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Adsorption of Tetramethylammonium Hydroxide on Activated Carbon Devarly Prahas1; J. C. Liu2; Suryadi Ismadji3; and Meng-Jiy Wang4 Abstract:

> 7**Tetramethylammonium hydroxide (TMAH) is widely used**

in manufacturing thin-film transistor liquid crystal displays (TFT-LCD) and semiconductors. Because of its toxicity and nitrogen content,

> 7**TMAH-containing wastewater has to be properly treated before**

discharge. In this study, several commercial activated carbons were characterized and used for TMAH adsorption. Activated carbon with micropores showed higher adsorption capacity for TMAH. The adsorption kinetics could be represented by pseudo-second-order model, and the Langmuir model fitted the adsorption of TMAH on activated carbon under different pH adsorption well. Higher pH was favorable for TMAH adsorption, while there was no TMAH adsorption at pH 4:7 0:2. The adsorption was spontaneous and exothermic. Exhausted carbon could be easily regenerated by 0.1 N HCl, with no considerable reduction in performance even after five cycles of adsorption- desorption. It was proposed that electrostatic interaction was the main mechanism of TMAH adsorption on the activated carbon.

Adsorption; Activated carbon; pH; Tetramethylammonium hydroxide (TMAH); Thin-film transistor liquid crystal display (TFT-LCD); Wastewater. Introduction In Taiwan, thin-film transistor liquid crystal displays (TFT-LCD) and semiconductors are currently the most important industries. Tetramethylammonium hydroxide (TMAH) is a major ingredient of photoresist developer in the lithography step of the LCD manu-facturing process (Sugawara et al. 2002). TMAH is used as an alkaline etchant and as a cleaning solution in semiconductor manu- facturing (Thong et al. 1997). Consequently, a high amount of TMAH-containing wastewater from these industries can be ex- pected. The typical TMAH concentration ranges from a few to hun- dreds of milligram per liter, depending upon the manufacturing process and its operation. TMAH is highly toxic and several symp- toms of poisoning caused by TMAH have been reported (Chang et al. 2008). While this wastewater is toxic to humans, its nitrogen content can be a nutrient source to the water environment. As such, the Taiwan Environmental Protection Administration has es- tablished a new effluent standard of NH4þ N < 10 mg=L in water protection zones and < 20 mg=L in other areas as applied to semiconductor and optoelectronic industries. In addition, these

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13Chemical Engineering, Widya Mandala Catholic Univ., Jl. Kalijudan 37, Surabaya 60114, Indonesia. 4Associate Professor, Dept. of Chemical Engineering, National Taiwan Univ. of Science and Technology, 43 Keelung Rd., Section 4, Taipei 106, Taiwan.

industries are currently studying technologies to recover and remove TMAH from wastewater since eco-toxicity tests will be commonly required for their effluent. Therefore,

7TMAH- containing wastewater has to be properly treated before it can be discharged to the environment.

Research conducted to treat the wastewater includes catalytic oxidation (Hirano et al. 2001), biodegradation by aerobic process (Tsuzaki and Nakamoto 1990), anaerobic process (Chang et al. 2008), aerobic and anoxic/oxic sequencing batch reactors (Lei et al. 2010), and reclama- tion and reuse by a combination of electrodialysis and ion exchange technology (Sugawara et al. 2002; Shibata et al. 2006). Among existing conventional methods for treating industrial wastewater, adsorption is the most widely used process due to its simplicity and capability to produce effluents containing very low levels of dissolved organic compounds (Wibowo et al. 2007). Along with other commonly used adsorbents, such as alumina, silica gel, and zeolite, activated carbon is best known for its large surface area from internal microporosity (Do 1998). Despite the versatile use of activated carbon, currently there is still no study about TMAH adsorption on activated carbon. The only study about adsorption of TMAH uses cubic mesoporous silicate (CMS) and modified CMSs as adsorbents (Kelleher et al. 2001, 2002). The main objective of this study is to investigate the adsorption behav- ior of TMAH onto activated carbon. Materials and Methods Different commercial activated carbons with similar surface area were obtained from Acros activated charcoal (SAC), Norit SA- 2, decolorizing), Wako activated charcoal (WAC), Sigma-Aldrich activated carbon (ZAC), and Merck activated carbon (MAC). Prior to use, all activated carbons were washed with ultra pure water repetitively until the pH of the washing water was constant and the conductivity was below 5 µS=cm. The carbons were then dried in an oven at 105°C overnight and sieved until the particles were below 0.149 mm (100 mesh). A stock solution was prepared by diluting aqueous solution of TMAH (25%, w/w, Megaunion) using ultra pure water (Millipore). BET surface area (SBET); micropore (Vmi), mesopore (Vme), and total pore volume (Vtotal); as well as

