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13**Microporous and Mesoporous Materials** 246 (2017) 166e177 **Contents lists available at ScienceDirect Microporous and Mesoporous Materials journal homepage: www.elsevier.com/locate/micromeso** Investigation **of** heavy **metal** adsorption **in**

26**binary system by nanocrystalline cellulose** e **Bentonite nanocomposite: Improvement on extended Langmuir isotherm model** Jindrayani Nyoo **Putro** a, Shella Permatasari **Santoso** a, Suryadi **Ismadji**

a, b, *,

9**Yi-Hsu** Ju **a,** ** a **Department of Chemical Engineering, National Taiwan University of Science and Technology,** No. 43, **Sec 4, Keelung Rd,** Da'an District, **Taipei** City, 106, **Taiwan b Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya, 60114, Indonesia**

Bentonite Nanocellulose Composite Isotherms Adsorption abstract The preparation of NCC e bentonite nanocomposite using waste paper as the source of NCC was con- ducted in this study. The adsorption performance of the composite was tested

10**for the removal of Pb(II) and Hg(II) from aqueous solution in single and binary systems.** Langmuir **and**

Freundlich

3**adsorption isotherms were employed to correlate** pure component **adsorption**

isotherm.

1**Langmuir equation can represent the experimental data better than Freundlich, the** qm **for** lead **is higher than** mercury **in both systems (single system qm ¼ 0.44 mmol/g (Pb) and 0.23 mmol/g** (Hg) **for composite). All systems exhibit endothermic process, except for bentonite which shows the exothermic process.**

The modification of extended Langmuir model for a binary system with the inclusion of fractional loading and heat of adsorption was proposed in this study. The modified extended

24**Langmuir model could represent the experimental data better**

than original extended Langmuir equation. © 2017 Elsevier Inc. All rights reserved. 1. Introduction The rapid grow of industrialization in the 21st century makes the human life much easier. On the other hand, these rapid de- velopments ruin the environment with many kinds of industrial hazardous wastes. One of the biggest problems that the human encountered today is clean water shortage and severe water pollution. Contamination of water resources with various kind of industrial hazardous substances becomes one of the biggest prob- lems for underdeveloped and some of developing countries. Heavy metals are some of the most harmful contaminants which usually were found in the polluted water environments. Heavy metals in contaminated water such as lead and mercury can highly damage human health and other living organisms. Pro- longed exposure to these metals can cause blood and brain * Corresponding author.

5**Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya, 60114, Indonesia.** ** Corresponding author. **Department of Chemical Engineering, National Taiwan University of Science and Technology, No. 43, Sec 4, Keelung Rd,** Da'an District, **Taipei** City, 106, **Taiwan.**

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disorders. Reducing or eliminating the heavy metals content of wastewater before discharging to the water environment is a way to handle this major environment problem. Adsorption is one of the various techniques which is widely used for removing contami- nants in water. This process is a very efficient and economical method which results in high-quality water decontamination [1]. Recently, natural polymer adsorbents have been given tremen- dous attention

6**as biosorbents due to their ubiquitous,** biodegrad- ability, **and non-toxic nature.**

One of the natural polymers that has potential application as biosorbent

6**is cellulose. Cellulose is** considered as **the most abundant natural material in the world,**

which

6**is composed** of **linear polysaccharides consisted of two anhydroglucose rings linked by repeated** b **-1,4 glycoside bonds** [2]. **Cellulose is an important raw material for** many kinds of **industries,**

especially for pulp and paper industries. In 2014, the total graphic papers (newsprint, uncoated mechanical, uncoated woodfree, and coated papers) consumption was 56 Mt for Europe and Northern America region; then it can be assumed that the waste paper has the same amount of the total consumption number [3].

Waste pa- pers usually are used as feedstocks for making recycled paper. However, after several times of recycling, cellulose fibers become short and has lower economic value than long cellulose fibers. To increase the added value of waste paper, the possibility of utilizing

> 1 **waste paper as raw material for nanocrystalline cellulose (NCC)**

production was explored in this study. Cellulose has hydroxyl functional groups that can be modified to enhance its adsorption ability as an adsorbent. Currently, several methods are available for the modification of cellulose such as esterification, etherification, cationization, oxidation, amidation, and grafting. Among these methods, esterification through acid hydrolysis has been shown to improve cellulose properties excel- lently. Acid hydrolysis is a simple method to modify cellulose. Basically the acid will attack the amorphous part in cellulose fiber and extract the nanocrystalline cellulose (NCC). Sulfuric acid pre- pared NCC is well known for excellent thermal stability property due to the attachment of sulfate esters on the NCC surface. The presence of sulfate ester in the NCC surface increases the adsorp- tion capacity two times of that of the original NCC, which means that modification of functional groups indeed has a major impact on adsorption capacity [4]. Bentonite is one kind of clay material which has

