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3 Adsorption of Acid Blue 129 from Aqueous Solutions onto Raw and Surfactant-modified Bentonite: Application of

Temperature- dependent Forms of Adsorption Isotherms Yesi, Fiona Patricia Sisnandy, Yi-Hsu Ju, Felycia Edi Soetaredjo and Suryadi Ismadji

6 Reprinted from Adsorption Science & Technology 2010 Volume 28 Number 10 Multi-Science Publishing Co. Ltd. 5 Wates Way, Brentwood, Essex CM15 9TB, United Kingdom Adsorption of Acid Blue 129 from Aqueous Solutions

onto Raw and Surfactant-modified Bentonite: Application of Temperature-dependent Forms of Adsorption Isotherms Yesi^{1,2}, Fiona Patricia Sisnandy^{1,2}, Yi-Hsu Ju¹, Felycia Edi Soetaredjo² and Suryadi Ismadji^{2*}

7(1) Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, sec. 4 Keelung Rd., Taipei, 106 Taiwan. (2) Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia.

(Received 25 September 2010; revised form accepted 15 December 2010) ABSTRACT: Modification of raw bentonite from Ponorogo, East Java, Indonesia by microwave irradiation using cetyltrimethylammonium bromide (CTAB) was studied. The adsorption capabilities of raw bentonite and its modified form were examined through their use in the removal of Acid Blue 129 from aqueous solution. The adsorption isotherm and kinetic experiments were conducted at four temperatures (25, 30, 40 and 50 °C). The fitting of the corresponding experimental data was tested using the temperature-dependent forms of the Langmuir, Freundlich, Sips and Toth equations. The Sips equation gave a better representation of the adsorption data, together with reasonable values of the fitted parameters. Two well-known kinetic models, the pseudo-first- and pseudo-second- order, were used to correlate the adsorption kinetic data, with the pseudo-first-order

model giving the better results. Both physical and chemical adsorption mechanisms occurred during the adsorption process, with the main controlling mechanism being physical adsorption. INTRODUCTION Thousands of synthetic dyes have been produced for various kinds of purposes. These synthetic dyes are available in a vast range of colours and they possess better properties than natural dyes. Most synthetic dyes are synthesized from benzene and its derivatives. Some synthetic dyes are quite safe, but some are extremely toxic (carcinogenic) to the environment. Synthetic dyes are widely used to colour fabrics, and in every fabric-dyeing process a solution of dye in water is used into which the fabrics are dipped and then washed. Most countries have regulations that require fabric factories to treat dye effluent before it is discharged into the water system. However, for small factories such as home industries which are widely found in Indonesia and other developing countries, building facilities to treat dye-containing wastewater would be very expensive, and the easiest and cheapest way to handle dye effluents in their cases is to dump them into a river. Due to the complex chemical structures of these synthetic dyes, they are usually resistant to breakdown by chemical, physical and biological treatments. Furthermore, any degradation by such treatments often produces a small amount of toxic and carcinogenic products (Eren and Afsin 2008). It is now recognized that adsorption using a low-cost adsorbent provides an effective technique for removing non-biodegradable dyes from aqueous streams, due to its

6*Author to whom all correspondence should be addressed. E-mail:

suryadiismadji@yahoo.

com. 848 Yesi

2et al./Adsorption Science & Technology Vol. 28 No. 10 2010

efficiency, high adsorption capacity and applicability in a large-scale operation (Aksu et al. 2008; Ziólkowska et al. 2009; Guiza et al. 2004; Paula et al. 2009). Bentonite

40is widely used in many fields of material science technology (Zhou 2010) and the utilization of this clay material for the treatment of wastewater containing

dyes is receiving increasing attention, since it offers a very attractive method for pollution remediation. In addition, bentonite is plentiful, inexpensive and available in many countries. Indonesia has a huge bentonite reserve located in several provinces. However, studies regarding the utilization of bentonite originating from Indonesia for the treatment of dye effluents are still very scarce. In the present study, raw bentonite from Ponorogo (East Java, Indonesia) was used as the raw material for organobentonite preparation. A cationic surfactant, cetyltrimethylammonium bromide (CTAB), was employed as the modifying agent. The relevant equilibrium adsorption data provide the most important information for understanding a given adsorption process, since these are needed for the design and analysis of adsorption systems (Ismadji and Bhatia 2000). Authors of most studies on liquid-phase adsorption, especially the removal of organic compounds or heavy metal ions using various kinds of adsorbents, have only fitted the corresponding experimental results with isotherm equations obtained at a single temperature. It is also important that the experimental data obtained at various temperatures should be correlated by different isotherms equations. In the present study, several temperature-dependent adsorption models (Langmuir, Freundlich, Sips and Toth) have been employed to correlate the experimental adsorption data obtained. The temperature-dependent forms of these equations were originally developed for gas-phase adsorption processes; here, they

19have been used to the correlate the experimental data for the

adsorption of the dye

11Acid Blue 129 from the aqueous phase onto

an organobentonite. The validity and physical meaning of the equation parameters employed for correlating the adsorption experimental data has also been discussed. TEMPERATURE-DEPENDENT FORMS OF ISOTHERM MODELS Adsorption

37equilibrium data, commonly known as adsorption isotherms, are the basic requirements for the design of adsorption systems. These data provide fundamental physicochemical information for evaluating the applicability of

an adsorption process as a unit operation as well as for design purposes. For optimizing the design of an adsorption system,

8 It is important to establish the most appropriate correlation for the experimental equilibrium curve. Hence, the correlation of equilibrium data using either a theoretical or an empirical equation is essential for the interpretation of the adsorption

process and for predicting the extent of adsorption. Different adsorption models have been developed and applied successfully for correlating adsorption data for various systems. Most of these models were originally developed for gas-phase adsorption data, but later these models were extended to liquid-phase adsorption processes. Since the adsorption of an adsorbate onto an adsorbent is affected by temperature, it is important that the isotherm models employed should also possess temperature-dependent forms. Four adsorption isotherm models together with their temperature-dependent forms were used in the present study. They were the Langmuir, Freundlich, Toth and Sips isotherms. The Langmuir isotherm The Langmuir adsorption isotherm has been successfully applied to many real sorption processes (Almeida et al. 2009) and