> 15**pore size distribution by density functional theory (DFT) and Barret-Joyner-Halenda (BJH) models were determined from** N2 **adsorption-desorption isotherms**

at 196°C by a Quantachrome, Autosorb-1 instrument. Prior to the

> 10**measurements, the activated** carbons were **degassed at 200°C in a vacuum condition for at least** 24 **h.** SBET **was** then **determined by**

standard BET equation applied to the adsorption-desorption

> 23**data in the** relative **pressure (P=P0) range** of **0.05 to 0.3** while **pore** size distribution **was** modeled **from the**

data in the P=P0 range of 0.05 to 0.98 using Quantachrome, Autosorb-1 software package.

> 9**Isoelectric point (pHIEP)** and **point of zero charge (pHPZC) of the activated**

carbons were both deter- mined by zeta potential measurement and pH drift method (El- Sayed and Bandosz 2004), respectively, with 0.01 N NaCl (Acros) as background electrolyte. pHIEP could be deduced when pH versus zeta potential line crossed the line at which zeta potential equals the zero. pHPZC could be found when the final pH equals the initial pH. The widely used Boehm titration was used to semi quantitatively address surface acidity and basicity of the activated carbons (Boehm 1994, 2002). Initial Concentrations of 20, 50, 100, 150, 200, 250, 300, and 500 mg=L were added to 50 mL of TMAH in several. Into several Erlenmeyer flasks 50 mL of TMAH solution. The pH of the sol- ution was adjusted by 0.05 N HCl (Acros) and 0.05 N NaOH (Fischer Scientific) and

> **14**0.2 g (1%) **of** activated **carbon was added** into **each flask** then **the**

flask was covered tightly. The flasks were shaken at 25°C and 80 rpm shaking speed until equilibrium was reached (24 h) in a temperature-controlled water bath shaker. Amount of TMAH adsorbent, qe ðmg=gÞ, was then defined as

> **6qe ¼ ðC0 CeÞ · V m Where C0**

> **3is the** initial **concentration of adsorbate (mg=L),** Ce **is the** final **volume of liquid (L), and m is the mass of adsorbent (g).**

To ensure data validity,

> **6experiments were carried out in triplicate** analysis **with**

relative standard deviation lower than 10% in every adsorption isotherm experiment. Measurement of TMAH concen- tration was by ion chromatography system (Dionex ICS-1000) equipped with autosampler (Spectra System, AS-1000) with the retention time of 20 min. To study effect of temperature on adsorp- tion, the flasks were shaken at 25, 40, and 55°C, respectively, with identical procedures as aforementioned. Five hundredths

> **6mL of** TMAH **solution with initial** concentra- tion **of** 300 **mg=L**

was put into a glass reactor. The solution in the reactor was stirred by a magnetic stirrer (Corning) at the speed of 360 rpm. The pH of the solution was adjusted by 0.05 N HCl and 0.05 N NaOH so that desired pH could be obtained. Two grams (1%)

> **24of activated carbon was added into** the reactor **and** then **the**

reactor was covered. Right after the activated carbon was added, the time was recorded. It was sampled at different intervals for analysis. The amount of TMAH adsorbed onto activated carbon at a given time, qt (mg=g), was then defined as: qt ¼ ðC0 CtÞ · V m Where C0