> 34 **2:1 layer structure in which the octahedral sheet is sandwiched between two tetrahedral silica**

sheets, with water and metal cations existing between the spaces of the layers [5]. The layers are negatively charged and held together by charge-balancing counterions like Ca^{2+} and Na^{+}. Natural bentonite has been known to have moderate adsorption capacity towards heavy metals and certain organic substances due to high cation exchange capacity (CEC), which is around 40e130 meq/100 g and high surface charge in their lattice structure [6]. However, due to its hydrophilic nature, natural bentonite is not a good adsorbent for many organic compounds. Therefore, modification of natural bentonite

> 18 **is necessary to** in- crease **its adsorption capacity. The** combination **of**

clay and other materials such as metal oxides and polymers has gained much attention from researchers in recent years. These clay based com- posite materials have excellent capability for removing various organic and inorganic contaminants [5,7]. The aim of this study was to use

> 1 **waste paper as raw material for the synthesis of NCC, and combining this NCC with bentonite to produce a nanocomposite material for removing** Pb^{2+} **and** Hg^{2+} **in single and binary systems.**

Improvement of extended Langmuir model to represent the adsorption isotherms of the binary system was also given in this study. The adsorption performance of the adsorbents was also tested. The mechanism of the adsorption was investigated from isotherm and thermodynamic viewpoints. 2. Materials and methods 2.1. Materials Waste printing paper used in this study was obtained from our laboratory. The ink type for printing in this waste paper was toner from HP LaserJet Q7553A. Bentonite was obtained from

> 11 **Pacitan, East Java, Indonesia. The cation exchange capacity of** this natural **bentonite was**

44.7 meq/100 g. The

> 19 **chemical composition of natural bentonite was analyzed using**

PANalytical

> 15 **MiniPal QC energy dispersive X-ray fluorescence, and the results are as follows:**

Al_2O_3 ¼ 19.21%, SiO_2 ¼ 61.98%, Na_2O ¼ 2.22%, CaO ¼ 3.59%, K_2O ¼ 1.78%, MgO ¼ 1.98%, Fe_2O_3 ¼ 2.97%, MnO ¼ 0.22%, and TiO_2 ¼ 0.09%. Analytical grade NaOH, HCl, KNO_3, $Pb(NO_3)_2$, $HgCl_2$, chloroform, dimethyl sulfoxide, sulfuric acid, hydrogen peroxide, were used without further purification. 2.2. Pretreatment of waste paper and bentonite Waste paper (5 g) was soaked in tap water overnight and shredded using a blender. The shredded paper was then deinked with 100 ml organic solvent that was 30%

chloroform (99% purity) Fig. 1. ATR-FTIR result of waste paper, paper after treatment, bentonite, NCC, and composite. and 70% dimethyl sulfoxide (99.7% purity). Deinking was conducted under continuous stirring for 2 h at room temperature. Subse- quently, the solution was sonicated for 15 min, and the waste paper was filtered. The collected waste paper was dried in an oven overnight and kept in a desiccator for further use. Before use,

11**bentonite was purified** in 30% **hydrogen peroxide solution**

18**at room temperature for 24 h under continuous** stirring **to remove** organic impurities. **The**

weight ratio of bentonite and hydrogen peroxide solution was 1:5. Then the mixture was heated in boiling water for 2 h

