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paper text:

10Investigation on the montmorillonite adsorption of biocidal compounds incorporating thermodynamical-based multicomponent adsorption isotherm L.K. Ong a, F.E. Soetaredjo a, A. Kurniawan a, A. Ayucitra a, Jhy-Chern Liu

b, S.

9Ismadji a,⇑ a Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia b Department of Chemical Engineering, National Taiwan University of Science and Technology, No. 43, Sec. 4, Keelung Rd., Taipei City 106, Taiwan,

ROC highlights Microwave power level determined the characters of organo-bentonite. Organo-bentonite increased the removal percentage of triclosan. Intercalated organic cation reduced the adsoption site for benzalkonium chloride. pH value affects the adsorption of benzalkonium chloride and triclosan. Incorporation of thermodynamical spontaneity ratio improved extended Langmuir model.

4-**bentonite abstract Sublethal concentration of biocides, namely triclosan and benzalkonium chloride, have been known to raise severe environmental problems such as pathogens resistance and the existence of the toxic** compounds **in reclaimed water. Simple adsorption process of those biocides onto the bentonite modified by dodecyltricetyl ammonium bromide (DTAB) cation, show a remarkable increase on the removal** effi- ciency **of triclosan, regardless of the pH value. It was found that organophilic cation facilitates the** anchor- ing **of hydrophobic triclosan, but slightly limits the adsorption of benzalkonium chloride by occupying the active cation exchange site in the bentonite structure. Adsorption of a single system can be described properly by Langmuir isotherm equation. Incorporation of the Gibb's free energy on the affinity constant of the extended Langmuir equation may attribute robust predictive ability on the binary adsorption model.** Ó 2013 **Elsevier B.V.**

1. Introduction Biodegradation is a common part of the proper life cycle in this nature. However, in some cases, biodegradation is undesired for its destructive effect towards the natural products. In addition, the microbes, which have been acknowledged to be the main subject of this natural phenomenon, slowly release some toxic compounds, which are responsible for many diseases. To overcome those prob- lems, human have invented several chemical compounds, the bio- cides,

2**which can inhibit the metabolism, even eliminate the**

microorganisms. There are many biocides available today showing broad spectrum of antimicrobial activity, which may extend its application ranges. Two types of commonly used biocides are benzalkonium chloride and triclosan, which can be classified as quaternary ⇑ Corresponding author.

15**Tel.: +62 31** 389 1264; **fax: +62 31** 389 1267. **E-mail address: suryadiismadji@yahoo.com (S. Ismadji).**

12.001 ammonium and chlorophenol compounds. Many consumer prod- uct, for example, cosmetic and cleaning products, also contain these compounds. Notably, benzalkonium chloride and triclosan are frequently found to be used in many household disinfection products. Those biocides are known to have a vast susceptibility range of microorganisms and non-corrosive properties; therefore, they have been utilized in many industries (i.e., food industries, textile industries, paper industries, oil and gas industries, plastic industries, etc.) to prevent biofouling in the pipelines and product deterioration. A massive use of biocides in daily life generates a wastewater, which contains the excess of those biocides [1]. Although wastewater treatment plant has reduced much of those com- pounds, there are a number of biocides in the scale of ng/L to mg/L that still remaining [2–3]. Some researchers denote that sub- lethal concentration of remaining biocides found in the nature, particularly in the reclaimed water, may accumulate in the microbial cells and elicit microbial resistance on the biocides itself and some antibiotics, which may impact on the human health [4–6]. In the other hands,

2**some toxic organic compounds such as the** trihalomethanes, **dioxins, and benzenes, which are known to be carcinogenic substances**

have been reported to be exist as the deg- radation products of those biocides and poisoning many aquatic organisms [7–9]. As the result,

2**supplementary treatment process on the regular wastewater treatment plant should be** involved **to manage a maximum elimination of those hazardous residues.**

Several processes have been proposed to remove those micro- pollutants such as UV/TiO2 photocatalysis [7,10], membrane biore- actor [11], chemical oxidation [12], chlorination [9,13], ozonisation [12,14], and activated carbon adsorption [14–15]. Amongst those processes, adsorption shows a promising prospect in removal effi- ciency and cost feasibility. However, the utilization of powdered activated carbon often raises a drawback on the cost of adsorbent. Bentonite, which has been known as a low cost and abundantly available natural adsorbent material in Indonesia, is mostly used in its form of organo-bentonite as alternative substitution of acti- vated carbon to perform the adsorption of several organic moieties including antibiotic agents [16–17]. However, investigation on the adsorption of trace household biocide compounds in the water is still rare among all adsorption studies using pristine and organo- clay. In this study, the effect of microwave power output on the interlayer distance of organo-bentonite has been carefully exam- ined to get an effective modification parameter, which can be used further to achieve high removal efficiency of biocides

adsorption. Utilization of the saponin extract of Sapindus rarak pericarp was also tested as the promising green modification agent. This natural surfactant shows considerable possibility to substitute synthetic surfactant. Investigation on the fundamental mechanism of the biocide compounds adsorption at various pH and different mont- morillonite surface condition may contribute key concept for a bet- ter understanding on the practical biocides removal. Finally, a novel extended Langmuir model incorporating thermodynamical spontaneity ratio was assessed to prove its ability in performing an easy and critical evaluation on the adsorption data of the binary system (i.e., benzalkonium chloride and triclosan). 2. Materials and methods 2.1. Materials Benzalkonium chloride (P95%) and triclosan (HPLC Grade, P97%) were acquired from Sigma Aldrich and Fluka,