8 is most widely used for the adsorption of pollutants from liquid solutions

due to its simplicity. The

4 Langmuir model was derived on the basis of three assumptions and may be written in the form: $q_e = \frac{q_{max} C_e}{1 + K_L C_e}$

1 + $K_L C_e$

4(1) where q_{max} is the maximum amount of adsorbate adsorbed by the adsorbent to achieve complete monolayer coverage of the adsorbent surface (mmol /g) and K_L is the Langmuir affinity constant (?/mmol). The variables q_e (mmol /g) and C_e (mmol/?) are the amounts of dye adsorbed per unit weight of adsorbent and the equilibrium concentration, respectively. The parameter q_{max} is assumed to correspond to saturation of a fixed number of identical surface sites and

should logically be independent of the temperature. In real situations, however,

16 q_{max} is variable and depends on the adsorption temperature. This means that the

5 saturation limit is associated with the surface functional groups rather than with a set of identical surface sites.

The

16 saturation limit can be affected by several factors, such as the number of sites on the adsorbent surface and the affinity between the adsorbate and the

adsorbent (Febrianto et al. 2009). The parameter K_L , which is related to the adsorption energy, can also be used to determine the type of adsorption process involved. If the value of K_L decreases with increasing temperature, this means that an exothermic adsorption process has occurred and that the adsorption mechanism is dominated by physical adsorption. The reverse trend indicates the occurrence of an endothermic adsorption process with chemical adsorption dominating.

5 In physical sorption, the bonding between the adsorbate and the active sites on the adsorbent weakens at higher temperature; in contrast,

in chemical sorption processes the bonding becomes stronger with increasing temperature (Febrianto et al. 2009). The temperature dependence of the Langmuir isotherm parameters, q_{\max} and K_L , may be expressed by the following equations: $q_{\max} = q_{0\max} \exp[\delta(T_0 - T)]$ (2) and $K_L = K_0 \exp\left(\frac{E}{R(T - T_0)}\right)$ (3) where $q_{0\max}$ (mmol/g) is the maximum adsorption capacity, δ

28 is a constant representing the temperature coefficient of expansion of the adsorbate, K_0 is the

Langmuir affinity constant at the reference temperature, E is the heat of adsorption and T_0 is the reference temperature (Ismadji and Bhatia 2001; Do 1998). The Freundlich isotherm The Freundlich equation is the earliest known adsorption equation and is amongst one of the most widely used isotherms for describing adsorption equilibrium. The isotherm assumes that the adsorbent surface sites exhibit a spectrum of different binding energies (Almeida et al. 2009). Although the Freundlich isotherm is basically an empirical equation, it is often useful as a means of data description. The Freundlich isotherm can also be employed to predict adsorption 850 Yesi

2et al./Adsorption Science & Technology Vol. 28 No. 10 2010 equilibrium data and

also to describe heterogeneous systems and reversible adsorption processes, since it is not restricted to the formation of an adsorbate monolayer (Özcan et al. 2005). It is capable of describing the adsorption of organic and inorganic compounds onto a wide variety of adsorbents (Febrianto et al. 2009). The Freundlich isotherm is generally found to be better suited for characterizing multi-layer adsorption processes. It may be expressed by the relationship: $q_e = K_F C_e^{1/n}$ (4) where K_F (mmol/g)(mmol)⁻ⁿ and n are the Freundlich constants, K_F indicates the Freundlich adsorption capacity, while n indicates the adsorption intensity and can also characterize the heterogeneity of the system. The quantities K_F and n in equation (4) are temperature-dependent. On the basis of the assumption that a solid surface is composed of sites having a distribution of surface adsorption potential the temperature-dependent forms of the Freundlich isotherm (Do 1998) may be written as: $K_F = K_F^0 \exp\left(\frac{A_0}{RT}\right) - \alpha RT$ (5) and $1/n = \frac{A_0}{RT} - \alpha$ (6) where K_F^0 is the adsorption capacity at the reference temperature T_0 and α/A_0 is a constant. Equations (5) and (6) suggest that K_F and n are not independent. For most practical systems, the parameter n is usually greater than unity; hence, equation (6) indicates that the characteristic surface adsorption energy is greater than the molar thermal energy, RT (Do 1998). The Sips equation The

24 Sips isotherm is a combination of the Langmuir and Freundlich expressions. It was developed for predicting adsorption in heterogeneous systems by circumventing the limitation of increasing adsorbate concentration associated with the Freundlich isotherm model

(Do 1998; Abramian and El-Rassy 2009; Sips 1948). This equation has a finite limit. Thus, when the concentration is sufficiently high, the equation may be written as: $q_e = q_{\max} (K_S C_e)^{1/n} / [1 + (K_S C_e)^{1/n}]$ (7) where K_S is the Sips constant which is related to the affinity (mmol^{1/n})^{1/n} and n characterizes the heterogeneity of the system. If

15 n is unity, equation (7) becomes the Langmuir equation applicable for ideal surfaces (Do 1998). In the

Sips equation, the temperature dependency is represented via q_{\max} , K_S and n . The temperature-dependent form of q_{\max} may be expressed by equation (2), while K_S and n have the following forms: $K_S = K_S^0 \exp\left(\frac{E}{R(T - T_0)}\right)$ (8) and $n = \frac{1}{1 - n_0 + \eta} \left[1 - \frac{E}{RT_0}\right]$ (9) The magnitude of K_S^0 in equation (8) is a measure of the affinity between the adsorbate and the adsorbent at the reference temperature T_0 , while n_0 and η represent the magnitude of

15 n at the same reference temperature and a constant, respectively (Do 1998). The Toth equation The