11**to remove excess hydrogen peroxide. The** purified **bentonite was**

separated from the solution by centrifuga- tion and washed with distilled water, then dried at 110 C for 24 h. 2.3. Preparation of NCC/Bentonite composite The deinked waste paper (1 g) was dissolved in 1 M NaOH (9 g) to remove impurities and swell the cellulose fiber. The solution was stirred for 3 h at room temperature and dried in an oven at 50 C for 6 h. Then 1 g of waste paper was treated with 20 ml of 64 wt.% H2SO4 at 45 C for 60 min under continuous stirring. After hydro- lysis, the solid and liquid were separated by centrifugation (9503 g, 10 min). The turbid supernatant was collected and placed in a dialysis tube for 3 days. The suspension was sonicated for 30 min in an ice-water bath to avoid overheating and kept in a ?20 C refrigerator for 24 h. Subsequently, the suspension was freeze-dried to obtain the NCC powder. Preparation of NCC - bentonite nanocomposite was conducted according to the previous method [8] with modifications. Bentonite (0.6 g) was dispersed in DI water (30 ml), stirred for 1 h and sub- sequently sonicated for 1 h. The bentonite was added to 0.1% of NCC dispersion (30 g) and stirred for 24 h. Then the solution was soni- cated for 1 h. The nanocomposite formed was poured into a poly- styrene Petri dish and oven dried at 50 C for 1 day.

29**2.4. Characterization Field emission scanning electron microscope (FESEM,** JEOL **JSM-** 6500F) **was** employed for obtaining **the surface morphology of**

Fig. 2. Morphological image of (A) waste paper, (B) paper after treatment, (C) bentonite, (D) NCC, (E) composite, and (F) TEM of NCC. samples. Prior to FESEM imaging, the

21**sample was coated with a thin layer of platinum**

by a fine auto coater (JFC-1600, JEOL, Ltd., Japan) for 90 s in an argon atmosphere. The FESEM analysis was conducted at 10 kV and 15 kV with 10.4 mm working distance. Transmission electron microscope (TEM, Tecnai F20 G2 FEI-TEM) was conducted at 80 kV to know the NCC morphology. The sample was prepared on a 300 mesh Cu grids with 2% uranyl acetate for staining. The attenuated total reflectance (ATR) FTIR (Bio-Rad Model FTS-3500) analysis was operated in the frequency range of 4000e650 cm?1 with 4 cm?1 scanning resolution, and the signal was accumulated from 100 scans. X-ray diffraction (XRD,

8**Philips X'pert X-ray Diffractometer) patterns were acquired at 40 kV and 30 mA using** a **monochromatic high-intensity**

Cu Ka1 radiation (l ¼ 0.15405 nm). The surface charge of NCC, bentonite, and composite were deter- mined using

8**a zeta meter (Zeta Potential Analyzer, Brookhaven 90Plus). The** thermal stability **of**

NCC, bentonite, and composite was determined by thermal gravimetry analysis (TGA)

31**using a Perkin Elmer Diamond TG/DTA thermal analyzer** with **a heating** and cooling **rate of 10** C **min?**

1 up to 600

5**C under continuous nitrogen gas flow of** 150 **ml min?** 1. Sample **mass in each** experiment **was**

about 5 mg. 2.5. Adsorption experiment Adsorption of lead and mercury was conducted in batch mode. For single system, a stock solution of Pb(II) or Hg(II) was prepared by dissolving 159.85 mg of Pb(NO3)2 or 135.36 mg of HgCl2 into a liter of distilled water. The adsorption experiments were conducted by introducing various masses (0.1e2.0 g) of NCC, bentonite, nanocomposite

24**into a series of conical flasks containing** 50 **ml of**

Fig. 3. X-ray diffraction of adsorbents. Fig. 4. TGA curve for the characterization of bentonite, NCC and composite. Fig. 5. Surface charge of adsorbents. lead or mercury at a certain pH value. The pH was previously fixed at a range of 2e7 by adding 0.1 M HCl or NaOH solution into the heavy metal solution. The effect of temperature on adsorption isotherm was studied by carrying out the adsorption at 30, 40, and 50 C. After equilibrium

19**condition was reached, the** solution **was separated from the** adsorbent **by centrifugation**

(6082 g, 10 min). The final concentration

7**of Pb(II) and Hg(II) was**

measured using ICP- OES. Adsorbed Pb(II) and Hg(II) at equilibrium condition per unit mass of adsorbent (qe)

22**was calculated using the** following **equation: qe** ¼ Co ? **Ce V m (1) where qe is the amount of Pb(II)**

or Hg

20**(II) adsorbed on the adsorbent** (mmol/g) **at equilibrium** condition, Co **and**

12**Ce are the initial and equilibrium concentrations (mmol/L), respectively. V is the volume of solution** (L), **and m is the mass of adsorbent (g).**

For a binary system, a known amount of Pb (159.85 mg, 319.70 mg, 479.55 mg) was added into 1 L Hg solution (135.36 mg). The binary adsorption was conducted at 30 C and pH 2, 6 and 5 for NCC, bentonite and composite, respectively. The

