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Organo-bentonite Bentonite Adsorption abstract The capability of surfactant modified-bentonite for adsorption of dyestuff from aqueous solution was investigated. The so-called "organo-bentonite" was obtained by modifying the raw bentonite obtained from Pacitan, Indonesia using cetyl trimethylammonium bromide (CTAB) and later employed as adsorbent for Acid Green 25 removal. Isotherm and kinetic

22experiments were carried out on three different temperatures (30, 40 and 50 °C).

Langmuir and Freundlich models were chosen for isotherm equilibria data correlation, of which the former showed better suitability. On kinetic data representation, pseudo-first and second order models were used, with the last model gave better correlation. © 2009 Elsevier B.V. All rights reserved. 1. Introduction Dyes are used widely as coloring agents in many industries, such as textiles, cosmetics, leather, printing, foods and plastics. Due to their resistance to degradation, they might be present on wastewater at substantial quantity. Though not particularly toxic, dyes might be harmful to human beings and hazardous to aquatic organisms; not to mention their adverse aesthetic effects as they are quite visible. The presence of color also reduces aquatic diversity by blocking the passage of light through water (Khenifi et al., 2007). In some cases, aquatic organisms and plants that normally use light as an energy resource die. In human, these agents can cause several mutagenic and/or carcinogenic effects. Severe damage to reproductive system, liver, brain and dysfunction of kidneys for example, have been pointed out (Baskaralingam et al., 2006).

10Acid dyes which comprise the largest class of dye in the Color Index (CI) are anionic compounds mainly used for dyeing nitrogen-containing fabrics like wool, polyamide, modified acryl and silk. These compounds are the

most difficult to remove, even by activated carbon. Acid Green 25 (1, 4-di-[(2-sulfono-4-methylphenyl) amino]-9, 10-anthracenedione, disodium salt) in particular belongs to the commercial acid dye often used in textile, hair dye formulation and cosmetic product. This dye has also been known as Acid Green Anthraquinone, Alizarin Cyanine Green F, Japan Green 201 and/or D&C Green No. 5. Acid Green 25 is stable (not readily decomposed) in water at 20 °C up to 7 days. As a result, some aquatic organisms and plants' presence might be compromised. □ Corresponding author.

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23address: suryadiismadji @yahoo.com (S. Ismadji). 0169-1317/\$ – see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.clay.

2009.11.023 Moreover, this compound also brought about a slight or spotty discoloration in the orbital tissue of some animals at 10% aqueous solution, very mild irritation at 15% aqueous solution and dermal irritation at 50% aqueous solution in 1% CMC (carboxymethyl cellulose). Adsorption using activated carbon or ion exchange resins is the most popular technique for dyes removal due to its efficiency. Adsorbents remove dyes from wastewater, either by adsorption (anionic dyes) or by combined adsorption and ion exchange (cationic dyes). Although most adsorbents do not remove all dyes, due to the existence of different types of dyes (non-ionic, anionic or cationic dyes), activated carbon in particular is capable of adsorbing many different dyes with high capacity.

1 However, due to the high price and regeneration cost

(as desorption of dye molecules is not easily achieved),

1 activated carbon becomes infeasible as adsorbent

(Khaled et al., 2009; Leung et al., 2009; Al-Degs et al., 2009; Amin, 2009). Therefore, another cheaper and more economic alternative adsorbent has either been sought after or developed, such as bentonite. The chemical nature and pore structure of bentonites generally determine their adsorption ability. Yet, due to the hydrophilicity induced by the exchangeable metal cations, bentonites normally are not effective in adsorbing organic compounds such as dyes. Therefore, to improve the adsorption capacity of these adsorbents, surface modification has been conducted and investigated (Juang et al., 2002; Lee et al., 2002; Yilmaz and Yapar, 2004; Özcan et al., 2004; Yoo et al., 2004; Erdemoglu et al., 2004; Zeng et al., 2006; Sanchez-Martin et al., 2006; Richards and Bouazza, 2007; Khenifi et al., 2007; Akimbaeva and Ergozhin, 2007; Ma and Zhu, 2007; Zhu et al., 2008; Koyuncu, 2008). Two types of surface modification exist: (1) Impregnation of organic molecules on bentonite surface, classified as a physical process and (2) organo-functionalization or grafting of organic molecules on bentonite surfaces, classified as a chemical process. Impregnation or organic modification process is accomplished through the replacement of inorganic exchangeable cations, like Na⁺, K⁺, Al³⁺ and Ca²⁺, by organic cations, typically with quaternary ammonium cations. The surface nature of these bentonites can be changed from hydrophilic to hydrophobic or organophilic by organo-functional molecules with surface hydroxyl groups, Lewis and Bronsted acidic sites, etc., by grafting organic groups on the bentonite mineral surface (Erdemoglu et al., 2004). The adsorption ability of bentonite can also be improved by treatment with strong inorganic acid, usually carried out at high temperature.