Toth equation follows Henry's law at very low concentrations and possesses a finite saturation limit at high concentrations. This model was developed on the basis of potential theory and provides a good description of many systems with sub-monolayer coverage (Do 1998): $q_e = (K_{Th} q_{\max} + C_e C_{Te})^{1/t}$ (10) where K_{Th} [(mmol

18/?]t is the Toth isotherm constant representing the

affinity coefficient, while t characterizes the heterogeneity of the system and is a dimensionless constant which is

18 usually less than unity. The parameters K_{Th} and t are specific to particular adsorbate/adsorbent systems. The greater the deviation of t from unity, the more heterogeneous is the system (Do 1998). The

parameters K_{Th} and t are also temperature-dependent. The temperature-dependent forms of the Thoth parameters are: $K_{Th} = K_{Th0} \exp \left[\frac{E}{R(T - T_0)} \right]$ and $t = t_0 + \frac{1}{1 + T_0/T}$ (11) (12) where K_{Th0} is the affinity coefficient at the reference temperature T_0 , t_0

15 is the parameter t at the same reference temperature and η is a constant parameter.

MATERIALS AND METHODS Materials The

39 bentonite used in this study was obtained from a bentonite mine located in

Ponorogo,

26 East Java, Indonesia. Elemental analysis of the bentonite via an atomic absorption flame emission spectrophotometer (AA-6200, Shimadzu) gave the following results:

Al₂O₃, 30.71%; SiO₂, 48.22%; FeO, 3.14%; CaO, 3.76%; MgO, 0.56%; K₂O, 0.17%; Na₂O, 1.42%; MnO, 0.4%. In order to remove its organic impurities, the raw bentonite was treated by immersing it in a 30% solution of hydrogen peroxide for 24 h. The excess hydrogen peroxide was removed by heating the mixture at ca. 100 °C. The resulting purified raw bentonite was separated from the mixture and dried at 110 °C

3 for 24 h. The dried raw bentonite was then crushed using a Janke & Kunkel micro-hammer mill to obtain powdered raw bentonite with particle

sizes in the range 100–120 mesh. The

39 cation-exchange capacity (CEC) of the raw bentonite was determined via the ASTM C837-99 procedure

when a value of 57 mequiv/100 g was obtained. A.R. grade cationic surfactant (CTAB) and hydrogen peroxide were purchased from Merck while Acid Blue 129 dye (C₂₃H₁₉N₂NaO₅S) was obtained as the commercial grade. These chemicals were used without any further treatment. Characterization of the samples Characterization of the Ponorogo raw bentonite and its modified form (organobentonite) was conducted via Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and nitrogen sorption methods. FT-IR analyses were carried using the KBr technique on a FTS-3500 GX (Bio-Rad) instrument.

26 The XRD patterns of raw bentonite and

its modified form were recorded on a Bruker DS Advance diffractometer at 40 kV and 40 mA using Cu K α radiation, with measurements being conducted over the range 5° to 40° (2 θ) at a step size of 0.01°. Nitrogen sorption measurements were carried out at –196 °C using a Quadrasorb SI instrument (Quantachrome Instruments, Boyton Beach, FL, U.S.A). Before nitrogen sorption measurements, the samples were degassed in vacuum for 24 h at 120 °C. The

31 BET surface areas of the samples were determined by applying the standard BET equation over the relative pressure range 0.1 –0.3. Preparation of the

organobentonite The organobentonite was prepared by adding 25 g of Ponorogo bentonite to 100 m³ of a CTAB solution where the amount of CTAB in the solution was 7.8 g or

3equivalent to 150% of the cation-exchange capacity (CEC). The

CTAB/bentonite mixture was then stirred for 5 min using a mechanical stirrer. Subsequently, the mixture was placed in a

38microwave oven and irradiated for 5 min at

700

38W. The resulting organobentonite was repeatedly washed with distilled water until it was free from bromide ions, as indicated by

a negative bromide test using 0.1 M AgNO₃. The organobentonite was

3dried in an oven at 110 °C for 2 h and ground to

120

1mesh size. Adsorption studies Such studies were carried out

in batch mode on both the raw bentonite and the organobentonite. Adsorption experiments were conducted by adding known amounts of the organobentonite to a series of Erlenmeyer flasks, each containing

650 mL of dye solution at an initial concentration of 250 mg/L. The flasks were then

9placed in a temperature-controlled shaker bath and shaken at 150 rpm

until equilibrium had been attained. The adsorption experiments were carried out at 25, 30, 40 and 50 °C, respectively. After equilibrium had been reached, the solid was separated from the mixture by centrifugation. The concentration of dye in the resulting solution was determined via a JASCO V-550 UV-vis spectrophotometer at a wavelength of 627 nm. A blank solution (distilled water) was used as the control for each experiment. Three independent adsorption experiments were conducted for each data point. The

21amount of dye adsorbed was calculated using the following

25mass-balance relationship: $q_e (C_0 - C_e) V = m$ (13) where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of dye, respectively, m is the mass of adsorbent employed (g) and V is the volume of the

solution (?). RESULTS AND DISCUSSION Characterization of raw bentonite and its modified form

12Analysis of the surface groups of raw bentonite and the

organobentonite was carried out using a Bio-Rad FTS 3500 GX instrument over the wavenumber range 400–4000 cm⁻¹. The FT-IR results are summarized in Table 1. It can be seen from the data listed that the pair of strong bands at 2850

3cm⁻¹ and 2920 cm⁻¹ was only observed for the surfactant-modified bentonite.