7**amount of Pb(II) and Hg(II)**

27**adsorbed at equilibrium** condition **per unit mass of adsorbent** (qe) **was calculated using the following equation: qe;** i=j ¼ **Co;**

i=j ? Ce;i=j m V (2) where qe;i and qe;j are the amount of Pb(II) and Hg(II) adsorbed on the adsorbent (mmol/g) at equilibrium condition, respectively, Co,i/j and Ce,i/j are the initial and equilibrium concentrations (mmol/L), respectively. 3. Results and discussion 3.1. ATR FTIR analysis ATR-FTIR is the most widely used technique for characterization of materials based on the vibrations of atoms within the molecules. Fig. 1 represents the spectra of waste paper, deinked waste paper, purified bentonite, NCC, and composite. Both waste paper and deinked waste paper spectra show the cellulose characteristic peaks as indicated by CeO/CeC stretching (1045 cm?1), CeH bonding (1357 cm?1), and CH2 symmetrical stretching (2841 cm?1) [9,10]. From these spectra, there are two prominent different peaks. The peak at 1730 cm?1 for waste paper corresponds to carbonyl band that is usually found in toner such as styrene acrylate copolymer [11,12]. The

appearance of eOH group (3291 cm?1) in deinked waste paper can be explained by the removal of toner that previously covered up the eOH groups on the cellulose fiber [9]. All the characteristics of cellulose from deinked waste paper are retained in NCC. New peak appears for NCC in 1407 cm?1 which indicates the presence of sulfate esters due to sulfuric acid hydro- lysis. FTIR spectrum of bentonite shows the characteristics of montmorillonite clays as demonstrated by Al(Mg)eOH stretching (3612 cm?1), HeOeH stretching (3441 cm?1), eOH bending for adsorbed water (1641 cm?1) and SieOeSi stretching of the tetra- hedral sheet (1041 cm?1) [5,13,14]. The characteristic peaks of NCC and bentonite seem to be retained as indicated in the nano- composite spectrum. The wavenumber 1083 cm?1 indicates the SieO in bentonite, the shifting of the peak of silica from 1041 cm?1 to 1083 cm?1 was possibly due to the exfoliated off the tetrahedral sheet by NCC. The wavenumber of AleOHeMg appears at 3640 cm?1 which was slightly altered from 3612 cm?1. The wave- numbers of 2775 cm?1 and 3207 cm?1 corresponded to the CeH bond and bonded OH from NCC, respectively.

7**Fig. 6. Effect of** pH **on the** adsorption **of (a) Pb** single, **(b) Hg**

single, (c) Pb binary and (d) Hg binary. 3.2. Surface morphology analysis The surface morphologies of waste paper, deinked waste paper, bentonite, NCC, and nanocomposite are shown in Fig. 2. It can be seen from the image of waste paper that there were toner particles on the surface of cellulose fiber (Fig. 2a). After pretreatment, toner particles were removed and the fiber seems to be swollen due to NaOH pretreatment (Fig. 2b). The swelling of cellulose fibers helped to create homogeneous NCC particles. The SEM image of bentonite (Fig. 2c) reveals that the surface topography of bentonite consists of stacked sheets with heterogeneous surfaces. It can be seen from the surface topography of NCC (Fig. 2d) that NCC has a crystal structure. The TEM result of NCC (Fig. 2f) indicates that NCC possesses a rod crystal morphology with length around 157 nm. The morphology of composite (Fig. 2e) is similar to the bentonite morphology but with a smoother surface. 3.3. X-ray diffraction The crystalline phase of materials was observed by XRD. The characteristic peaks of montmorillonite in bentonite (Fig. 3) are at 19.7 and 22 . The other diffraction peaks belong to quartz (26.5 , 42.1 , and 51) and FeCaCO3 (35.8) [15]. Crystal plane of 200 at 22.3 represents the crystalline part of cellulose in NCC diffraction graph, the broad peak around 14 e16.5 indicates the crystal plane of 110 [16]. Continuous and broad peak was observed in XRD pattern of composite between 21.7 and 23 denoting the combi- nation of the crystalline part between bentonite and NCC which have been exfoliated within each other. 3.4. Thermal gravimetry analysis (TGA) The thermal characteristic of NCC, bentonite, and composite was characterized using thermogravimetry analysis, and the results are given in Fig. 4. TGA result of NCC shows that three different stages of weight loss occurred during the heating process. The first stage of weight loss was due to the evaporation of moisture content (30e200 C) and it was found that the moisture content of NCC was around 6.5%. The second stage of the weight loss occurred at 245e315 C. In this stage, the weight loss of the sample (~58.3%) was mostly due to thermal degradation (dehydration and depoly- merization of cellulose). In the last stage, the weight loss was mostly due to the carbonization of intermediate chars [17]. For bentonite, it was observed that there are two stages in TGA curve. The first stage corresponds to the evaporation of moisture content and the second stage was due to the dehydroxylation of alumino- silicate in bentonite [18]. The thermogravimetric curve of the composite shows a similar trend to that of the thermal degradation of the composite of NCC and bentonite, with the degradation of cellulose starting at between 215 and 315 C and dehydroxylation phase at 315e590 C. Fig. 7. Adsorption mechanism between each adsorbents (A: bentonite, B: NCC, C: composite) and metal (Mρ: Pb or Hg). 3.5. Zeta potential Zeta potential of each adsorbent was measured to obtain the isoelectric point. From Fig. 5, it can be seen that the surface charge of bentonite and composite is pH dependent. The iso- electric point is where the adsorbent has no charge at specific pH value. Isoelectric points for bentonite and composite are at pH 5.4 and 3.6, respectively. The surface charge of NCC is pH indepen- dent as seen in Fig. 5. The surface charge of NCC is almost con- stant (~?20 mV) at all pH which indicates excellent stability of NCC at various pH. 3.6. Effect of pH pH has been known to have a strong influence