3 When bentonites are acid-activated by hot mineral acid solutions, hydrogen ions attack the aluminosilicate layers via the interlayer region. This process alters the structure, chemical composition, and physical properties of the bentonite while increasing its adsorption capacity resulting in the

so-called "organo-bentonite". Organo-bentonite used for wastewater treatment applications in today's industry is strongly recommended due to their local availability, technical feasibility, engineering applications and cost effectiveness. Numerous studies have investigated the use of organo-bentonite as potential sorbent for organic contaminants in a wide variety of environmental applications (Juang et al., 2002; Lee et al., 2002; Erdemoglu et al., 2004; Yoo et al., 2004; Yilmaz and Yapar, 2004; Özcan et al., 2004; Sanchez-Martin et al., 2006; Zeng et al., 2006; Khenifi et al., 2007; Richards and Bouazza, 2007; Ma and Zhu, 2007; Akimbaeva and Ergozhin, 2007; Koyuncu, 2008; Zhu et al., 2008). These studies revealed organo-bentonite's performance and prospects as adsorbents. Bentonite deposit in East Java, Indonesia, is mainly of Ca-Mg type bentonite. This type of bentonite is generally suitable as a raw material for adsorbent and bleaching earth. In East Java, bentonite reserves can be found in several areas such as Pacitan, Ponorogo, Blitar, Trenggalek, etc., with total reserve more than 500 million tons. Currently, the major use of this material is for the purification of crude palm oil and as drilling mud. As far as we know, systematic studies on the modification of bentonite originated from Indonesia for acid dyes removal purpose has not yet existed. It is our hope that via this study, a better understanding on this aspect can be obtained. Therefore, this paper is focused on the preparation and characterization of "organo-bentonite" made from this bentonite. Different process variables were used to obtain bentonite with specific chemical and surface characteristic nature followed by bentonite modification using cationic surfactants. The standard procedures for characterizing

porous materials were then employed to characterize the bentonite and organo-bentonite. The organo-bentonite was subsequently employed for acid dye adsorption equilibria and kinetic study.

192. Material and methods 2.1. Materials Acid Green 25 **was obtained from** Semarang, Indonesia **and used without** any pretreatment. **The**

surfactant was cetyl trimethylammonium bromide (CTAB) which was purchased from Sigma-Aldrich Singapore (purity 99%). Bentonite was acquired from mining site on Pacitan, East Java, Indonesia. Initially, as-collected bentonite was dried in forced-circulation

22oven at 110 °C to remove excess **moisture** content. **The** drying process **was**

carried out for 24 h. Subsequently, dried bentonite was crushed using JANKE & KUNKEL micro hammer mill to obtain powder bentonite with a particle size of 60/80 mesh. The bentonite powder was later dispersed in hydrogen peroxide for 24 h to remove organic impurities. To remove peroxide, the mixture was gently heated

16in a boiling water bath. As **-purified** bentonite **was** then **suspended in distilled water and allowed to settle.** **The water was siphoned off and the** bentonite **was dried**

and crushed. The

2cation exchange capacity of bentonite **was determined to be** 45 **meq/100 g** on **the**

basis ASTM C837-99 procedure. 2.2. Preparation of organo-bentonite Organo-bentonite was made by mixing 10 g bentonite in 100 mL of solution containing CTAB at CTAB amount equivalent to 150% of cation exchange capacity (CEC). The suspensions were irradiated on microwave with a power of 600 W for 10 min. The organo-bentonite was washed repeatedly