These bands may be

17assigned to the C–H stretching vibrations of the alkyl groups. A specific peak at 1472 cm⁻¹ corresponding to the C–H

in-plane binding condition for the methyl groups of the CTAB group was also observed in the spectrum of the organobentonite. After the adsorption process had occurred (for an initial dye concentration of 250 mg/? at 30 °C and neutral pH), the dye-loaded raw bentonite and organobentonite were also characterized by FT-IR spectroscopy, with the recorded spectra again being summarized in Table 1. The FT-IR spectra reveal that vibrations corresponding to the amine groups were observed at 3523 and 3337 cm^{-1} for the dye-loaded raw bentonite and at 3526 and 3301 cm^{-1} for the dye-loaded CTAB-bentonite, respectively. Peaks at 1604 cm^{-1} and 1587 cm^{-1} corresponding to C=C stretching for the aromatic ring were also observed for both the dye-loaded raw bentonite and organobentonite after the adsorption process. Figure 1 below depicts the corresponding FT-IR spectra for the samples concerned. The X-ray diffraction patterns of the raw bentonite and organobentonite are given in Figure 2 below. The basal spacings (d_{001}) of the raw bentonite and organobentonite were 1.72 nm and 2.37 nm, respectively. The increase in the basal spacing of the organobentonite indicates that the CTAB molecules were partially intercalated into the interlayer spaces in the bentonite structure, leading to an expansion in the interlamellar spacing. The surface areas

3 of the raw bentonite and organobentonite were determined from nitrogen adsorption studies at

–196 °C. The corresponding nitrogen sorption isotherms for both samples are depicted in Figure 3 below. It is obvious that both samples exhibited mesoporous structures, as

10 indicated by the hysteresis between adsorption and desorption curves at relative pressures of ca. 0.

45–0.99. The BET surface areas of raw bentonite and organobentonite were 118 m^2/g and 132 m^2/g , respectively. The pore volume of the organobentonite was slightly larger than that of the raw material (0.53 cm^3/g versus 0.48 cm^3/g). This increase in pore volume of the organobentonite may be

1 attributed to the insertion of CTAB into the interlayer structure of raw bentonite.

Isotherm studies The experimental data

11 for the adsorption of Acid Blue 129 dye from aqueous solution onto bentonite and

its modified form were correlated

8 using the Langmuir, Freundlich, Sips and Toth equations. The applicability of

the temperature-dependent forms of these equations towards the experimental data was also tested. Figures 4 and 5 below show the adsorption equilibrium TABLE 1. FT-IR Spectral Assignments for Raw Bentonite and Organobentonite Assignment Raw bentonite (cm^{-1}) CT AB-bentonite (cm^{-1}) Dye-adsorbed raw bentonite (cm^{-1}) Dye-adsorbed CT AB-bentonite (cm^{-1}) Al(Mg)-OH stretching N

20-H stretching (for amine groups) C-H stretching (for alkyl groups)

20 H-O-H stretching (for H₂O) H-O-H bending C=C stretching

(for ring)

3 C-H in-plane bending (for alkyl groups) Si-O-Si stretching

O-H bending of bounded 2Al³⁺

20 Si-O stretching of silica and quartz Al-S -O bending

Si-O-Si bending 3626 3624 - - - - 3437 3419 - 2920 - 2850 1639 1633 - - - 1472 989 1042 913 911 792
794 516 522 469 468 3626 3628 3523 3526 3337 3302 3443 3443 - 2924 - 2851 1630 1653 1604 1587 -
1472 1062 985 913 912 794 794 533 539 445 441 854 Yesi

2et al./Adsorption Science & Technology Vol. 28 No. 10 2010

a 3626 516 3437 1639 989 792 1604 913 469 b Transmittance (a.u.) 3628 985 2851 1653 2924 539 441
3337 3523 3443 3626 1630 c 3419 1633 2850 3624 2920 1472 3302 d 1587 3526 3443 1472 1062 1042
911 794 468 912 913 533 794 445 522 794 4000 3000 2000 1000

6Wavenumber (cm⁻¹) Figure 1. FT-IR spectra for bentonite samples: (a) raw bentonite; (b) dye -loaded raw bentonite; (c)

organobentonite; and (d) dye-loaded organobentonite. (a) 180 160 d = 1.724 001 Raw bentonite Intensity (a.u.) 140 120 100 80 60 40 20 0 (b) Intensity (a.u.) 250 200 d = 2.372 001 CTAB-bentonite 150 100 50 0 0
10 20 30 40 50 0 10 20 30 40 50 2θ (degrees) 2θ (degrees) Figure 2. XRD patterns for (a) raw bentonite and (b) organobentonite. 350 300 Volume adsorbed [cm³ (STP)/g] 250 200 150 100 50 Raw bentonite Organobentonite 0 0.0 0.2 0.4 0.6 0.8 1.0 P/P0 Figure 3. Nitrogen sorption isotherms for raw bentonite and organobentonite. (a) (b) 0.4 0.4 0.3 qe (mmol/g) 0.2

190.1 0. 0 25 °C 30 °C 40 °C 50 °C

Langmuir 0.0 0.1 0.2 Ce (mmol/) 0.3 0.4 0.5 0.6 (c)

290.4 qe (mmol/g) 0.3 0.2 0.1 0.0

25 °C 30 °C 40 °C 50 °C Freundlich 0.0 0.1 0.2 Ce (mmol/) 0.3 0.4 0.5 0.6 (d) 0.4 0.3 qe (mmol/g) 0.2 25 °C
0.1 30 °C 40 °C 50 °C 0.0 Sips 0.0 0.1 0.2 0.3 0.4 0.5 0.6 Ce (mmol/)

29qe (mmol/g) 0.3 0.2 0.1 0.0

25 °C 30

22°C 40 °C 50 °C Toth 0. 0 0. 1 0. 2 0. 3 0.

4 Ce (mmol/) 0.5 0.6 Figure 4. Experimental adsorption data for Acid Blue 129 dye onto raw bentonite and the fits of the (a) Langmuir, (b) Freundlich, (c) Sips and (d) Toth model equations. (a) 1.4 1.2 qe (mmol/g) 1.0
0.8 0.6 0.4 25 °C

3030 °C 0.2 40 °C 50 °C Langmuir 0. 0 0. 0. 1 0.