33**on the adsorption of heavy metals onto** various adsorbents. **Fig.** 6 depicts the **effect of pH on the adsorption of**

7**Pb(II) and Hg(II)** onto bentonite, NCC, **and** nanocomposite. **The**

pH optimum for

8**adsorption of Pb(II) and** Hg **(II)** onto bentonite both **in the single** or **binary**

system was achieved at pH 6. For NCC in single system, the pH optimum for adsorption of Hg(II) was pH 2 while for Pb(II) was pH 3. For the adsorption of Hg(II) and Pb(II) onto nanocomposite, the pH optimum in single system for adsorption Hg(II) was pH 4, while for Pb(II) was pH 5. In binary adsorption process, the optimum pH for NCC was 2 and 5 for composite. Slight change in the optimum pH of binary adsorption

process for NCC and composite denotes that surface charge of NCC has a quite significant role in the binary adsorption, as discussed previously that NCC has good stability at the various condition of pH. The isoelectric point of bentonite is at pH 5.4 as indicated in Fig. 5. Below this isoelectric point, the bentonite is positively charged while above this point the bentonite is negatively Fig. 8. Adsorption isotherms of single system in 30, 40, and 50 C (solid line: Langmuir fitting, dashed line: Freundlich fitting). charged. At pH 6, lead ions are present in the forms of Pb(II) and PbOHþ. Since the surface of the bentonite is negatively charged, therefore, electrostatic interaction between lead cations and the surface of bentonite occurred,

> 21**resulting in the** increased **amount of** lead cations **adsorbed onto the surface**

of bentonite. A similar phenomenon also took place in the adsorption of Hg(II) onto bentonite. At pH 6, the mercury ions exist in the forms of HgOHþ and HgOHCl [19,20] and the interaction between the surface of bentonite and HgOHþ is electrostatic, while with HgOHCl it is through van der Waals force. Table 1 Langmuir and Freundlich parameters for single adsorption system at various temperatures. Adsorbent Adsorbate T (C) Langmuir parameters Freundlich parameters qm