> 3**is the initial concentration of adsorbate (mg=L), Ct is the concentration of adsorbate at** a given reaction **time (mg=L), V is the volume of liquid (L), and m is the mass of adsorbent (g).**

For desorption experiments,

> 6**50 mL of** TMAH **solution with** ini- tial **concentrations of** 50 **mg=L**

was added into each Erlenmeyer flasks. The pH of the solution was controlled by 0.05 N HCl and 0.05 N NaOH so that equilibrium pH was 11:8 0:2. Fixed amount

> 14**(0.2 g) of** activated **carbon was added** into **each flask** and tightly covered. **The** flasks **were** shaken **at** 80 rpm shaking **speed**

at 25°C until equilibrium was reached. After equilibrium was reached, the activated carbon was separated from the solution by filtration. It was mixed with either 50 mL of 0.1 N HCl or warm water (65°C) and was then shaken at 80 rpm for 6 h. The amount of desorbed TMAH was analyzed after samples were diluted and neutralized. The adsorbent was collected again by filtration and oven-dried at 105°C overnight before undergoing subsequent adsorption ex- periment. The cycle of such adsorption and desorption was repeated for five times in triplicate analysis. Results and Discussion Characteristics of Activated Carbons The pore size distribution of the activated carbons was assessed by both the density function theory (DFT) and the Barret-Joyner- Halenda (BJH) models. DFT model covers pore size distribution from micropore to mesopore range (i.e., 4.2 to 50 Å). Fig. 1(a) illustrates that up to 20 Å, WAC activated carbon had the highest cumulative pore volume, and there was no further increase for pore size ranging from 20 to 50 Å. SAC, ZAC, and MAC had less cumulative pore volume for pore width < 20 Å, yet they showed 0.4 Cumulative Pore Volume (cc/g) 0.3 0.2 0.1 SA-2 WSIAGKMOA MERCK 0.0 0 10 20 30 40 50 60 (a) Pore Width (Å) 0.5 Cumulative Pore Volume (cc/g) SA-2 0.4 WAKO SIGMA MERCK 0.3 0.2 0.1 0.0 10 100 1000 10000 (b)

> 8**Pore Width (Å) Fig.** 1. (a) cumulative **pore size distribution of activated carbons by DFT**

model; (b) cumulative

> 8**pore size distribution of activated carbons by**

BJH model further increase in cumulative pore volume in the pore size range of 20 to 50 Å. Similar tendency in

8**pore size distribution** of **the** acti- vated **carbons was** also found **by**

BJH model [Fig. 1(b).] For pore width < 20 Å, WAC had the highest pore volume, followed by MAC, ZAC, and SAC. However, as the pore size range shifted to mesopore range (20 to 500 Å), SAC had higher mesopore vol- ume, and eventually reached the highest cumulative macropore volume (500 Å to > 2;000 Å). While for WAC, no further cumu- lative pore volume in mesopore and macropore range could be observed. Even though the surface areas were approximately equal, the pore size distribution of each activated carbon was different (Table 1). WAC had the lowest pore volume, followed by both MAC and ZAC, and then SAC. The ratio of mesopore to micropore revealed that WAC had the lowest value, implying that this acti- vated carbon was more microporous as compared with other car- bons. From pHPZC values (Table 2), it was known that SAC was a basic carbon while the others were neutral carbons. Activated carbons with a predominantly basic surface may show an isoelec- tric point in the acidic range since electrokinetic behavior is deter- mined by the charge on the external surface of the carbon particles (Corapcioglu and Huang 1987; Boehm 2002). Thus, as depicted in Table 2, the pHIEP of activated carbons was always lower than pHPZC. The nature of oxygen functional groups distribution caused denser oxygen surface functional groups on the external surface (Menéndez et al. 1995).