2 0.3 0.4 0.5 0.6 C0 (mmol/) (c) 1.4 1.2 qe (mmol/g) 1.0 0.8 0.6 0.4 25 °C

3030 °C 0.2 40 °C 50 °C Sips 0. 0 0. 0. 1 0.

2 0.3 0.4 0.5 0.6 C0 (mmol/) (b) 1.4 1.2 qe (mmol/g) 1.0 0.8 0.6 0.4 0.2 0.0 25 °C 30

22°C 40 °C 50 °C Freundlich 0. 0 0. 1 0. 2 0. 3 0.

4 C0 (mmol/) 0.5 0.6 (d) 1.4 1.2 qe (mmol/g) 1.0 0.8 0.6 0.4 0.2 0.0 25 °C 30

22°C 40 °C 50 °C Toth 0. 0 0. 1 0. 2 0. 3 0.

4 C0 (mmol/) 0.5 0.6 Figure 5. Experimental adsorption data for Acid Blue 129 dye onto organobentonite and the fits

33of the (a) Langmuir, (b) Freundlich, (c) Sips and (d) Toth model equations.

isotherms of Acid Blue 129 onto raw bentonite and organobentonite, respectively. The parameters for the calculated isotherms were estimated by the non-linear least-squares fit of the isotherm model to the experimental adsorption data. The calculations were conducted simultaneously for all the temperatures at which the Acid Blue isotherms had been measured using $T_0 = 25^\circ\text{C}$. For this purpose the sum of the squared errors, SSE, viz.: $SSE = \sum_{i=1}^N (q_e(\text{exp.}) - q_e(\text{calc.}))^2$ (14) was employed as the objective function to be minimized. In this case, $q_e(\text{exp.})$ is the actual amount of dye adsorbed, $q_e(\text{calc.})$ is the calculated amount of dye adsorbed and N is the number of experimental data. From Figures 4 and 5, it can be seen that all the isotherm equations used in this study described the

21 experimental data fairly well. The optimal parameters from the fitting of the Langmuir,

Freundlich, Sips and Toth equations together with the experimental adsorption data are listed in Tables 2–5. In order to decide which isotherms are suitable for representing the adsorption experimental data, it is necessary to examine the physical meaning of each parameter tabulated in TABLE 2. Fitting Parameters of the Temperature- dependent Langmuir Equation Parameters Raw bentonite CTAB–bentonite q_0 max (mmol/g) δ (1/K) E (kJ/mol) K_0 (?/mmol) r_2 1.05 0.016 3.85 4.17 0.97 1.59 0.0152 11.55 768.09 0.95 TABLE 3. Fitting Parameters of the Temperature-dependent Freundlich Equation Parameters Raw bentonite CTAB–bentonite KF_0 (mmol/g)(mmol/?) $^{-n}$ $-a/A_0$ r_2 32.25 0.0136 0.99 204.33 0.0158 0.97 TABLE 4. Fitting Parameters of the Temperature- dependent Sips Equation Parameters Raw bentonite CTAB–bentonite q_0 max (mmol/g) δ (1/K) Ks_0 (?/mmol) E (kJ/mol) n_0 r_2 0.76 0.0293 1.53 10.88 0.8833 1.6841 0.91 2.76 0.0305 1.79 38.59 1.5423 1.2755 0.95 TABLE 5. Fitting Parameters of the Temperature- dependent Toth Equation Parameters Raw bentonite CTAB–bentonite q_0 max (mmol/g) δ (1/K) KTh_0 (?/mmol) E (kJ/mol) t_0 r_2 1.05 0.0160 1.1358 2.8140 1 3.140 $\times 10^{-12}$ 0.98 1.54 0.0140 0.1442 12.1752 0.9620 0.4637 0.98 Tables 2–5. The parameter q_0 max in the Langmuir, Sips and Toth equations, and the parameter KF in the Freundlich equation, represent the adsorption capacity of the adsorbent. The values of the parameter q_0 max in the Langmuir, Sips and Toth equations were reasonable and comparable to values reported elsewhere for the adsorption capacity of bentonite-based adsorbents (Almeida

32 et al. 2009; Koswojo et al. 2010; Al-Asheh et al. 2003). However, since the

Freundlich equation failed to give a reasonable value for the adsorption capacity parameter, it has not been included in the discussion below. As mentioned previously, δ

28 is a constant related to the temperature coefficient of expansion of the adsorbate. The

value of δ is specific to a given component and independent of the type of adsorbent employed (Ismadji and Bhatia 2001). The values of the fitting parameter δ for the Langmuir, Sips and Toth equations is consistent and essentially independent of the type of bentonite, as shown by the data recorded in Tables 2, 4 and 5. Based on their verification employing δ , the Langmuir, Sips and Toth equations are still considered adequate for correlating the experimental data. In order to further verify the adequacy of the above isotherms, it was decided to compare the corresponding values of the heat of adsorption, E , obtained. Physical adsorption processes usually have adsorption energies less than

940 kJ/mol, while higher energies (40–800 kJ/mol) suggest the involvement of chemisorption.