> 1**respectively. The molecular structure and some**

specific information of those biocide compounds are given in Table 1. Dodecyltricethylammoni- um bromide (DTAB) (P99%), hydrogen peroxide solution (35%), hydrochloric acid (37%), and sodium hydroxide (P98%) were obtained

> 1**from Sigma–Aldrich, Singapore and used as-supplied.**

Tropical fruit of Sapindus rarak was collected from Klaten, Central Java, Indonesia and extracted using the same procedure that was reported previously [18]. 2.2. Preparation of organo-bentonite

> 8**Bentonite was** obtained **from a mining site located on** Pacitan, **East Java, Indonesia. Prior to the use, bentonite was purified**

by means of 0.5% H2O2 solution with an impregnation

> 1**ratio of 1:10 (w/v)**

for 24

> 1**h under** a **mechanical stirring at** 200 **rpm. The** result- ing bentonite **was**

filtered,

> 1**dried at 373.15 K for 24 h,** crushed, **and screened with 100/120 sieves to obtain** the **size**

fraction between 125 lm and 152 lm. The

6**cation exchange capacity (CEC) of** the **bentonite was** measured according to **the ASTM C837-99** proce- dure **and found to be**

39.5 meq/100 g bentonite. Organo-bentonite was engineered by referring on this following procedure: 50.0 g of bentonite was dispersed in the 250 mL of dis- tilled water containing surfactant (i.e., DTAB or saponin)

8**with the amount equivalent to 1.5 times of the CEC of** pristine bentonite. **The suspension was stirred at** 500 rpm **for** 15 min **and**

then sub- jected into a microwave oven at the heating power of 450, 810 and 900 W for 60 s. The organo

8**-bentonite was repeatedly washed with** distilled **water to remove the**

excess of surfactant

13**and dried in an oven at 105 °C for** 24 **h.** Dried lump of **organo-bentonite was crushed** and **sieved**

through 100/+120 mesh screen. Organo-bentonite that was fabricated by using synthetic surfactant (i.e. DTAB) was labeled as DTA-bentonite, while the one that used saponin was S-bentonite. 2.3. Characterizations of the pristine and organo-bentonite The Brunner–Emmet–Taylor (BET) specific surface area, pore volume, and average pore diameter of the original and organo- bentonite were quantified from nitrogen adsorption–desorption isotherms performed in a

7**Micromeritics ASAP-2010 volumetric sorption analyzer at 77.** 15 K **over a relative pressure (p/p0) range** of **10 5**

to 0.995. Prior to the analyses, the samples were degassed in a vacuum condition at 423.15 K for 24 h. The powder X-ray Diffraction (XRD) patterns of the samples were taken by XRD Philip Expert Diffractometer at 030 kV and 15 mA

6**with a Ni-filtered** Cu Ka **radiation** (k = **1.** 54056 AÅ) **at a step size of 0.01°.**

Fourier Transform Infra Red (FTIR) analysis was also performed to identify the surface functional groups of the benton- ite

7**before and after** modification. **The analysis was conducted in a Shimadzu FTIR-8400S spectrophotometer based on the KBr disk** method **with cumulative scans of 200. The spectra data of the** sam- ples **were recorded in a wavenumber range**

of 4000–500 cm 1. To understand the surface charge behavior of the pristine, syn- thetic organo-bentonite, and natural organo-bentonite in the water,

6**pHpzc (point of zero charge) of**

all samples were analyzed using the

6**pH-drift procedure** [19], **and found to be 2.** 92, 3.12 **and 3.** 08, **respectively.**

Table 1 Physical and chemical information about benzalkonium chloride and triclosan. Benzalkonium chloride Triclosan Molecular structure Physical state Molecular mass (g/mol) Chemical formula Water solubility, 25 °C (g/L) pKa n = 12 White solid 360 [C22H40N]Cl 100 – White solid 289.54 C12H17Cl3O2 12 7.9 2.4. Adsorption experiments Stock solution of benzalkonium chloride (BAC) and triclosan (TCS) were prepared at the concentration of 20 lmol/L by dissolv- ing 7.2 mg of BAC or 5.8

20**mg of** TCS **into a** litre **of distilled water. Adsorption** isotherm **experiments**

of the single system were con- ducted by introducing

6**various mass of adsorbent into a series of conical flasks containing** 100 mL **of** the stock **solution**

(i.e., ben- zalkonium chloride or triclosan solution) with a certain pH value that gave relatively maximum adsorption of both species. The pH value was previously determined at the pH range of 2–9 by an appropriate addition of 0.1 N HCl or NaOH solution into the solu- tion. For the next step, the flasks were shaken at various tempera- ture

1**(303.15 K, 313.15 K and 323.15 K)** within the equilibrium **time**

(1 h) in a Memmert shaking water bath. The solution was then cen- trifuged in a Hettich EBA-20 centrifugal separator at 4000 rpm for 5 min to separate the suspended solid particles. The residual con- centration was measured

6**using a Shimadzu UV/Vis-1700** spectro- photometer **at** the **maximum** wavelength **of**

256.8 nm for BAC and 277.9 nm for TCS. Adsorbed biocide at equilibrium condition

18**per unit** mass **of adsorbent (qe) was calculated using** this **following equation: qe** ¼ ðC0 **Ce**Þ m V ð1Þ **where** qe **are the equilibrium** capacity **of**