> 32**(mmol/g) KL (L/mmol) R2 KF ((mmol/g)(mmol/L)1/n) n R2**

Bentonite NCC Composite Pb 30 40 50 Hg 30 40 50 Pb 30 40 50 Hg 30 40 50 Pb 30 40 50 Hg 30 40 50 0.25 11.52 0.22 10.50 0.20 9.37 0.13 6.59 0.10 4.65 0.09 2.54 0.30 15.51 0.33 16.14 0.35 18.19 0.16 9.68 0.18 11.96 0.22 13.31 0.40 17.25 0.43 17.46 0.44 19.33 0.19 13.50 0.21 15.13 0.23 15.87 0.99 0.47 0.99 0.41 0.99 0.32 0.99 0.18 0.95 0.13 0.95 0.09 0.99 0.42 0.99 0.49 0.99 0.57 0.98 0.20 0.99 0.25 0.99 0.31 0.99 0.80 0.99 0.88 0.99 0.92 0.99 0.24 0.99 0.26 0.99 0.29 1.72 1.67 1.79 1.85 1.77 1.51 2.83 2.58 2.42 2.43 2.50 2.54 2.00 1.99 2.01 3.05 3.26 3.23 0.99 0.98 0.99 0.98 0.98 0.97 0.99 0.99 0.99 0.96 0.99 0.99 0.98 0.98 0.98 0.99 0.98 0.99 In the case of the adsorption of heavy metals onto NCC, since the surface of the NCC is negatively charged at all pH, the adsorption mechanism is obviously electrostatic interaction between negatively charged NCC and metal cations. The presence of hydroxyl and sulfonate functional groups on the surface of NCC also enhanced the

> 14**adsorption capacity of** NCC towards **Pb(II) and Hg(II). The** combination **of** bentonite **and**

NCC as nanocomposite greatly enhanced the adsorption removal of Pb(II) and Hg(II) as can be seen in Fig. 6. The mechanism of the adsorption

> 14**of Pb(II) and Hg(II)** onto nanocomposite is **the** electrostatic interaction **between metal ions and**

negatively charged surface of the nanocomposite. In general, for all adsorbents the adsorption of Pb(II) is more prefer- able to Hg(II) (including in the binary system). Based on the elec- tronegativity values (2.00 for Hg and 1.87 for Pb), the adsorption behavior should be opposite, i.e. Hg(II) should be adsorbed easier onto the surface of the adsorbents than Pb(II) [21]. Since this adsorption phenomenon cannot be explained by the electronega- tivity of the metals, we will explain it further with the effect of van der Walls radius (150 pm for Pb and 200 pm for Hg) which is defined as the half of the internuclear distance of two atoms [22]. With a larger van der Walls radius, the forces in mercury are weaker than in lead. Thus the chance of mercury to create higher affinity is better than lead. However the results (Fig. 6c and d) indicate that the adsorbents have better interaction with Pb(II) than Hg(II). Since the van der Walls radii concept also cannot explain this adsorption phenomenon, we will try another approach. Pearson's

> 17**principle states that hard acids prefer to bind to hard bases and soft acids to soft bases.** Hg2þ **is a**

soft acid while Pb2þ is a borderline acid [23]. For bentonite, interaction with Pb(II) is pref- erable because in its structure there are exchangeable cations (hard acid) and water (hard base) in the midst of bentonite layers, hence Pb(II) can form attractive forces with hard acid and a hard base. Since NCC has hydroxyl and sulfite anion which are hard base and borderline base, respectively and the pH is acid (2e3) which makes low Hg(II) affinity towards adsorbents hence adsorption is not as strong as in the case of Pb(II). The schematic diagram of this adsorption mechanism can be seen in Fig. 7. 3.7. Adsorption isotherms in single system Various

> 4**models have been developed to represent liquid phase adsorption equilibria data. The most common used adsorption isotherms models are**

Langmuir and

Freundlich. Both isotherm equations consist of two parameters. Langmuir adsorption isotherm

4**is based on assuming homogeneous surface and energy on the adsorbent surface,**

while Freundlich is an empirical model for heterogeneous systems.

4**Both models have been extensively used to represent huge numbers of adsorption experimental data**

since these equations are simple and can fit the data in a specific concentration range. Langmuir (Eq. (3)) and Freundlich (Eq. (4)) models are mathematically expressed as follows: qe ¼ qm1 þKLKCLeCe (3) qe ¼ KF Ce1=n (4) where qm is the Langmuir constant which indicates the maximum adsorption capacity of the adsorbent with monolayer surface coverage ðmmol=gÞ, and KL is the adsorption affinity constant (L/ mmol). KF is the Freundlich constant which expresses the adsorp- tion capacity [(mmol/g)(mmol/L)1/n] and n is the dimensionless unit representing the surface heterogeneity. A higher n reflects that the adsorption system is more heterogeneous. The adsorption experimental data were fitted to the adsorp- tion equations using nonlinear regression fitting, and the results are shown in Fig. 8. It can be seen that the fitting results (Table 1) indicate that Langmuir model fits the experimental data better than Freundlich model. Correlation coefficient factors (R2) for Langmuir models are around 0.95e0.99.