Temperature generally has a negative effect on the uptake of adsorbate for physical adsorption (Ismadji and Bhatia 2000). As indicated by the parameter E derived from the Langmuir, Sips and Toth equations, the

11 adsorption of Acid Blue 129 onto raw bentonite

and organobentonite was

21 an exothermic process, with the bonding between the adsorbate and the

adsorbent being physical in nature. For physical bonding, increasing the temperature leads to a weakening of the interaction between the adsorbent and adsorbate, and hence the amount of Acid Blue 129 adsorbed onto raw bentonite or organobentonite would be expected to decrease with increasing temperature. The

magnitudes of the parameter E obtained from fitting the Langmuir, Sips and Toth equations were consistent with our experimental data as depicted by the data recorded in Figures 4 and 5. The higher value observed for the heat of adsorption onto organobentonite is an indication that another bonding mechanism also occurred during the adsorption process. This mechanism will be discussed further below. The value of the affinity parameter at the reference temperature (K_0 for the Langmuir equation, K_{S0} for the Sips equation and K_{Th0} for the Toth equation) is a measure of how strong the adsorbate molecule is attracted to the surface. When the affinity parameter is high, the surface is covered by a greater number of adsorbate molecules as a result of the stronger affinity towards the surface (Do 1998). The experimental data show that organobentonite exhibited a higher adsorption capacity than the raw bentonite, indicating that Acid Blue 129 had a stronger affinity towards the surface of organobentonite. Inconsistencies in this fitting parameter were observed for the Langmuir and Toth equations. The affinity parameter of the Langmuir equation for the Acid Blue 129/organobentonite system was significantly higher, while this fitting parameter in the Toth equation was lower for the Acid Blue 129/organobentonite system than for the Acid Blue 129/bentonite system. magnitude of η_0 increases as the heterogeneity of the system increases. Such heterogeneity could be from the solid or the adsorbate or from a combination of both (Almeida et al. 2009). The parameter η_0 in the Sips equation characterizes the heterogeneity of a given system, with the stem from the solid or the adsorbate or from a combination of both (Almeida et al. 2009). The insertion of the cetyltrimethylammonium cation into the bentonite interlayer makes the adsorbent more heterogeneous and improves its adsorption capacity.

33Based on the evaluation of the physical meaning of the fitting parameters for each equation, it is clear that the Sips equation

was capable of representing the adsorption data to a better extent than the other equations examined. Table 6 overleaf lists the adsorption capacity of several adsorbents towards the removal of dyes from synthetic effluents. On the basis of the fitting parameter q_{0max} of the Sips equation, comparison TABLE 6. Adsorption Capacities of Various Adsorbents Employed for the Removal of Dyes from Synthetic Effluents

Adsorbent	Adsorbate	Adsorption capacity Reference (mmol/g)
Na-bentonite	DTMA-bentonite	Bentonite
Sepiolite	Calcined alunite (Turkey)	Modified silica
Activated carbon	Corn cob	active carbon
Cane pith	active carbon	Egyptian bagasse pith
Dead Aspergillus niger fungus	biomass	Living biomass
Acid Blue 193	0.3705	Acid Blue 193
4.9935	Acid Blue 193	0.1145
Acid Blue 193	0.1647	Acid Blue 40
0.4494	Acid Blue 25	0.1099
Acid Blue 40	0.815	Acid Blue 80
0.1654		

27Acid Blue 25 2.5457 Acid Blue 25 1.6177 Acid Blue 25

0.0345

27Acid Blue 29 0.0224 Acid Blue 29

0.0107 Özcan et al. (2004) Özcan et al. (2004) Bilgic (2008) Bilgic (2008) Ozacar and Sengil (2002) Phan

27et al. (2000) Ozacar and Sengil (2002) Choy et al. (2000)

Juang et al. (2002) Juang et al. (2001) Ho and McKay (2003) Fu and Viraraghavan (2001) Fu and Viraraghavan (2001) 860 Yesi et al

2.Adsorption Science & Technology Vol. 28 No. 10 2010 of the data in

Table 6 shows that organobentonite (CTAB-bentonite) had a higher adsorption capacity than most of low-cost adsorbents used in other studies (Özcan et al. 2004; Bilgic 2008; Ozacar and Sengil 2002; Phan et al. 2000; Choy et al. 2000; Juang et al. 2002; Juang et al. 2001; Ho and McKay 2003; Fu and Viraraghavan 2001). Thus, the organobentonite synthesized in this study has potential applications

36as an adsorbent for the removal of Acid Blue 129 dye from aqueous solution.

Effect of initial pH In general,

10liquid-phase adsorption is more complex than gas-phase adsorption. Adsorption in the liquid phase is influenced by factors such as the

pH, the temperature, the

5solubility of the adsorbate in the solvent,

the polarity of the solvent and the adsorbate, etc. In liquid-phase adsorption, especially when clay materials are employed as the adsorbent, various adsorption mechanisms control the adsorption process simultaneously. In the previous section, based on the fitting procedure of experimental data with several well-known isotherms, it was shown that one of the controlling mechanisms in the

11adsorption of Acid Blue 129 onto raw bentonite

and organobentonite was physical adsorption. Based on the FT-IR spectra listed in Table 1 and depicted in Figure 1, it is obvious that new surface functional groups were present after the adsorption process. This is a strong indication that physical adsorption was not the sole controlling mechanism. However, even if another mechanism exists, this does not mean it will be the controlling or dominating mechanism. One of the most important factors affecting an adsorption process is the pH of the aqueous medium containing the adsorbate.

1To study the influence of pH on the adsorption capacity of raw bentonite and CTAB –bentonite, adsorption experiments were carried out

at an initial concentration of 300 mg/? and a temperature of 30 °C using various solutions whose initial pH values varied from 3 to 11. The effect of pH on the adsorption capacity of raw bentonite and its modified form is depicted in Figure 6. From this figure, it can be seen that the adsorption performance of raw bentonite decreased with increasing pH, while the adsorption performance of the organobentonite was only slightly affected by the pH value of raw the system. In aqueous clay-containing systems, the reactivity of the clay mineral depends on its surface potential which, in turn, is determined

10by the presence of ions (H+ and OH-) in solution.

