreases with increasing tempera- ture. This evidence indicates that longer time is required to reach an equilibrium condition. While k1 strongly dependent on the temperature, the parameter k2 essentially independent of temperature. Based on the experimental results (for all adsorption systems), at 30°C, the equilibrium condition was achieved after 360 min, and longer time was required

6**when the temperature of the solution was increased from** 30 **°C to** 40 and 50 **°C.** This evidence supports **the** validity of **the**

pseu- do-first order to represent the adsorption kinetic data. 3.4. Thermodynamic study To obtain a complete description on the phenomena of

4**adsorption of** Cu **(II) and** Pb **(II) onto bentonite and** benton- ite – biochar **nanocomposite, the**

assessment of several ther- modynamic properties of the adsorption system has also been conducted in this study. The thermodynamic feasibil- ity of the adsorption of Cu(II) and Pb(II) onto bentonite and nanocomposite was accessed through standard Gibb’s

24**free energy change (∆G°), standard** of **enthalpy change (∆H°), and standard** of **entropy change (∆S°).** Standard Gibb’s **free energy** change **was** determined by **the following equation** ∆Go = **−RT ln** KD **(15)**

where KD is thermodynamic distribution coefficient. The value of KD was obtained from the plots of ln(qe/Ce) vs Ce [24] as seen in Fig. 8. The correlation between thermody- namic distribution coefficients with ∆H° and ∆S° is given by the following equation: ∆So ∆H o ln KD = R − RT (16) The values of KD, ∆G°, ∆H° and ∆S° are summarized in Table 4. The spontaneity of the adsorption process is measured by standard Gibb’s free energy. The negative ∆G° indicates that the adsorption process is spontaneous; the large neg- ative value of ∆G° also indicates that the system has high adsorption affinity. The higher adsorption affinity, more heavy metal molecules will attach to the surface active sites of the adsorbent. The values of ∆G° are consistent with adsorption experimental data depicted in Figs. 5 and 6.

4**For adsorption of Pb(II) onto bentonite, the**

increase of tempera- ture also increase the value of ∆G° as indicated

28**in Table 4. The** positive **value of** ∆G° indicates **that the adsorption of Pb(II) onto**

bentonite at high temperature (40 and 50°C) is not spontaneous. With this condition, the adsorption and desorption of Pb(II) onto bentonite is not in a thermody- namic equilibrium condition [25]. Standard entropy change (∆S°) measures the random- ness of the adsorption system. The positive value of ∆S° shows the randomness of the interface between the bentonite or nanocomposite and the adsorption medium [26,27], while the

36**negative value of** ∆S° **indicates** an increase **of** orderliness **of the adsorption** systems. **The**

more order of the system, less

33**amount of adsorbate** molecules are **adsorbed on the surface of** the **adsorbent. The** values **of**

∆S° of all systems (Table 4) are negative, and the lowest one is Pb(II) – bentonite system. Ben- tonite is a clay mineral, which has ordered crystalline layered 198 ln(qe/Ce) ln(qe/Ce) F.E. Soetaredjo et al. / Desalination and Water Treatment 82 (2017) 188–200 1.5 1.0 T = 30oC Plot KD at 30oC T = 40oC 0.5 Plot KD at 40oC T = 50oC 0.0 Plot KD at 50oC -0.5 -1.0 -1.5 -2.0 (a) -2.5 0 20 40 60 80 100 120 140 160 180 C e 0.5 0.0 -0.5 -1.0 -1.5 -2.0 (c) -2.5 0 20 40 60 80 100 120 140 160 C e ln(qe/Ce) ln(qe/Ce) 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 (b) -1.5 0 20 40 60 80 100 120 140 160 180 C e 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 (d) -2.0 0 20 40 60 80 100 120 140 160 Ce Fig. 8. Thermodynamic distribution coefficient. (a) Cu(II) – bentonite, (b) Cu(II) – nanocomposite, (c) Pb(II) – bentonite, and (d) Pb(II) – nanocomposite. Table 4 Thermodynamic parameters of adsorption of Cu(II) and Pb(II) onto bentonite and bentonite – biochar composite System Cu(II) – bentonite Cu(II) – nanocomposite Pb(II) – bentonite Pb(II) – nanocomposite Temperature, °C Ln KD 30 0.648 40 0.611 50 0.309 30 1.561 40 1.360 50 1.339 30 0.043 40 –0.210 50 –0.511 30 0.944 40 0.687 50 0.647 ∆G°, J/mol –1,632 –1,590 –830 –3,932 –3,539 –3,595 –108 546 1,372 –2,378 –1,787 –1,737 ∆S°, J/mol. K –39.32 –17.29 –73.82 –32.59 ∆H°, J/mol –13,688 –9,103 –22,505 –12,171 F.E. Soetaredjo et al. / Desalination and Water Treatment 82 (2017) 188–200 199 structure composed of polymeric sheets of SiO4 tetrahedral [2] R. Mallampati, L. Xuanjun, A. Adin, S. Valiyaveetill, Fruit linked into sheets of (Al, Mg, Fe) (O,OH)6 octahedral [28]. As peels as efficient renewable adsorbents for removal of dis- mentioned in the previous section, during the thermal pro- solved heavy metals and dyes from water, ACS Sustain. Chem. cess in the preparation of nanocomposite, the breakdown of Eng., 3 (2015) 1117–1124. the lignocellulosic structure created some pores in the struc- [3] M.S.

5**Islam, M.S. Rahaman,** J.H. **Yeum, Electrospun novel**

ture of the nanocomposite, the creation of these new pores

5**super-absorbent based on polysaccharide–polyvinyl alcohol–montmorillonite clay nanocomposites,** Carbohydrate Pol., **115**

made the structure of the nanocomposite become disorder, (2015) 69–77. and it increased the randomness of the adsorption system. [4] R. Bhattacharyya, S.K. Ray, Removal of congo red and methyl The increase of the randomness of the system also increases violet from water using nano clay filled composite hydrogels the value of ∆S° as indicated in Table 4.