BAC or TCS on the adsor- bent (lmol/g), C0 and Ce symbolize the

11**initial and equilibrium con- centrations of** adsorbate **in the solution** (lmol **/L), m is the mass of the adsorbent used (g), and V is the volume of the**

effluent (L). To make

20**a binary** solution **system, a known amount of**

benzalko- nium chloride (7.2 mg, 5.4 mg or 3.6 mg) was added into 1 L of the triclosan solution with a concentration of 20 lmol/L. The binary adsorption experiment was then conducted under the same condi- tion as the single system. The equilibrium concentration of each bio- cide was measured using the multicomponent photometric mode, which is available within the same spectrophotometer apparatus. 3. Results and discussion 3.1. Characteristics of the adsorbents Modification of bentonite using synthetic DTAB and natural saponin surfactant under microwave irradiation certainly change the genuine characteristics of the bentonite. Table 2 encloses the effect of the microwave irradiation power level towards the char- acteristics of the produced organo-bentonite in this study. It is obvious that the specific surface area (SBET) and the total pore vol- ume (VT) of the organo-bentonite are dramatically decreased along with the increase of the microwave power level. These reveal that higher microwave irradiation power facilitates more blockades of some internal pores by means of the organic modifier that may hinder the sorption of N2 molecules. The other analogue evidence of the pore blockade is the diminishing of the sharp N2 desorption hysteresis loop (refer to Fig. S1 of Supporting Information) in the organo-bentonite (i.e., DTA-bentonite and S-bentonite) compared to that of the pristine one. A slight shift on the average pore size diameter approximately about 0.1–0.2 nm in organo-bentonite corresponding to the blockade of micropore by the intercalated or- ganic cation can also be seen in the Barrett–Joyner–Halenda (BJH) pore size distribution curves (inset of Fig. S1). The infrared spectral assignments of pristine and organo- bentonite are enlisted in Table S1. Several typical infrared absorption bands of montmorillonite mineral are similarly observed on the pristine and organo-bentonite. Those bands are O–H stretching, which corresponds to the

1**structural hydroxyl groups located at the surface and along the broken edges**

of tetrahedral sheets, O–H

1 **bending vibrations of** the hydroxyl **group in** adsorbed **water**

molecules,

1 **Si–O stretching, Al–Al–OH bending** vibration, **Al–O–Si bending** vibration, **and Si–O–Si bending**

vibration. These results suggested that the tetrahedral–octahedral–tetrahedral layered sheets of the pristine bentonite remains intact even after the organic modification treatment. The intercalation of organic cation into the interlayer spacing of DTA-bentonite and S-bentonite can be observed by the absorption peaks of C–H stretching at wave- numbers of

1 **2900–2800 cm 1 and C–H bending vibration at** 1500–1400 **cm 1.**

The existence of the acetyl group of S-bentonite in the IR pattern is also observed at 1712 cm 1 . Organic cation insertion may also impart an effect to the basal spacing of the bentonite. As shown in Table 2, reflection peak of the XRD pattern is shifted to the lower angle as the raise of micro- wave power level. In the beginning, a (0 0 1) reflection is seen at the 2h-angle of 6.32°, ascertaining the basal spacing of 1.40 nm while after the modification, the basal spacing is seen to be enlarged up to 2.24 and 2.27 nm at the largest microwave power output for the DTA-bentonite and S-bentonite, respectively. These results indi- cate the formation of pseudotrimolecular layer of alkyl chains, which consists of three alkyl chains forming a parallel interlocked array in the interlamellar space of the bentonite by the cation exchange mechanism between inorganic native cation of the bentonite and organic cation of DTAB or saponin. The existence of other peaks in the XRD patterns, such as quartz (Q), calcite (C), and feldspar (F) remains unchanged during the microwave induced organic modification treatment. Those XRD patterns of pristine and representation of organo-bentonite (DTA-bentonite and S-bentonite) can be found in Fig. S2 of Supporting Information section. Therefore, the surface chemical of the bentonite has been changed from hydrophilic to more organophilic by increasing microwave power level, which is more suitable to adsorb organic compounds. 3.2. Effect of pH to the adsorption The pH of the solution system contributes a crucial influence on the

16 **surface charge** density **of the** bentonite **and the ionization of** Table 2 **The**

characterization results of pristine bentonite and the organo-bentonite produced at the different microwave power output level. Bentonite d(0 0 1) (nm) SBET (m2/g) VT (cm3/g) Average pore diameter (nm) Pristine bentonite DTA-bentonite Power output (W) 450 810 900 S-bentonite Power output (W) 450 810 900 1.40 47.48 0.118 6.11 2.10 14.09 2.22 10.87 2.24 10.47 0.035 6.27 0.027 6.29 0.026 6.32 2.11 2.24 2.27 13.28 9.66 8.86 0.033 6.24 0.024 6.28 0.022 6.31 the adsorbate species, which may affect the removal effectivity. Based on the information in Table 1, the only adsorbate species that can be affected by pH is TCS, which has a pKa value of 7.9, while BAC, which has ionized instantly as a salt in the water, forms a stable

positively charged quaternary ammonium cation that can never be affected by the pH. However, the experimental result on the pH effect, which is described in Fig. 1, shows that the pH of the solution system still has some role in the adsorption of BAC. In Fig. 1, the adsorption of BAC by either pristine or organo-bentonite is seen to increase for the pH value of 2–6 and then reach a plateau at the pH above 7 while the adsorption of TCS shows a relatively stable uptake at the acidic condition and goes down gradually from neutral pH. This trend could be explained by the interaction between the