19**Therefore, the difference between pHPZC and pHIEP can be** regarded **as a** rough **measure of** the **surface charge distribution of carbon.**

Positive values indicate more nega- tively charged external particle surfaces than internal ones and values close to zero imply a more homogenous distribution of the surface charges (Menéndez et al. 1995). Furthermore, Boehm titration results showed good agreement with the trend of pHPZC, which were in the order of MAC < WAC < ZAC < SAC. The acidity of SAC and WAC was predominantly contributed by car- boxyliclike group, while ZAC and MAC by phenoliclike group. Even though WAC activated carbon had the densest carboxyliclike group, pHPZC of MAC (i.e., 6.4) was lower than WAC (i.e., 7.4) since MAC had the lowest amount of basic functional group. In contrast, SAC possessed highest basic functional group despite its high carboxyliclike group content, making it a basic acti- vated carbon. The amount of acidic and basic surface functional

16**Table 1.** Specific **Surface Area and Pore Volume** Distribution **of the Activated**

Carbons Pore volume (cc=g) Activated SBET V mi V me carbon m2 =g (DFT-Method) (BJH-method) V total V me =V mi SAC 619.80 0.1487 0.4185 0.5713 2.81 WAC 862.19 0.2544 0.1110 0.3609 0.44 ZAC 670.09 0.1698 0.3375 0.5119 1.99 MAC 854.94 0.1945 0.2686 0.4887 1.38

20**Table 2. Surface Properties** and Functional Groups **of the Activated Carbons**

pHpzc pHIEP Acidic groups (meq=g) Carboxylic Lactonic Phenolic Total Basic group (meq=g) 10.1 4.6 0.124 0.070 0.038 0.232 1.058 SAC 1.48

12**N/A N/A** 1.54 **N/A N/A** 7 **.4** 5.3 **0.**

179 0.134 0.160 0.473 0.459 WAC 19.99 0.0344 0.8850 20.50 0.0027 0.9719 7.9 7.6 0.011 0.110 0.416 0.537 0.652 ZAC 3.26 0.0945 0.8158 3.46 0.0367 0.9214 6.4 3.6 0.005 0.026 0.434 0.465 0.077 MAC 8.19 0.2435 0.8021 8.38 0.0496 0.9125 groups affected the total net surface charge of activated carbons significantly. Kinetic Study One of the widely used models to describe adsorption kinetics is

10**pseudo-first-order model. The equation** has **the**

form after integra- tion (Ho and McKay 1998) qt ¼ qeð1 expð k1tÞÞ ð1Þ where k1 is the rate constant for the first order (min 1) qe is equi- librium adsorption capacity, and qt is measured adsorption capacity at any time. Another is the pseudo-second-order kinetic model is as follows (Ho 2006): qt ¼ qe 1 þqekq2etk2t ð2Þ TMAH adsorption on SAC, WAC, ZAC, and MAC with respect to reaction time is illustrated and fitted by pseudo-first-order and pseudo-second-order kinetic models (Fig. 2).

22**It can be** found **that pseudo-second-order kinetic model** fitted **better than pseudo-first- order for** all kinds **of**

activated carbons, with

9**correlation coefficients higher than 0.** 90 (Table 3). **The**

models were not applicable for SAC since the type of kinetic curves was pseudo rectangular; indicating that the adsorption rapidly approached equilibrium (Chen and Wu 2004). Similar behavior was also observed on adsorption kinetics of TMAH on CMSs (Kelleher et al. 2001), cationic surfactant 20 SAC 15 WAC ZAC qt (mg/g) MAC Pseudo-first-Order Pseudo-secont-Order 10 5 0 0 500 1000 1500 2000 2500 3000 t (minutes) Fig. 2. Pseudo-first-order and pseudo-second-order kinetic plot of TMAH adsorption on SAC, WAC, ZAC, and MAC (C° ¼ 300 30 mg=L, volume ¼ 500 mL, adsorbent dose ¼ 4 g=L, pH ¼ 11:8 0:2) Table 3. Reaction Kinetics of TMAH Adsorption on SAC, WAC, ZAC, and MAC Pseudo-first-order Pseudo-second-order qt ¼ qeð1 expð k1tÞÞ qt ¼ qe 1þqeqke2kt2t Activated qe k1 qe k2 carbon (mg=g) (1= min) R 2 (meq=g) (meq=g) R 2 (i.e., cetyltrimethylammonium bromide) on activated carbon (Yalçin et al. 2005), as well as ammonium on sawdust (Wahab et al. 2010). In the current study, it is because generally experimental data are better represented by pseudo-second-order rather than pseudo-first-order model has been well discussed (Plazinski et al. 2009; Kosasih et al. 2010). Adsorption Isotherm Adsorption isotherms of WAC at different equilibrium pH are shown in Fig. 3. The experimental data were fitted by two- parameter isotherms, i.e., Langmuir and Freundlich equations.