5**of poly acrylic acid and polyethylene glycol, Chem. Eng. J., 260**

The nature of adsorption mechanism whether the (2015) 269–283. adsorption belongs to physisorption or chemisorption is [5]

6**R. Koswojo, R.P. Utomo, Y.H. Ju, A. Ayucitra, F.E. Soetaredjo, J.**

indicated by the standard of enthalpy change (ΔH°). The

25**Sunarso, S. Ismadji, Acid green 25 removal from wastewater by organo-bentonite from Pacitan, Appl. Clay Sci., 48 (2010) 81–86.** positive value **of**

ΔH° indicates that the adsorption process [6] Yesi, F.P. Sisnandy, Y.H. Ju, F.E. Soetaredjo, S. Ismadji, Adsorp- is an endothermic process, the uptake of adsorbate mole- tion of

2**acid blue 129 from aqueous solutions onto raw and** cules increase with **the** increase **of temperature.**

While the surfactant-modified bentonite: application of temperature-de- negative value of ΔH° indicates that the process is exother- pendent forms of adsorption isotherm, Adsorp. Sci. Technol., mic, the temperature gives adverse effect on the amount of 28 (2010) 847–868. adsorbate adsorbed by the adsorbent. The uptake of Cu(II) [7]

10**A. Kurniawan, H. Sutiono, Y.H. Ju, F.E. Soetaredjo, A. Ayucitra, A. Yudha, S. Ismadji, Utilization of rarasaponin natural**

surfac- and Pb(II) onto bentonite and nanocomposite decrease with tant

5**for organo-bentonite preparation: application for**

methy- the increasing of temperature as seen in Figs. 5 and 6. lene

10**blue removal from aqueous effluent, Micropor. Mesopor. Mater., 142 (2011) 184–193.**

[8]

39**E. Nathaniel, A. Kurniawan, F.E.** Soetaredjo, S. **Ismadji,**

Orga- 4. Conclusions no

5**-bentonite for the adsorption of Pb(II) from aqueous** solu- tion: **temperature dependent parameters of several adsorption**

Bentonite – biochar nanocomposite was prepared by equations, Desal. Wat. Treat., 36 (2011) 280–288. thermal treatment of natural bentonite and water hyacinth at [9]

2**A.K. Rahardjo, M.J.J. Susanto, A. Kurniawan, N. Indraswati, S.**

400°C under a combination of nitrogen and carbon dioxide

2**Ismadji, Modified Ponorogo bentonite for the removal of** ampi- cillin **from wastewater, J. Hazard. Mater., 190 (2011) 1001–1008.**

environment. Bentonite – biochar nanocomposite has both [10]

13**C.H. Zhou, D. Zhang, D.S. Tong, L.M. Wu, W.H. Yu, S. Ismadji, of**

microporous and mesoporous structures. The removal of

5**Paper-like composites of cellulose acetate–organo-**

montmoril- Cu

41**(II) and Pb(II) from aqueous solution** using **bentonite and**

lonite

13**for removal of hazardous anionic dye in water, Chem.**

bentonite – biochar nanocomposite was carried out isother- Eng. J., 209 (2012) 223–234. mally at 30, 40 and 50°C. The adsorption capability of Ben- [11]

9**M. Anggraini, A. Kurniawan, L.K. Ong, M.A. Martin, J.C. Liu,**

tonite – biochar nanocomposite was tested for the removal F.E. Soetaredjo,

2**N. Indraswati, S. Ismadji,** Antibiotic detoxifi- **of Cu(II)** and Pb(II) **from aqueous solution.**

Langmuir and cation

15**from synthetic and real effluents using a Novel MTAB surfactant-montmorillonite (organoclay) sorbent, RSC Adv., 4**

Freundlich adsorption

1**equations with their temperature** (2014) 16298–16311. **dependent forms were** employed **to** correlate **the adsorption**

[12]

4**R. Srinivasan, Advances in application of natural clay and its**

experimental data. Langmuir equation

30**and its** temperature **composites in removal of biological, organic, and inorganic**

dependent forms can correlate the experimental data better

30**contaminants from drinking water. Adv. Mater. Sci. Eng., 2011**

than Freundlich model. The adsorption capacities of benton- (2011) 1–17.

4**http://dx.doi.org/10.1155/2011/872531 (Article ID**

ite towards Cu(II) and Pb(II) are 32.5 mg/g and 27.2 mg/g, 872531). [13]

8**A.B. Dukic, K.R. Kumric, N.S. Vukelic, M.S. Dimitrijevic, Z.D.**

respectively. For bentonite-biochar nanocomposite, the max-

8**Bascarevic, S.V. Kurko, L.L. Matovic, Simultaneous removal of**

imum adsorption capacities are 78.1 mg/g and 44.7 mg/g

8**Pb2+, Cu2+, Zn2+ and Cd2+ from highly acidic solutions using**

for Cu(II) and Pb(II), respectively. The adsorption kinetic mechano chemically synthesized montmorillonite–kaolinite/ follows the pseudo-first-order kinetic model. Parameter k1

37**TiO2 composite, Appl. Clay Sci., 103 (2015) 20–27.**

41**strongly dependent on the temperature. The**

thermodynamic [14]

7**Z.M.O. Rzayev, A. Uzgoren-Baran, U. Bunyatova, Functional**

study indicated

14**that the adsorption of Cu(II) and Pb(II) onto**

organo-Mt/copolymer nano architectures: microwave-as- bentonite and nanocomposite were exothermic (physical sisted

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