3**From Table** 1 **it can be seen that** all of **the parameters** of Langmuir **and Freundlich** models **are** temperature **dependent.**

For heavy metals e bentonite system, qmax and KL decreased with increasing temperature, while for other systems, these parameters increase with the in- crease of temperature. The increase of uptake amount with temperature is a strong indication that chemisorption is the control mechanism of the adsorption process. Physical adsorption is the main control mechanism

20**of the adsorption of Pb(II) and Hg(II) onto**

bentonite. In chemisorption mechanism, the adsorbate molecules are strongly attached to the surface of the adsorbent. This phenom- enon is indicated by KL in Langmuir equation. The stronger the interaction between adsorbate and adsorbent, the higher the value of KL. The values of KL for NCC and nanocomposite systems Fig. 9. Plotting of experimental data against (a) original extended Langmuir and (b) modified extended Langmuir. are higher than those in heavy metals - bentonite system as indicated in Table 1. Both NCC and nanocomposite possess hy- droxyl and sulfonate functional groups on their surface, and usually, the binding of these functional groups and heavy metal ions are mostly through electrostatic interaction which is much stronger interaction than van der Walls force. The basic structure of bentonite

25**is a layer consisting of two inward-pointing** tetra- hedral **sheets with a central alumina octahedral sheet (2:1).**

In this 2:1 layer structure, water, and other cations exist and these layers also have intermolecular forces which can be much stronger than the interaction of heavy metal molecules, and the surface layer of bentonite, hence heavy metals ions are not able to penetrate into Stern-Gouy layer between those layers [24]. Therefore, lower adsorption affinity was observed for heavy metals e bentonite system. 3.8. Adsorption isotherms of binary system: improvement of extended Langmuir model Among of the available models for multicomponent adsorption, the extended Langmuir possibly is

3**the most widely used** one **to** describe binary **adsorption data,**

because it is simple and can represent the experimental data comparatively better than other models. The extended Langmuir is expressed as follows: qe;i ¼ qm;i1 þ SKjnL¼;i1CKe;Li;iCe;i (5) For binary system, Eq. (5) becomes qe;1 ¼ qm;11 þ KL;1KCLe;1;1Cþe;1KL;2Ce;2 (6) qe;2 ¼ qm;21 þ KL;1KCLe;2;1Cþe;2KL;2Ce;2 (7) where qm,i and KL,i in Eqs. (6) and (7) are Langmuir constants which are obtained from the fitting of adsorption experimental data of single system or pure component. This model has been developed for competitive multicomponent adsorption with respect to the energy of adsorption in system [25]. In real multicomponent adsorption system, competition between adsorbates molecules for

active sites always occur, and this phenomenon usually acts as the controlling mechanism. However, the shortcoming of the original extended Langmuir model is that it does not consider the compe- tition

> 3**of adsorbate molecules** on **the** active **adsorption sites of adsorbent. The** absence of **the**

competition between the adsorbates molecules in this model often results in overestimate of the theo- retical values of the isotherm [26]. Thus an improvement for this model is proposed in this work to predict the binary components adsorption equilibria. Regarding the competition of adsorption of molecules onto one of the available active surface sites, the Lang- muir constants qm and KL are modified in terms of fractional loading as follows: qm;1ðbinÞ ¼ qm;1q1 (8) qm;2ðbinÞ ¼ qm;2q2 (9) KL;1ðbinÞ ¼ KL;1ðsingleÞ Q1q1Q1þq1Q2q2 (10) KL;2ðbinÞ ¼ KL;2ðsingleÞ Q1q1Q2þq2Q2q2 (11) where q1 and q2 are the fractional loading of component 1 and 2 in the surface of adsorbent, respectively, while Q1 and Q2 are the heat of adsorption of component 1 and 2, respectively.