24The Freundlich equation is written as follows: $q_e \frac{1}{4} K_f$:

Ce1=n ð3Þ where qe

11is the mass of substance adsorbed per unit mass of adsorb- ent, Ce is the equilibrium concentration of the solute being adsorbed, while Kf and n are empirical constants.

The Langmuir isotherm is in the form of qe ¼ q0: 1 þb:Cb:eCe ð4Þ 25 20 15 qe(mg/g) 10 5 0 -5 0 100 200 300 400 500 Ce(mg/L) pH 11.8 ± 0.2 pH 7.8 ± 0.2 pH 7.0 ± 0.2 pH 4.7 ± 0.2 Langmuir Plot Freundlich Plot Fig. 3. Adsorption isotherms of TMAH on WAC at different pH as fitted by Langmuir and Freundlich isotherms (adsorbent dose ¼ 4 g=L, reaction time = 24 hours)

5where Ce is the equilibrium concentration (mg=L), qe is the amount adsorbed at equilibrium (mg=g), and q0 and b are Langmuir constants related to the adsorption capacity and energy of adsorp- tion, respectively. Langmuir and Freundlich fitting parameters are

summarized in Table 4. The pH greatly influenced TMAH adsorp- tion so that the higher the pH, the higher the TMAH adsorption capacity of WAC activated carbon. At equilibrium pH of 4:7 0:2, no adsorption of TMAH occurred, while at equilibrium pH of 11:8 0:2, the adsorption capacity was found to be the highest. The Langmuir model fitted very well with every adsorption iso- therm data of WAC, with correlation coefficient value higher than 0.97, better than Freundlich equation (0:91 < R2 < 0:97). Adsorp- tion density parameter, q0, changed with respect to pH, while the adsorption energy constant, b, was constant within entire pH range studied. Aside from fitting capability, the n values of the adsorption were between 1 and 10, indicating favorable adsorption isotherm type. A suitable fitting by Langmuir isotherm indicated formation of monolayer coverage of TMAH molecules at the adsorption sites of the adsorbent (Do 1998). Similar good correlation with Lang- muir isotherm was also found by Kelleher et al. (2001, 2002) on their CMSs in the range of equilibrium concentration of about 0 to ca. 300 mg=L of TMAH. Compared with the cubic mesopo- rous silicates (CMSs), the adsorption capacities of WAC activated carbon were less than one tenth. CMSs surface-area-to-volume ratios were very large, which suggests the dominant presence of microporosity, and the ratios were much higher than WAC. This fact indicates that microporosity had a very important role in adsorption of TMAH. Effect of Temperature As depicted in Fig. 4 and Table 5, Langmuir model fitted well ad- sorption of TMAH on WAC activated carbon at different temper- ature. The increase of temperature from 25°C to 55°C was disadvantageous not only to the b value, but also to the maximum adsorption capacity. The