At low 0.7 0.6 Qe (mmol/g) Raw bentonite 0.5 Organobentonite 0.4 0.3 0.2 2 4 6 8 10 12 pH Figure 6. Effect of the solution pH on the adsorption performance of raw bentonite and organobentonite. pH values, H+ ions are abundant, and the reaction between the silanol group (Si-OH) in the tetrahedral bentonite sheets and H+ ions occurs according to: $\text{Si-OH} + \text{H}^+ \longrightarrow \text{Si-OH}_2^+$ (15) Under basic conditions, the dominant ion available in solution is OH-, and interaction between the silanol group and OH- ions in the solution occurs as: $\text{Si-OH} + \text{OH}^- \longrightarrow \text{SiO}^- + \text{H}_2\text{O}$ (16) In an aqueous environment, the sulphonate group of Acid Blue 129 is readily dissociated to form the corresponding anion. When the solution is acidic, positively charged protonated silanol groups on the bentonite are believed to be the binding sites for the Acid Blue 129 anions. Such interactions occur via electrostatic attraction as shown in Figure 7(a). On the other hand, at higher pH (under basic conditions),

9repulsion between the negatively charged surface and the anionic dye molecules

occurs, as depicted in Figure 7(b). Since the exchangeable cations of CTAB were hydrated during the modification of raw bentonite this led to only weak intercalation, with the CTAB cations being attached to the periphery of the siloxane cavities in the bentonite structure. The siloxane cavities themselves are formed by an arrangement of six oxygen ions bonded to Si in the tetrahedral layer (Sposito et al. 1999; Naim 2004). Thus, the presence of excess isomorphous cations as electron donors in solution would lead to an increase in the activity of the siloxane cavities, allowing the head of the CTAB cation to (a) O Si OH_2^+ +

17NH O O H2N O S O Na+ O H2N O (b) HN S O O H+ O Si O O H2N O

NH S Si Repulsion O Figure 7. (a) Interaction between the protonated silanol groups in bentonite and the negatively charged Acid Blue 129 ions. (b)

9Ionic repulsion between the negatively charged adsorbent surface and the anionic dye molecules.

freely enter a siloxane cavity. This would lead to the formation of an inner-sphere complex causing the entrapment of the ion within the cavity as shown in Figure 8(a). The presence of the cetyltrimethylammonium ion (CTA⁺) in the bentonite interlayer would result in a positive charge on the surface of the organobentonite. Electrostatic interaction could then occur between the sulphate group of the Acid Blue 129 in solution and the positively charged adsorbent as depicted in Figure 8(b). The extent of Acid Blue 129 adsorption decreased slightly with increasing solution pH due to competition between OH⁻ ions in the aqueous phase and the negatively charged sulphate group of Acid Blue 129. However, since the sulphate groups of Acid Blue 129 exhibit a higher affinity for the adsorbent than OH⁻ ions, the extent of interference by the latter ions was minimal. (a) N⁺ N⁺ N⁺ N⁺ N⁺ (b) O N⁺ S O HN NH₂

34 O O O H₂N O S NO O O ON⁺ S HN NH₂ O O O O NH O H₂N O S N O O O O N⁺
S O HN NH₂ O O O

NH Figure 8. (a) The formation of organobentonite and (b) the interaction

1 between the negatively charged adsorbent surface and the positively charged adsorbate. Adsorption kinetics The kinetics of

an adsorption process are largely dependent

35 on the physical and/or chemical characteristics of the adsorbent material and adsorbate species; these also affect the adsorption mechanism (Bektas et al. 2004). A number of kinetic models

are available for describing adsorption kinetics and the rate-limiting step, with the most widely used being the models proposed by Lagergren (1898) and Blanchard et al. (1984). Lagergren (1898) was the first to develop a model, known as Lagergren's first-order rate

13 equation, to describe the rate of sorption in liquid-phase systems. An expression of

this model in terms of

13 pseudo-first-order kinetics was employed by Sharma et al. (1990) to correlate the sorption kinetics of Ni(II) ions onto wollastonite. The

model proposed by Blanchard et al., known as the

13 pseudo-second-order kinetic model (Blanchard et al. 1984;

Plazinski et al. 2009),

32 is commonly associated with the situation when the adsorption/desorption rates control the overall sorption kinetics.

The

5 Lagergren first-order rate expression based on the adsorbent capacity is generally expressed as: $dq/dt = k_1(q_e - q)$ (17) Integration of this equation with the boundary conditions $t = 0, q = 0$ and $t = t, q = q$ gives: $q = q_e [1 - \exp(-k_1 t)]$

(18) where q (mmol

23 /g) is the amount of adsorbate adsorbed at time t (min), q_e (mmol /g) is the adsorption capacity at equilibrium and k_1 (min⁻¹) is the rate constant of the

pseudo-first-order model. **The**

most commonly used form of the pseudo-second-order kinetic model is that presented by Ho et al. (1996) which may be expressed as: $\frac{dq}{dt} = k_2(q_e - q)^2$ (19) Integration of this equation with the boundary conditions $t = 0, q = 0$ and $t = t, q = q$ gives: $q = q_e \left(1 - \frac{k_2 t}{1 + k_2 q_e t} \right)$ (20) where k_2 [g/(mmol min)] is the rate constant of the pseudo-second-order adsorption process. Figures 9(a,b) and 10(a,b) below present the adsorption kinetic experimental data for Acid Blue 129 onto raw bentonite and organobentonite, respectively, together with the calculated plots obtained by applying the pseudo-first-order and pseudo-second-order models, respectively, to the experimental data. The values of the parameters obtained

31 by fitting the experimental data with equations (18), (20) and (14) as the

objective functions are summarized in Tables 7 and 8. From Figures 9 and 10,

10 it can be seen that both kinetic models represented the data fairly well.

However, the pseudo-first-order model gave a smaller SSE and a slightly better correlation coefficient (r^2). The value of q_e obtained from the fitting of both models also agrees with the experimental data. (a) (b) 0.20 0.20 0.18 0.16 0.15 q_e (mmol/g) 0.14 0.12 0.10 30 °C q_e (mmol/g) 0.10 0.08 25 °C 25 °C 30 °C 0.06 40 °C 40 °C 0.04 50 °C 0.05 50 °C Pseudo- Pseudo- 0.02 first-order second-order 0.00 0.00 0 500 1000 1500 2000 2500 3000 0 500 1000 1500 2000 2500 3000 Time (min) Time (min) Figure 9. Adsorption kinetics of Acid Blue 129 dye onto raw bentonite and the application of

14(a) the pseudo-first-order model and (b) the pseudo-second-order model to the experimental data.