2until a negative bromide **test was obtained with 0.1 M** of **AgNO₃.**

As-washed organo-bentonite was then dried in an oven at 105 °C for 2 h and then ground to obtain a particle size of 200 mesh. 2.3. Adsorption isotherm and kinetics studies Adsorption isotherm and kinetics experiments were done in a batch mode. For kinetic studies, 0.01 g of organo-bentonite was mixed with 150 mL of Acid Green 25 solution at various concentrations (600, 800 and 1000 mg/L). Each batch was conducted at various time intervals and temperatures (30, 40 and 50 °C) for 2 h to determine the period required to reach the adsorption equilibrium and maximum removal of dyes. The solutions were then separated from adsorbates. The remaining concentrations of each solution, c , were measured by spectrophotometer at 605 nm (the λ_{max} value for Acid Green 25). The amount of dye adsorbed onto organo-bentonite, q , was determined from the difference between the initial and remaining concentrations of dye solution. For isotherm studies, different amount of organo-bentonite (0.01, 0.02, 0.03, 0.04, 0.05, and 0.06 g) was contacted with 150 mL of Acid Green 25 solution at a concentration 1000 mg/L for 60 min at different constant temperatures (30, 40 and 50 °C). 2.4. Physical characterizations of adsorbent

11The pore structure characteristics of the

bentonite and organo-bentonite

20were determined by nitrogen adsorption at 77. 15 K using Quadrasorb SI. **The**

sample was degassed at 423.15 K in a vacuum condition for 24 h before gas adsorption measurements.

11 Nitrogen adsorption isotherms were measured over a relative pressure (P/P₀) range from approximately 10⁻³ to 0.995. The Brunauer–Emmett–Teller (BET) surface area, pore volume and pore size distribution of the

bentonite and organo-bentonite were determined using

6 Brunauer–Emmett–Teller and Dubinin–Asthakov (DA) analysis software available within the instrument, respectively. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range of 0.06 to 0.3.

The pore size distribution of the bentonite and its modified form was ascertained using density functional theory (DFT) software available within instrument using medium regularization. Fig. 1. Nitrogen adsorption isotherms. R. Koswojo et al. / Applied Clay Science 48 (2010) 81–86 Fig. 2. DFT result for bentonite (straight line) and organo-bentonite (dotted line). Powder X-ray diffraction (XRD) patterns of bentonite and organo-bentonite were recorded on a Rigaku Miniflex Goniometer at 30 kV and 15 mA, using Cu K α radiation at a step size of 0.01°. 2.5. Chemical characterizations of adsorbent Qualitative analysis of bentonite and organo-bentonite

1 was performed by FTIR transmission spectra using KBr technique. The analysis was carried out on Shimadzu 8400S FTIR instrument in the wavenumber range of 500–4000 cm⁻¹.

3. Result and discussion 3.1. Physical characterizations of adsorbent The

20 specific surface area and pore size distribution were determined by nitrogen adsorption at

its boiling point using Quadrasorb SI. Nitrogen sorption isotherms for both bentonite and organo-bentonite were shown in Fig. 1. Both bentonite and organo-bentonite have mesoporous structures. Mesoporous structure was shown by a hysteresis between adsorption and desorption curve after relative pressure (P/P₀) of 0.4. The difference between bentonite and organo-bentonite lies on its volumetric adsorption capacity (V_{ads}) and BET surface area. Organo-bentonite had larger V_{ads} than bentonite (0.70 cm³/g vs 0.48 cm³/g) but lower surface area (96 m²/g vs 118 m²/g) which indicates the formation of larger pore on organo-bentonite as compared to bentonite due to CTAB insertion at bentonite interlayer. The pore size distribution of bentonite and organo-bentonite analyzed using DFT (Fig. 2) indicated mesoporosity. XRD patterns of bentonite and organo-bentonite are shown in Fig. 3. Fig. 3 shows a basal spacing of 12.3 Å. After the modification process, this basal spacing is increased onto 25.1 Å. With the insertion of cethyl ammonium cation into the bentonite interlayer, the bentonite became hydrophobic; improving its organic adsorption capacity. 3.2. Chemical characterization FTIR spectra reveals

1 the specific surface functional groups on bentonite and organo-bentonite

13 surface qualitatively based on the characteristic absorbed energy for each bonds in certain groups

(Putra et al., 2009). The FTIR spectra of bentonite and organo-bentonite are shown in Figs. 4 and 5 and Table 1. Figs. 4 and 5 reveal the presence of Fig. 3. XRD pattern of: a) bentonite b) organo