18decrease in maximum adsorption capacity with the increase of temperature could be due to increasing ten- dency of

the TMAH molecules to escape from the solid phase to the bulk phase as adsorbate molecules possessed higher total en- ergy (Ho and McKay 1998) and that the adsorption process was dominated by physisorption, resulting in the bonding between the adsorbate and the active adsorbent sites that weakens at higher temperature, in contrast with chemisorption (Kosasih et al. 2010). Thermodynamic analysis of the adsorption reaction can be assessed utilizing van't Hoff equation: ΔH° ΔS° ln b ¼ RT þ R ð5Þ where b is the Langmuir constant, ΔH° the standard enthalpy change, ΔS° the standard entropy change, R the gas constant, Table 4. Isotherm Parameters of TMAH Adsorption on WAC at Different pH pH Isotherms Parameters 11:8 0:2 7:8 0:2 7:0 0:2 4:7 0:2 Freundlich (qe ¼ Kf :C1e=n) Langmuir (qe ¼ q0 · 1þb:bC·eCe) KFðmg=gÞðL=mgÞ1=n n 1=n R2 q0 (mg=g) b (L=mg) R2 2.44 2.61 0.383 0.9652 27.77 0.0118 0.9902 1.33 2.65 0.377 0.9687 14.62 0.0118 0.9768 0.67 2.81 0.356 0.9143 6.68 0.0118 0.9803

12N/A N/A N/A N/A N/A N/A N/A

25 20 qe(mg/g) 15 10 5 250 C 400 C 550 C Langmuir Plot 0 0 100 200 300 400 500 Ce

16(mg/L) Fig. 4. Effect of temperature on adsorption isotherms of

WAC (adsorbent dose ¼ 4 g=L, pH ¼ 11:8 0:2, reaction time = 24 hours) Table 5. Langmuir Constant of TMAH Adsorption at Different Temperature T (°C) q0 (mg=g) b (L=mg) R2 25 27.77 0.0118 0.9902 40 23.53 0.0110 0.9956 55 22.81 0.0105 0.926 and T the temperature. By the

20slope and intercept of linear regres- sion of van't Hoff

equation, the thermodynamic parameters in Table 6 could be determined. It is clear that the standard Gibbs' free energy change were all negative along the temperature varia- tions, indicating a spontaneous nature of TMAH adsorption on WAC activated carbon (Do 1998). The negative value of the en- thalpy change revealed

18that the adsorption was exothermic in nature. On the

contrary, CMSs showed poor adsorption when the temperature was set to low (i.e., 7°C) and when the temperature was increased from 23 to 40°C, b and q0 were increased, suggesting endothermic process (Kelleher et al. 2001). The typical enthalpy change in physisorption is in the range of 5–40 kJ=mol (1:19– 9:56 kcal=mol) and typical enthalpy change in ion exchange is below 2 kcal=mol (Helfferich 1995; Inglezakis and Poulopoulos 2006). The adsorption enthalpy range was in the range of a combi- nation of physisorption and ion exchange. Positive value of ΔS° suggests that adsorption process exhibits randomness behavior at the solid/solution surface (Kelleher et al. 2001; Kosasih et al. 2010). Desorption Study In five cycles of adsorption-desorption experiments, the TMAH- saturated activated carbon could be easily regenerated by 0.1 N HCl, while the regeneration could not be completed by warm water [Figs. 5(a) and 5(b)]. By using 0.1 N HCl, the amount of desorbed 120 100 desorbed TMAH (%) 80 60 40 20 0 1 HCl-regenerated water-regenerated (a) 2 number of batch adsorption experiment 3 4 5 6 7 8 9 100 HCl-regenerated water-