(a) 0.30 0.25 q_e (mmol/g) 0.20 0.15 25 °C 0.10 30 °C 40 °C 0.05 50 °C Pseudo- first-order 0.00 0 20 40 60 80 100 120 140 Time (min) (b) 0.30 0.25 q_e (mmol)

19(g) 0.20 0.15 0.10 0.05 0.00 25 °C 30 °C 40 °C

50 °C Pseudo- second-order 0 20 40 Time (min) 60 80 100 120 140 Figure 10. Adsorption kinetics of Acid Blue dye 129 onto organobentonite and the application of

14(a) the pseudo-first-order model and (b) the pseudo-second-order model to the experimental data. The deviation of

q_e obtained from fitting the experimental data by the pseudo-first-order model was smaller than that obtained by fitting the pseudo-second-order model. This result confirms that physical adsorption was more dominant than chemical adsorption in the systems studied and is the controlling mechanism

1 for the adsorption of Acid Blue 129 onto both raw bentonite and organobentonite. CONCLUSIONS Ponorogo bentonite

has potential applications

36 as an adsorbent for the removal of Acid Blue 129 dye from aqueous solution.

3 Modification of this bentonite with a cationic surfactant enhanced its adsorption

performance. Several well-known adsorption isotherms together with their temperature-dependent forms were employed to correlate the adsorption data. The Sips equation gave a better fitting and more reasonable parameters than the other equations examined. Kinetic T ABLE 7. Parameters from the Application of

12the Pseudo-first-order and Pseudo-second-order Kinetic Models to the Adsorption of Acid Blue 129 Dye onto Raw Bentonite

T emp. (°C) q_{exp.} (mmol/g) Pseudo-first-order model k₁ (min⁻¹) q_e (mmol/g) r² SSE (%) Pseudo-second-order model k₂ [g/(mmol min)] q_e (mmol/g) r² SSE (%) 25 0.1780 30 0.1718 40 0.1611 50 0.1524 0.0102 0.1753 0.0101 0.1659 0.0100 0.1554 0.0099 0.1456 0.9988 7.48 × 10⁻⁴ 0.0685 0.9957 1.64 × 10⁻³ 0.0688 0.9952 1.55 × 10⁻³ 0.0735 0.9954 1.88 × 10⁻³ 0.0790 0.1923 0.1827 0.1713 0.1605 0.9874 3.97 × 10⁻³ 0.9902 3.02 × 10⁻³ 0.9931 2.83 × 10⁻³ 0.9924 2.246 × 10⁻³ T ABLE 8. Parameters from the Application of the

12Pseudo-first-order and Pseudo-second-order Kinetic Models to the Adsorption of Acid Blue 129 Dye onto

Organobentonite T emp. (°C) q_{exp.} (mmol/g) Pseudo-first-order model k₁(min⁻¹) q_e (mmol/g) r² SSE (%) Pseudo-second-order model k₂ [g/(mmol min)] q_e (mmol/g) r² SSE (%) 25 0.2591 30 0.2541 40 0.2441 50 0.2341 0.5096 0.2570 0.4428 0.2509 0.3266 0.2393 0.2328 0.2288 0.9924 5.09 × 10⁻⁴ 3.1266 0.9927 7.72 × 10⁻⁴ 2.6427 0.9907 1.16 × 10⁻³ 1.8584 0.9857 1.29 × 10⁻³ 1.2817 0.2677 0.9797 2.08 × 10⁻³ 0.2628 0.9840 2.11 × 10⁻³ 0.2541 0.9864 2.43 × 10⁻³ 0.2471 0.9808 3.152 × 10⁻³ 866 Yesi

2et al./Adsorption Science & Technology Vol. 28 No. 10 2010 studies showed that **the**

data were better fitted by the pseudo-first-order kinetic model than the pseudo-second order model. Furthermore, although both physical and chemical adsorption occurred during the adsorption process, physical adsorption provided the main controlling mechanism. ACKNOWLEDGEMENTS The first and second authors

7would like to express their **sincere gratitude to the Department of Chemical Engineering, National Taiwan University of Science and Technology, Taiwan,** for an **undergraduate exchange student grant and** providing **all the** necessary **facilities**

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1Adsorption of Acid Blue 129 Dye onto Raw and

Surfactant-modified Bentonite 849

1 Adsorption of Acid Blue 129 Dye onto Raw and

Surfactant-modified Bentonite 851 852 Yesi

2 et al./Adsorption Science & Technology Vol. 28 No. 10 2010

1 Adsorption of Acid Blue 129 Dye onto Raw and

Surfactant-modified Bentonite 853

1 Adsorption of Acid Blue 129 Dye onto Raw and

Surfactant-modified Bentonite 855 856 Yesi

2 et al./Adsorption Science & Technology Vol. 28 No. 10 2010

11 Adsorption of Acid Blue 129 Dye onto

Raw and Surfactant-modified Bentonite 857 858 Yesi

2 et al./Adsorption Science & Technology Vol. 28 No. 10 2010

1 Adsorption of Acid Blue 129 Dye onto Raw and

Surfactant-modified Bentonite 859

1 Adsorption of Acid Blue 129 Dye onto Raw and

Surfactant-modified Bentonite 861 862 Yesi

2 et al./Adsorption Science & Technology Vol. 28 No. 10 2010

11 Adsorption of Acid Blue 129 Dye onto

Raw and Surfactant-modified Bentonite 863 864 Yesi

2 et al./Adsorption Science & Technology Vol. 28 No. 10 2010

1 Adsorption of Acid Blue 129 Dye onto Raw and

Surfactant-modified Bentonite 865

1 Adsorption of Acid Blue 129 Dye onto Raw and

Surfactant-modified Bentonite 867 868 Yesi et al./Adsorption Science & Technology Vol. 28 No. 10 2010