16**surface charge of the** bentonite **and the** ionic state **of the adsorbate**

at the various pH. At the low pH, to be more precisely below pHpzc of the bentonite, a net repulsion between positively charged silanol and aluminol sites of montmo- rillonite crystallites and the quaternary ammonium cation takes place thus lowering the adsorbed BAC amount while for the TCS molecules, the adsorption is quite high due to the formation of the cation-p interaction between the positively charged surface of the bentonite and partial negative charge of the aromatic ring within the TCS molecular structure. Right on the pHpzc of the ben- tonite, the neutral surface charge of the bentonite is occured, and this may nullify the net repulsion thus slightly increase the removal efficiency of BAC. The adsorption of TCS remains high because of the formation of hydrogen bonding between the alumi- nol and/or silanol with the phenolic group of the TCS molecule. At the higher pH, which is above pHpzc of the bentonite, the surface becomes deprotonated and negatively charged. At this point, the adsorption of BAC rises to its peak due to the electrostatic attrac- tion between the positive charged benzalkonium cation and the negatively charged surface; while the adsorption of TCS maintains its stability by the mechanism of anion-p interaction between the negative surface of the bentonite and partial positive charge of the chlorobenzene group of the TCS molecule. Starting at the pH of 7, a gradual decline on the adsorption of TCS was occurred as the result of the partial ionization of the phenolic group within the TCS structure thus creating the anionic form of TCS that leads to the electrostatic repulsion with the surface of the bentonite. The other remarkable case that can be noticed in Fig. 1 is the higher removal effectivity for the adsorption of TCS on the organo-bentonite and the lower one for the BAC. It can be implied that the exchange of interlayer inorganic cation with surfactant cat- ion is responsible for the occurrence of this phenomenon. In addi- tion to the expansion of the

1**interlayer and basal spacing, the intercalation of** surfactant **cation**

in the clay may induce a unique degree of intermolecular attraction force, such as van der Waals A 20 18 %Removal 16 14 12 Pristine bentonite DTA-bentonite S-bentonite 10 2 4 6 8 10 pH force with specific hydrophobic molecule, for example, TCS molecule in this study, which gives beneficial properties to- wards its adsorption process in spite of the constriction of its initial specific surface area and pore volume. On the contrary, BAC mole- cules, which may also serve as the organic cation in the solution sys- tem, have lost the most of possibility to form strong electrostatic attraction force due to the prior surfactant cation intercalation, leav- ing the weak van der Waals force as the single force that develops the adsorption. This force diminution leads to the abatement of its adsorption on the surface of organo-bentonite. However, it can be seen from Fig. 1 that the depression of the BAC removal is not so sig- nificant as the previous theory may reveal. This could be explained by the propensity of van der Waals attraction force that becomes larger for a larger molecules. The greater molecular weight of BAC compared to TCS contributes a greater van der Waals attraction force that may withstand the rate of the removal capacity reduction due to the loss of strong electrostatic force. 3.3. Adsorption isotherms of a single component Up to date, there are many available

adsorption isotherm mod- els, which posses a number of parameters that can be used to describe the equilibrium adsorption of certain adsorbate. Among all isotherm equation, Langmuir and Freundlich isotherm equation have satisfactorily used for the evaluation of many adsorption sys- tems. In most of the recorded adsorption studies, Langmuir iso- therm has been well known to be superior against Freundlich isotherm in representing adsorption equilibria data since it fea- tured the Henry's law limit at low concentration and possesses sat- uration capacity at high concentration domain. In contrast to the Langmuir isotherm, the lack of fundamental thermodynamics con- sideration in pure empirical Freundlich isotherm equation may form an infinite adsorption as the increasing equilibrium concen- tration value. Thereby, Langmuir may offer the

> 1**simplest and most useful model for**

the best understanding of the both

> 1**physical and chemical adsorption in gas and liquid systems.**

The Freundlich equation was developed empirically for express- ing an isothermic

> 1**quantity of gas adsorbed by unit mass of** adsor- bent **with pressure.**

The equation can be written as follows: qe ¼ KF C1e=n ð2Þ where KF is the Freundlich constant reflecting the adsorption affinity [(lg/g) (L/lg) n or (lmol/g) (L/lmol)

> 1**n] and n is a dimensionless intensity** index of **the surface heterogeneity degree. The**

> 1**adsorption favorability can be** determined by judging **on the n values,** whether it **favorable (2**< n < 10), **moderately difficult**

B 22 20 18 %Removal 16 14 Pristine bentonite 12 DTA-bentonite S-bentonite 10 2 4 6 8 10 pH Fig. 1. Effect of the pH on the adsorption of benzalkonium chloride (A) and triclosan (B) onto the pristine bentonite, DTA-bentonite and S-bentonite (m adsorbent = 0.1 g, T = 303.15 K, t = 1 h). (1 < n < 2) or poor (n < 1). The n value that is higher than 10 indi- cates non-reversible behavior of the adsorption isotherms. On the other side, Langmuir equation is essentially postulated from a simple equilibrium kinetic mechanism theoretical basis with several underlying assumptions, which state that the surface of the adsorbent has a fixed number of uniform site with identical adsorption enthalpy and affinity; the adsorbed molecules do not interact; the adsorption occurs through the same mechanism, and the adsorbed molecules can only form a monolayer on the out- er surface of adsorbent. The mathematical expression of Langmuir isotherm is shown by the following equation: qe ¼ qm 1 þKLKCLeCe ð3Þ where qm