8-symmetric and

asymmetric stretching vibration at wavelength bands of 2819.97 cm^{-1} and 2920.40 cm^{-1} . These bands are associated with the

2-symmetric and asymmetric stretching vibrations of the methylene and methyl group CH_2 , CH_3 of the aliphatic chain of the surfactant

(Khenifi et al., 2007). Also, a

15-bending vibration of the methylene groups can be seen at wavelength bands of 1475.19 cm^{-1} , verifying the intercalation of surfactant molecules between the silica layers

(Özcan et al., 2004). All these bands (at wavelengths of 1475.19 cm^{-1} , 2819.97 cm^{-1} and 2920.40 cm^{-1}) are only detected for organo-bentonite. 3.3. Adsorption studies Due to instability of Acid Green 25 at several pH values (pH 5), the adsorption experiments were conducted at pH 6 corresponding to the pH of Acid green solutions. 3.3.1. Adsorption isotherms The isotherm data for adsorption of Acid Green 25 onto organo-bentonite were fitted by Langmuir and Freundlich models. The Langmuir model is expressed as $q_e = \frac{q_{\text{max}} \cdot C_e}{K_L + C_e}$ Fig. 5. FTIR spectra of organo-bentonite. Table 1 FTIR spectra data of bentonite and organo-bentonite. Assignment Bentonite, cm^{-1} Organo-bentonite, cm^{-1}

9-Al(Mg)-O-H stretching H-O-H stretching (for H_2O)

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

alkyl groups)

9-Si-O-Si stretching OH bending bounded Fe^{3+} and Al^{3+}

Si-O stretching 3600.1700 3349.8600 – – 1675.4210 – 1061.4521 904.1560 786.4410 3640.1300
3399.6700 2920.4000 2819.9700 1650.1200 1475.1900 1050.0400 899.9170 799.8350

5-where q_e is the equilibrium dye concentration on adsorbent (mmol g^{-1}), C_e is the equilibrium dye concentration in solution (mmol L^{-1}), q_{max} is the monolayer capacity of the adsorbent (mmol g^{-1}) and K_L is the Langmuir adsorption constant (L mmol^{-1}).

Eq. (1) is often written at

12-its linear form $C_e/q_e = \frac{1}{q_{\text{max}}} + \frac{K_L}{q_{\text{max}}} C_e$

$q_{\text{max}} \times K_L$: The characteristic of the Langmuir isotherm can also be expressed using a dimensionless constant called equilibrium parameter (RL), which has the form $RL = \frac{C_0}{1 + C_0 \times K_L}$ where C_0 is the initial dye concentration in solution (mmol L^{-1}), RL value indicates the isotherm type, whether it is unfavorable ($RL < 1$), linear ($RL = 1$), favorable ($0 < RL < 1$) or irreversible ($RL = 0$) (Ozcan et al., 2007). Fig. 6 shows that the Langmuir model represented the adsorption data better than Freundlich model, and the parameters of the Langmuir model are given in Table 2. Comparing with other low cost adsorbent such as walnut shell (Aydın et al., 2009), spent brewery grains (Jaikumar and Ramamurthi, 2009), shells of bittim

(Aydin and Baysal, 2006), activated palm ash (Hameed et al., 2007), chitosan (Gibbs et al., 2003), and crab shell (Cheung et al., 2007) the adsorption capacity of this organo-bentonite is higher, indicate that this adsorbent has potential application for industrial scale wastewater treatment process. Fig. 6. Adsorption isotherms of AG 25 onto organo-bentonite. R. Koswojo et al. / Applied Clay Science 48 (2010) 81–86 85 Table 2 The Langmuir isotherm constants for the adsorption of AG 25. T (°C) Langmuir q_{max} (mmol g⁻¹) KL (L mmol⁻¹) rL2 RL 30 2.9838 40 3.3386 50 3.7230 4.521 0.9573 4.5807 0.9782 4.9015 0.9773 0.1210 0.1197 0.1127 3.3.2. Adsorption kinetics

14 **Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the adsorbate in the solid–solution interface.** In here, two kinetic models are

chosen, i.e.: pseudo-first and second order kinetic models. The pseudo-first order has the form $dq/dt = k_1(q_e - q)$. The integration of Eq. (6) with the boundary conditions as follows: $t = 0 - t$ and $q = 0 - q_t$, gives $\log(q_e - q_t) = \log(q_e - q_0) - k_1 t$.