regenerated 80 TMAH removal (%) 60 40 20 0 1 2 3 4 5 6 (b) number of batch adsorption experiment Fig. 5. (a) regeneration of WAC by 0.1 N HCl and water (C° ¼ 50 5 mg=L, adsorbent dose = 4 g=L, pH ¼ 11:8 0:2, reac- tion time = 24 hours); (b) batch adsorption cycles of WAC (C° ¼ 50 5 mg=L, adsorbent dose ¼ 4 g=L, adsorbent dose ¼ 4 g=L, reaction time = 24 hours) TMAH could always reach 100% even after five cycles of adsorption-desorption. Even though there was an increase in the percentage of desorbed TMAH with the increase of cycle time, re- generation efficiency of the water actually stayed the same while WAC activated carbon was actually more and more exhausted. Eventually, removal efficiency of TMAH stabilized at a low value (ca. 15%), with the same amount of TMAH that could be desorbed. Overall, this relatively easy desorption suggested that the bond be- tween TMAH and activated carbon surface was a weak physical one and the adsorption was reversible. Mechanism Since activated carbon is amphoteric in nature, its surface charge changes as the solution pH varies. Since TMAH remains Table 6. Thermodynamic Parameters of TMAH Adsorption at Different Temperature T (°C) 1=Tð1=KÞ b0 L=mol lnb0 ΔG° (kcal=mol) ΔH° (kcal=mol) ΔS° (cal=½mol:kŠ) 25 0.003354 40 0.003193 55 0.003047 1075.57 1002.65 957.08 6.9806 6.9104 6.8639 4:13 0:76 11.32 4:30 4:47 permanently ionized over any pH range, its adsorption depended strongly on the pH of the solution that determines the surface charge of the activated carbons. When the pH was shifted to a re- gion lower than the pHPZC of the WAC activated carbon, the ad- sorption capacity decreased significantly until there was practically no adsorption. Since no adsorption of TMAH could be observed when the pH was lower than pHPZC (i.e., at pH ¼ 4:7 0:2), it suggested that hydrophobic interaction was not a dominant driving force for the adsorption of TMAH on acti- vated carbon. On the contrary, as the pH shifted from pHPZC to higher pH region, the adsorption density increased dramatically. Effect of pH on TMAH adsorption suggested that the electrostatic interaction was the main driving force for the adsorption. As demonstrated by results from Boehm titration, the activated carbons contained polar functional

21**groups, such as carboxylic, lactonic, and** phenoliclike **groups.** Therefore, **the**

reaction between TMAH and the surface of the activated carbons can be represented as XO þ TMAþ⇌XO TMA ð6Þ X could be carbon or oxygen element, representing carboxylic, lactonic, and phenoliclike functional groups whose amounts were semi quantitatively characterized by Boehm titration. For adsorption at high pH, complete ionization of the

21**carboxylic, lactonic, and phenolic** functional **groups** on **the surface of**

acti- vated carbon unleashed its maximum surface charge density. This situation is schematically illustrated at Fig. 6. In general, adsorption of TMAH on activated carbon can be visualized as follow. First, delocalized π electrons of the graphite planes may act as Lewis basic sites accepting protons as governed by this reaction scheme (Lopez-Ramon et al. 1999; László 2001): Cπ þ H3Oþ H⇌þ;K1 CπH3Oþ←ðrepulsionÞ→TMAþ ð7Þ which is disadvantageous to TMAH adsorption. Secondly, the presence of acidic functional group is beneficial to TMAH adsorp- tion, particularly when solution pH is higher than pHPZC. It was the negatively charged surface oxides tend to attract TMAþ as follows (Lopez-Ramon et al. 1999): Fig. 6. Schematic representation of TMAþ attracted to ionized acidic surface functional groups of the activated carbon XOH2þ H⇌þ;K1 Hþ; K2 XOH ⇌ XO ð→attrac←tionÞ TMAþ ð8Þ This was the first work in which activated carbon was utilized for TMAH adsorption. Judging from experimental results, activated carbon was in general very effective, particularly those with micro- pores and low pHPZC. It can be used as a pretreatment of TMAH- containing wastewater prior to its biological treatment unit, so that the wastewater