1**is the Langmuir constant** defining the **maximum sorption capacity when the solid is covered with a monolayer** (lg **/g or** lmol **/g)**

13**and KL is the adsorption affinity constant** (L/lg **or L/**

lmol). Those constants also can be used to determine the practical limit of the adsorption capacity and aid the identification of relative adsorption performance. By knowing those adsorption parameters, a dimensionless constant expressed by RL, also

1**can be calculated using a** mathematical equation **proposed by Weber and Chakravorti**

[20]: RL ¼ 1 ð4Þ 1 þ KLC0 where C0 is the initial concentration of adsorbate in the solution. The value of RL is useful to

22**indicate the** adsorption **nature to be favorable** (0 <**RL < 1), unfavorable (RL > 1), linear (RL = 1), or**

highly favorable and non-reversible (RL = 0). Adsorption affinity (KF and KL) and the other parameter (qm for Langmuir isotherm or n value for Freundlich isotherm) may pro- vide a glimpse of light to understand the occurring adsorption mechanism. At this present, there are three possible adsorption mechanism: physisorption, chemisorption or combination thereof. To distinguish the mechanism, quantification of adsorption heat is generally done. The distinct difference can be observed on the physisorption and chemisorption while the combination appears as the transitional value of those two. This thermodynamical prin- ciple, therefore, allows the temperature to affect the adsorption process. Naturally, the adsorbed amount of adsorbate in physisorption shows a decreasing behavior towards the temperature increase, whereas on the chemisorption, the contrary result is found until a certain temperature is reached. This tendency may arise because of the fundamentally different existed bond formation between the physisorption and chemisorption, the weak intermolecular bond and strong chemical bond (i.e., ionic or covalent bond) formation. While the adsorption is usually an exothermic process due to reduction of surface entropy, higher temperature may lead to the desorption as prescribed by the principle of Le Chatelier but a fair requirement of activation energy in chemisorption phenomena, which is needed to be surpassed to form a chemical bond, promote the system to absorb a certain extent of thermal energy thus main- tains the adsorption to increase spontaneously. Based on that, physisorption can be typically characterized by a decrease on the values of adsorption parameters along with the rising temperature while the chemisorption generally shows the opposite. The correlation between experimental adsorption equilibrium data and the isotherm model was analyzed by applying nonlinear regression fitting in the SigmaPlot 11.0 software (Systat Software Inc.). Fig. 2 depicts the comparison of the fitting using

1Freundlich and Langmuir isotherm **models** on the **single adsorption** experiment **data**

while the

17values of the fitted parameters **are** enlisted **in Table 3.** From **the adsorption**

parameters evaluation, it is obvious that the values of constant n show an erratic pattern and instead of increasing surface heterogeneity due to the intercalation of surfac- tant organic cation, the magnitude of constant n for organo- bentonite is lower than that of the pristine-bentonite. In addition to that, the assessment of R2 values also indicate that

1Langmuir isotherm describes experimental data better than Freundlich isotherm.

Therefore, compared to Freundlich isotherm, Langmuir isotherm prevails as an excellent way to evaluate adsorption equilibria data for single component system. As presented in Table 3, the adsorption affinity (KL) and maxi- mum adsorption capacity (qm) onto the pristine and organo-ben- tonite are diminishing with increasing temperature. This indicates that higher temperature facilitates the solubilization of adsorbate molecules in the solution thus preventing the adsorp- tion. In addition, this phenomenon reveal that adsorption of BAC and TCS mainly occurs due to the physisorption. Although the adsorption of BAC onto the pristine bentonite theoretically takes place by the electrostatic attraction, which is identical to the chemisorption, the physisorption appears as the governing adsorp- tion mechanism. This can be analyzed from the possible bonding strength that can be formed between the small amount of organic cation (dilute BAC concentration) and inorganic oxide anion on the montmorillonite surface. In dry montmorillonites, the bonding force between exchangeable cations and the montmorillonite sheets

14is relatively strong, but **when** the **wet conditions occur, water is drawn into the interlayer space between sheets and causes the clay to swell dramatically**

thus weakens the bonding force [21]. All RL values assert that the adsorption of BAC and TCS are favored over the temperature range of this study. 3.4. Thermodynamic parameters of the single system Thermodynamics aspect is useful to reveal the precise nature of the adsorption system. Thermodynamics parameters,

1such as activation energy (Ea, **kJ/mol), the Gibb's free energy change (DG°, kJ/mol), standard enthalpy change (DH°, kJ/mol), standard entropy change (DS°, kJ/mol K), and isosteric heat of adsorption** (DHx, **kJ/mol)**

cannot be obtained directly from the experiment but can be calculated from the adsorption data. The Gibb's free en- ergy change has already known as the most fundamental

> 1criterion for the spontaneity of a process and

its relation to the adsorption can be defined by the following equation: DG ¼ RT ln KD ð5Þ

> 1where R is the ideal gas constant (8.314 10 3 kJ mol 1 K 1), T is the temperature (K), and KD is the linear sorption distribution coef- ficient. The values of

KD are simply obtained as the intercept of a straight line plot of ln (qe/Ce) versus Ce (figures are not shown), fol- lowing Khan and Singh method [22]. The correlation of constant KD and Gibb's free energy change then can be reformed to an expres- sion of

> 1standard enthalpy change and standard entropy change by applying the classical van't Hoff

equation: lnKD ¼ DS R DH R 1 T ð6Þ where the value of DH° and DS° are the slope and intercept of a lin- ear fitting of ln KD vs. 1/T, respectively.