> 3**As mentioned in the previous section,**

the Langmuir affinity constant

> 3**measures how strong the adsorbate molecules are attached or attracted onto the surface of**

the adsorbent. Basically, the frac- tional loading q and heat of adsorption Q will influence the Langmuir affinity constant as indicated in Eqs. (10) and (11). In Eqs. (10) and (11), the competition between adsorbate molecules is expressed as the ratio of the multiplication between the heat of adsorption and fractional loading of certain adsorbate to the summation of those values for both components. Taking into account that the competition occurred in the adsorption system, adsorption affinity in the binary

> 15**system should be** lower **than in single system.**

The introduction of fractional loading in Eqs. (10) and (11) indicates that the contribution of surface coverage of a Fig. 10. Modified extended Langmuir isotherm for lead and mercury in binary system for bentonite, NCC and composite. Table 2 Adsorption parameters for extended Langmuir model. Adsorbent Initial concentration q1 q2 qm,1 (mmol/g) qm,2 (mmol/g) KL,1 (L/mmol) KL,2 (L/mmol) Q1 (kJ/mol) Q2 (kJ/mol) Co,Pb (mmol/L) Co,Hg (mmol/L) Bentonite NCC Composite 0.48 0.50 0.97 0.50 1.45 0.50 0.48 0.50 0.97 0.50 1.45 0.50 0.48 0.50 0.97 0.50 1.45 0.50 0.66 0.34 0.67 0.33 0.67 0.33 0.68 0.32 0.68 0.32 0.69 0.31 0.70 0.30 0.70 0.30 0.70 0.30 0.16 0.05 0.17 0.05 0.17 0.05 0.21 0.05 0.21 0.05 0.21 0.05 0.28 0.06 0.28 0.06 0.28 0.06 5.21 3.61 5.23 3.60 5.26 3.59 8.18 4.57 8.22 4.55 8.27 4.52 10.87 4.99 10.91 4.96 10.97 4.92 8.31 ?6.62 ?4.74 20.00 ?12.61 ?6.46 particular component towards the heat of adsorption. The orig- inal Langmuir equation assumes that

> 30**there is no interaction** be- tween **adsorbed molecules** implying **that the heat of adsorption is independent of coverage**

[27], and for real multicomponent sys- tem this assumption is not truly correct. By substituting Eqs. (8)e(11), the extended Langmuir model becomes qe;1 ¼ qm;1q11 þ KL;1ðsingleÞ QK1qL1;þ1QðQs1i2qnð11gÞ leqÞ1Þ CQe;11q1þþQQK12qLð1;12?ðsqi1nÞgleCÞe;1 Q1qQ12þðQ1?2ðq11?Þq1Þ Ce;2 (12) qe;2 ¼ qm;2ð1 ? q1Þ KL;2ðsingleÞ Q1qQ12þðQ1?2ðq11?Þq1Þ Ce;2 (13) 1 þ KL;1ðsingleÞ Q1q1 Q1q1þQ2ð1? q1Þ Ce;1 þ KL;2ðsingleÞ Q1qQ1þð2ðQ1?2ðq11?Þq1Þ Ce;2 This fractional loading ðqÞ was originally developed by Langmuir experimental data for the single system. The value of optimum pH which represents the fraction of the surface [28]. Now by assuming for binary systems is not much different with the single system, monolayer coverage of surface active sites, then in the binary sys- which confirms that the adsorption mechanism in both of single tem, the total of fractional loading must be equal to unity and binary systems was similar. The adsorption capacity for lead is ðq1 þ q2 ¼ 1Þ since the surface active sites will be occupied by either higher than mercury in both systems; this phenomenon indicated

> 7**of Pb(II)** or **Hg(II)** to form **the** monolayer **surface**

coverage. The value

> 10**that functional group plays a major role in the adsorption**

mecha- of Q can be obtained by the following equations: nisms. The modified model could represent the binary experi- KL;1ðsingleÞðTÞ ¼ KLo;1 exp RT Q mental data very well. 1 (14) References KL;2ðsingleÞðTÞ ¼ KLo;2 exp RT Q 2 (15) [1] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, Prog. Polym. Sci. 30 (2005) 38e70. [2] S.J. Einchorn, A. Dufresne, M. Aranguren, N.E. Marcovich, J.R. Capadona, where R is the ideal gas constant (0.008314 kJ K?1 mol?1), T is the S.J. Rowan, S. Weder, W. Thielemans, M. Roman, S. Renneckar, W. Gindl, S. Veigel, J. Keckes, H. Yano, K. Abe, M. Nogi, A.N. Nakagaito, A. Mangalam, temperature (K), KL is the Langmuir affinity constant that can be J. Simonsen, A.S. Benight, A. Bismarck, L.A. Berglund, T. Peijs, Review: current determined from a single system (L/mmol). The value of KLo and Q international research into cellulose nanofibers and nanocomposites, J. Mater. 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