8 **The pseudo-second order, on the other hand has the**

form $dq/dt = k_2(q_e - q)^2$. Fig. 7. The kinetic experimental data and model predicted from (a) pseudo-first order and (b) pseudo-second order. Table 3 The pseudo-first and pseudo-second order rate constants for the adsorption of AG 25. T (°C) Pseudo-first order k_1 r12 Pseudo-second order k_2 r22

12 **(mmol g⁻¹) (min⁻¹) (mmol g⁻¹) (g mmol⁻¹ min⁻¹)**

30 1.0048 40 1.7466 50 1.3937 0.0652 0.7821 0.0656 0.8669 0.0420 0.7897 2.8024 0.0359 3.2488 0.0292 3.5063 0.0232 0.9855 0.9896 0.9747 The integration of Eq. (8) with the same boundary conditions as those of Eq. (6), gives $t = 1 + t: 1/q_t = 1/k_2 + q_e^2/k_2(q_e - q)^2$. The kinetic data obtained using the

13 **pseudo-first and pseudo-second order** is depicted in Fig. 7. Parameters for **pseudo-first** and second **order**

models from linear regression are also summarized in Table 3. Fig. 7 and Table 3 demonstrate that the pseudo-second order model represents the kinetic data better than the pseudo-first order. The equilibrium sorption capacity was improved from 2.8024 mmol g⁻¹ to 3.5063 mmol g⁻¹ within a 20 °C temperature margin increase (30 to 50 °C). The enhanced adsorption capacity indicates that the adsorption of Acid Green 25 onto organo-bentonite is an endothermic process. The values of the

8 **pseudo-second order rate constant, k_2 were found to decrease from**

0.0359

12 **g mmol⁻¹ min⁻¹ to 0.0232 g mmol⁻¹ min⁻¹**

for a 20 °C temperature margin increase. This trend suggests a chemisorption reaction as a predominant

8 **rate-controlling step. The relationship between the pseudo-second rate constant**

and

19 temperature was then probed to determine the activation energy of the

adsorption based on Arrhenius equation. $k_2 = k_0 \cdot \exp\left(-\frac{E_a}{RT}\right)$ where k_2 is the rate constant of sorption ($\text{g mmol}^{-1} \text{ min}^{-1}$), k_0 is the temperature independent rate constant of sorption

7 ($\text{g mmol}^{-1} \text{ min}^{-1}$), E_a is the activation energy of sorption (kJ mol^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the solution temperature (K).
The

linear regression of $\ln k$ vs. T^{-1} was plotted in Fig. 8 to evaluate E_a (supposedly be the plot's slope). The relationship between k and T was then represented in Arrhenius equation as $k_2 = 0.00003 \cdot \exp\left(-\frac{290.1442}{T}\right)$. The activation energy of adsorption is $290.1442 \text{ kJ mol}^{-1}$ while the temperature independent rate constant of sorption is $0.00003 \text{ g mmol}^{-1} \text{ min}^{-1}$. Therefore, adsorption of Acid Green 25 onto organo-bentonite is determined as an endothermic process, due to the positive sign of its activation energy. Fig. 8. Arrhenius plot for the adsorption of AG 25 onto organo-bentonite. 4. Conclusion The so-called "organo-bentonite" made from bentonite obtained within Pacitan, Indonesia was probed in terms of its adsorption potential to remove Acid Green 25 from aqueous solution. The Langmuir model fitted well the experimental data. The pseudo-second order model represented the experimental kinetic data in a better manner than the pseudo-first order model, indicating chemisorption as the controlling step of adsorption. Acknowledgements The authors acknowledge the funding of this work through the National Taiwan University of Science and Technology–Widya Mandala Surabaya Catholic University joint research project with contract no RP09-01 and the Directorate General of Higher Education Republic of Indonesia through competitive grant for international publication with contract number 676/SP2H/PP/DP2M/VII/2009. This work is also partially funded by the Directorate Higher Education, Indonesia through PKMP Student Grant 2009. References Akimbaeva, A.M., Ergozhin, E.E., 2007. Estimation of structural and sorption characteristics of activated bentonite. *Colloid Journal* 69, 401–406. Al-Degs, Y.S., Khraisheh, M.A.M., Allen, S.J., Ahmad, M.N., 2009. 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