> 1Table 4 shows the values of the thermodynamic parameters for the adsorption of BAC and TCS. The

negative values of the Gibb's free energy change exhibit that all adsorption occur spontaneously. The free energy change of adsorption (DG°) was found to decrease with an increase in temperature indicating that higher tempera- ture causes the adsorption process to be easier even though the DH° value features a negative sign, which refers to an exothermic behavior of the adsorption process. This could be thermodynami- cally explained by the positive value of DS° that reflects the strong Fig. 2.

> 1Freundlich and Langmuir model fittings towards single adsorption data of benzalkonium chloride and

triclosan on the pristine bentonite, DTA-bentonite and S-bentonite. confinement of adsorbate species towards the sorption sites on the surface

21**and the** increased **randomness at the solid-solution** inter- face **during the adsorption process.** In addition, **the** increasing mobility **of the** adsorbate molecules in **the**

solution with the tem- perature rise may intensify the adsorption chance of the adsorbate towards the surface. In agreement with the evaluation of adsorption isotherm parameters, the magnitude of the negative Gibb's free energy change exhibits

15**that the adsorption of** TCS **onto organo-bentonite** solid **is**

preferred rather than its adsorption onto the pristine ben- tonite at a given temperature while the adsorption of BAC is more favored on the pristine bentonite. Furthermore, the DH° value indi- cates that the adsorption process truly belongs to physisorption (i.e., 20.9 kJ/mol), is not chemisorption (i.e., 80–200 kJ mol 1). These facts confirm that the thermodynamic parameters may have a strong correlation towards the adsorption isotherm parameters; therefore the parameters may be harnessed further in the model- ing of multicomponent isotherm. 3.5. Adsorption isotherms of a binary system Proper model of multi-component adsorption equilibria

2**data may provide a complete description of the adsorption process in the practical application, yet, it is a challenging task to build it.** Multicomponent **adsorption**

is mainly controlled by the com- petition

1**phenomena in the solution and/** or **the** interface of the **solid** and the **solution,**

which is hard to be incorporated to the isotherm equation due to its complexity. Thereby,

2**most of the available empirical or semi-empirical adsorption models often lack of the theoretical basis and may not be able to accurately predict the adsorption behavior.**

It is undeniable too that

1**to correlate multicomponent adsorption equilibria data** Table 3 **The**

adsorption parameters of

1**Freundlich and Langmuir** isotherm for **single adsorption of**

benzalkonium chloride and triclosan.

6**Adsorbent Adsorbate T (K)** Freundlich **parameters** Langmuir **parameters** KF (lmol **/g) (L/**

lmol) n n R2 qm (lmol/g) KL (L/lmol) R2 RL Pristine bentonite Triclosan Benzalkonium chloride DTA-bentonite Triclosan Benzalkonium chloride S-bentonite Triclosan Benzalkonium chloride 303.15 313.15 323.15 303.15 313.15 323.15 0.4419 0.4336 0.4228 0.7548 0.7578 0.7603 303.15 313.15 323.15 303.15 313.15 323.15 0.4767 0.4649 0.4565 0.7082 0.7072 0.7077 303.15 313.15 323.15 303.15 313.15 323.15 0.4894 0.4861 0.4850 0.7098 0.7081 0.7073 1.2756 1.2786 1.2756 1.7329 1.7455 1.7605 0.85 0.84 0.84 0.98 0.98 0.97 1.2706 1.2669 1.2645 1.7567 1.7578 1.7591 0.87 0.86 0.86 0.97 0.97 0.97 1.2704 1.2695 1.2697 1.7571 1.7561 1.7557 0.87 0.87 0.87 0.97 0.97 0.97 11.6136 11.4123 11.1817 5.9914 5.9696 5.9331 0.0306 0.0303 0.0302 0.0939 0.0938 0.0937 12.3287 12.3215 12.2803 5.6478 5.6394 5.6389 0.0315 0.0307 0.0302 0.0902 0.0901 0.0901 12.5316 12.5076 12.5028 5.6528 5.6495 5.6448 0.0319 0.0318 0.0317 0.0904 0.0902 0.0902 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.9999 0.9999 0.9991 0.3474 0.3477 0.3479 0.6135 0.6195 0.6231 0.3566 0.3568 0.3569 0.6103 0.6114 0.6121 0.3561 0.3566 0.3566

1**Table 4 Thermodynamic parameters for** benzalkonium chloride **and** triclosan adsorption **in single systems**

onto bentonite and TTA-bentonite. Adsorbent T (K) Benzalkonium chloride Triclosan

1**DG° (kJ/mol) DS°** (kJ **/mol K) DH° (kJ/mol) DG° (kJ/mol) DS°** (kJ **/mol K) DH° (kJ/mol)**

Pristine bentonite DTA bentonite S bentonite 303.15 313.15 323.15 303.15 313.15 323.15 303.15 313.15 323.15 4.7175 4.8758 5.0341 0.0158 0.0821 4.4773 4.6127 4.7481 0.0135 0.3732 4.6906 4.8452 4.9998 0.0155 0.0359 4.5133 4.6518 4.7901 0.0138 0.3178 4.6919 4.8456 4.9994 0.0154 0.0313 4.5260 4.6730 4.8201 0.0147 0.0676 satisfactorily an advanced computer is required to perform a complex algorithm such as those in the

1**ideal adsorption solution theory (IAST) and its**

modified forms,

1**fast-IAS and real** adsorp- tion **solution theory**

(RAST).

1**On the other hand, extended-Langmuir** offers the **simple**

isotherm models that adequately built on the thermodynamic and kinetic basis to describe multicomponent adsorption equilib- ria. Competitive adsorption in the multicomponent system of this study is simply described by the extended Langmuir isotherm in these following mathematical equations: qe;1 ¼ 1 þ KqLm;1;1 CKe;1L;1þ KCLe;;21 qe;2 ¼ 1 þ KqLm;1;2 CKe;1L;2þ KCLe;;22 Ce;2 Ce;2 ð7Þ ð8Þ where qm,1 and qm,2 are the maximum sorption capacity of adsor- bent for TCS and BAC, while KL,1 and KL,2 are adsorption affinity constants of TCS and BAC, respectively. All Langmuir parameters (qm,1, qm,2, KL,1 and KL,2) are obtained from single adsorption iso- therm data of each component and introduced to Eqs. (7) and (8) for calculating the predicted qe values of each component. To as- sess the fitting, an error calculation between predicted and mea- sured qe values is performed. Although extended-Langmuir model has been reported successfully in predicting liquid phase binary adsorption equilibrium data just

1**based on the** minimal **error** be- tween **predicted and measured,**

such approach still lacks in reflecting the involvement of the competition between adsorbate molecules

1**in the solution and on the active surface sites.**

There- fore, a few slight mathematical modification should be proposed

1**to improve the accuracy of predictions and theoretical** basis **of the extended-Langmuir model.**

1**In the binary** adsorption, **the active sorption sites**

on the solid surface are occupied by two kinds of adsorbate molecule with a specific coverage reflecting its competition effect. The competi- tion may arise until a certain component prevails from the other, but the

1**total monolayer surface coverage by both** components **should not exceed unity**

as postulated by the basic Langmuir equation. The competition then can be depicted by natural loga- rithmic plots that reflect the equilibrium condition of the single adsorption and the competition itself. Therefore, the binary max- imum sorption capacity in the equilibrium condition can be as- sumed

2equal to the log mean value of each maximum sorption capacity of the solute in single adsorption **system**

that can be formulated mathematically as follows: qm;2ðsingleÞ qm;1ðsingleÞ qm;bin ¼ ln qqmm;;21ðð ssiinngglleeÞ�þ ; with qm;2ðsingleÞ > qm;1ðsingleÞ ð9Þ The affinity constant (KL) measures the attraction strength of the adsorbate molecule towards the surface active site that is the higher the affinity, the adsorbate molecules that tend to cov- er the surface.

6Since the competition of **adsorbate** components **in** the **binary** adsorption **system** existed, **the** affinity **of**

each Table 5 Sum of square error (SSE) values for the extended Langmuir and its modified model of the binary adsorption of benzalkonium chloride and triclosan at various mixtures and temperatures. Adsorbent Initial concentration (lmol/L) T (K) Extended Langmuir Modified extended Langmuir Co,triclosan Co,benzalkoniumchloride SSEtriclosan SSEbenzalkoniumchloride SSEtriclosan SSEbenzalkoniumchloride Pristine bentonite 20 DTA-bentonite S-bentonite 20 20 20 20 20 20 20 20 20 20 20 20 20 20 20 20 20 20 20 20 20 20 20 20 20 15 10 20 15 10 20 15 10 303.15 313.15 323.15 20 15 10 20 15 10 20 15 10 303.15 313.15 323.15 20 15 10 20 15 10 20 15 10 303.15 313.15 323.15 10.440970 20.133187 38.450752 9.814283 19.076506 36.571842 9.230475 18.035454 34.781394 15.020413 27.499932 50.375994 14.960781 27.234831 50.000504 14.808665 27.122724 49.426541 14.104274 25.987715 47.568724 13.678340 25.186422 46.456712 13.314371 24.536537 45.318928 0.157378 0.237884 0.759162 0.172429 0.196068 0.693595 0.197028 0.163540 0.625388 0.311061 0.794490 1.372068 0.289328 0.755964 1.318352 0.310190 0.770065 1.274867 0.247219 0.681162 1.258606 0.231163 0.660619 1.223793 0.238611 0.640252 1.198186 0.000284 0.000151 0.000119 0.000161 0.000190 0.000117 0.000289 0.000171 0.000242 0.000310 0.000353 0.000145 0.000198 0.000179 0.000144 0.000270 0.000134 0.000245 0.000269 0.000378 0.000160 0.001198 0.000245 0.000772 0.000249 0.000111 0.000116 0.0003886 0.000298 0.000260 0.000350 0.000295 0.000394 0.000155 0.000201 0.000242 0.000430 0.000341 0.000241 0.000149 0.000445 0.000423 0.000117 0.000273 0.000279 0.000177 0.000115 0.000150 0.001686 0.000588 0.001807 0.000161 0.000281 0.014387 component should be weaker than those

1in the single adsorption system making **the** direct use **of**

the single adsorption affinity constant to be invalid. Therefore, the KL from single isotherm data could be corrected by the equations below: KL;1ðbinÞ ¼ KL;1ðsingleÞ DG1ðsingleÞ C0;1 DG1ðsingleÞ C0;1 þ DG2ðsingleÞ C0;2 ! KL;2ðbinÞ ¼ KL;2ðsingleÞ DG2ðsingleÞ C0;2 DG1ðsingleÞ C0;1 þ DG2ðsingleÞ C0;2 ! ð10Þ ð11Þ In Eqs. (9) and (10), the competitive behavior of the adsorbate components are expressed

2as the ratio of the multiplication value between standard Gibb's free energy change and initial concentra- tion **of certain** adsorbate **to the summation of those values for both**

components. It can be noticed that in Eqs. (10) and (11), the

> **2adsorption affinity of an adsorbate species in the binary adsorption system is reduced from its adsorption affinity in the single** adsorp- tion **system** by **the presence of** adsorbates **competition.**

Introduc- tion of the

> **17initial concentration of the adsorbate** species **in** this equation represents **the** increasing tendency **of**

adsorption affinity or the shifting act of equilibrium condition towards the adsorption along with the increasing initial concentration, which is in confor- mance with the Le Chatelier's principle. Here, the standard Gibb's free energy is constrained to be less than or equal to zero, which also means that only the spontaneous one is concerned to the com- petition phenomena. Substitution of Eqs. (9)–(11) into Eqs. (7) and (8) gives the following mathematical expressions: qe;1ðbinÞ ¼ 1 þ KL;1ðqbmin;ÞbinCeK;1Lðb;1inðbÞinþÞ KCL;e2;1ðbðbininÞÞ Ce;2ðbinÞ ð12Þ qe;2ðbinÞ 1 þ KL;1ðqbmin;ÞbinCeK;1ðLb;2inðbÞinþÞ KCLe;2;2ðbðbininÞÞ Ce;2ðbinÞ ¼ ð13Þ Eqs.

> **1(12) and (13) are** assigned **as the** modified **extended- Langmuir** isotherm **model**

in this study, and its prediction per- formance is tested in terms of the sum of square error towards the experimental binary adsorption isotherm data. The quantifi- cation of adsorbed equilibrium capacity and its sum of square error (SSE) against the experimental data are performed by Microsoft Office Excel 2007. To observe the improvisation, the SSE values of the predicted equilibrium adsorption capacity from the original extended Langmuir model are also counted. The result of the SSE quantification is summarized in Table 5, while some representation plots that show the aptness between the calculated and experimental adsorption data are illustrated in Fig. 3. The incorporation of the

> **2log mean value of maximum adsorption capacity and the Gibb's free energy ratio in the extended Langmuir model gave better representation of the experimental data than the original extended Langmuir model**

as indicated in Table 5 and Fig. 3. Judging from the SSE, original extended Langmuir equation produces relatively small error only on the adsorption of BAC that can be presumed as its limited well-reputed capability in performing binary adsorption data prediction of a component with a high affinity relative to its molecular competitor while the modified extended Langmuir is capable to predict both adsorbates system due to the incorpora- tion of the thermodynamical favorability ratio, which may give a proportional relative affinity of an adsorbate to the adsorbent surface. In the real experimental data view, the competition be-

tween adsorbate species during the adsorption was indicated by the decreasing adsorbed amount, whereas the presence of either BAC or TCS decrease the uptake capacity of the other relative to the single adsorption data. However, it should be noticed that the significance decrease on TCS uptake is observed on the organo-bentonite (i.e., S-bentonite and DTA-bentonite), while Extended Langmuir Original Modified A B C Fig. 3. The aptness of original and

> 1**modified extended Langmuir** models **against** experimental **binary adsorption**
>
> **data of**

benzalkonium chloride (BAC-) and triclosan (TCS-) at 303.15 K onto S-bentonite using. (A) Co benzalkonium chloride = 20 lmol/L, Cotriclosan = 20 lmol/L, (B) Co benzalkonium chloride = 15 lmol/L, Co triclosan = 20 lmol/L, (C) Co benzalkonium chloride = 10 lmol/L, Co triclosan = 20 lmol/L. the decreasing the BAC uptake is seen on the pristine bentonite. This could be possible because of the nature of each adsorption affinity, that is, a strong adsorption affinity of certain species on either pristine or organo-bentonite contributes an ability to pre- serve its uptake in the middle of molecular competition. 4. Conclusions Removal of micro-pollutant compounds, namely, benzalkonium chloride (BAC) and triclosan (TCS) from synthetic wastewater was studied using pristine and organo-bentonite. The organo-bentonite was modified with two kinds of surfactant: synthetic DTAB surfac- tant and natural saponin surfactant under microwave irradiation. Microwave irradiation contributes positive effect on the intercala- tion of organic cation that can be seen by interlamellar space broadening and pore blockage. The uptake capacity of the BAC is at its greatest point when it is adsorbed by the pristine bentonite while the maximum adsorption of TCS is achieved by applying the organo-bentonite. The optimum pH for both adsorption is lied on the slightly acidic condition (pH of 6). The Langmuir model for

> 2**single component adsorption** and **the** thermodynamically modified **extended**
>
> **Langmuir model** are able **to** represent **the**

single and bin- ary component adsorption data, respectively. Acknowledgement

> 3**Appendix A. Supplementary material Supplementary data associated with**
>
> **this article can be found, in the online version, at**
>
> **http://dx.doi.org/10.1016/j.cej.2013.**

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