becomes more biodegradable. Or, it can be a post- treatment following biological process to further polish secondary effluent to lower the effluent eco-toxicity. Some column study is needed to assess adsorption reactions in more detail before pilot study. Subsequent treatment of loaded activated carbon is relatively easy if the removal of TMAH only is desired. Since TMAH is com- pletely decomposed at temperature of 135–140°C, the TMAH- exhausted activated carbon can be heat-treated and washed instead of incinerated (Feng et al. 2008). Alternatively, since TMAH could be desorbed completely by 0.1 N HCl, the concentrated wastewater generated from activated carbon desorption can be further recov- ered via membrane processes. Surely, further feasibility study and cost analysis should be considered. Conclusions Adsorption of TMAH on activated carbons was carried out in this study. Based on the experimental results and discussion, the follow- ing conclusions could be drawn: 1. In the adsorption of TMAH on activated carbons, the activated carbon with micropores was favored. 2. The adsorption kinetics could be represented by pseudo- second-order model. 3. The adsorption of TMAH on activated carbon followed monolayer adsorption as indicated by good fitting by Lang- muir isotherm. The highest adsorption capacity among activated carbons studied was 27:77 mg=g as achieved by WAC. 4. Adsorption of TMAH was noticeable only when solution pH was higher than the pHPZC of the activated carbon, and it was mainly driven by electrostatic adsorption mechanism. 5. Adsorption process was spontaneous and exothermic in nature with standard enthalpy change in the typical range between physical adsorption and ion exchange. 6. From the desorption study, exhausted activated carbon could be regenerated by 0.1 N HCl without significant reduction in TMAH removal. The desorption study also confirmed that the bonding between TMAH

9**and the** active **adsorption** sites **of activated carbon was** weak and **of**

physical nature. Acknowledgments Devarly Prahas would like to acknowledge the full international scholarship awarded by National Taiwan University of Science and Technology during his master study. References Boehm, H. P. (1994). "Some aspects of the surface chemistry of carbon blacks and other carbons." Carbon, 32(5), 759–769. Boehm, H. P. (2002). "Surface oxides on carbon and their analysis: A criti- cal assessment." Carbon, 40(2), 145–149. Chang, K. F., Yang, S. Y., You, H. S., and Pan, J. R. (2008). "Anaerobic treatment of tetra-methylammonium hydroxide (TMAH) containing wastewater." IEEE Trans. Semicond. Manuf., 21(3), 486–491. Chen, J. P., and Wu, S. (2004). "Acid/base-treated activated carbons: Char- acterization of functional groups and metal adsorptive properties." Langmuir, 20(6), 2233–2242. Corapcioglu, M. O., and Huang, C. P. (1987). "The surface acidity and characterization of some commercial activated carbons." Carbon, 25(4), 569–578. Do, D. D. (1998). Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London. El-Sayed, Y., and Bandosz, T. J. (2004). "Adsorption of valeric acid from aqueous solution onto activated carbons: Role of surface basic sites." J. Colloid Interface Sci., 273(1), 64–72. Feng, H., Huang, C., and Xu, T. (2008). "Production of tetramethyl am- monim hydroxide using bipolar membrane electrodialysis." Ind. Eng. Chem. Res., 47(20), 7552–7557. Helfferich, F. (1995). Ion exchange, Dover Publications, NY, 166. Hirano, K., Okamura, J., Taira, T., Sano, K., Toyoda, A., and Ikeda, M. (2001). "An efficient treatment technique for TMAH wastewater by catalytic oxidation." IEEE Trans. Semicond. Manuf., 14(3), 202–206. Ho, Y. (2006). "Review of second-order models for adsorption systems." J. Hazard. Mater., 136(3), 681–689. Ho, Y. S., and McKay, G. (1998). "Kinetic models for the sorption of dye from aqueous solution by wood." Process Saf. Environ. Prot., 76(2), 183–191. Inglezakis, V. J., and Poulopoulos, S. G. (2006). Adsorption, ion exchange, and catalysis: Design operations and environmental applications, Elsevier, Amsterdam, 31–33. Kelleher, B. P., Doyle, A. M., Hodnett, B. K., and O'Dwyer, T. F. (2002). "An investigation into the adsorption characteristics of grafted mesopo- rous silicates for the removal of tetramethyl ammonium hydroxide from aqueous solution." Adsorpt. Sci. Technol., 20(8), 787–796. Kelleher,

B. P., Doyle, A. M., O'Dwyer, T. F., and Hodnett, B. K. (2001). "Preparation and use of a mesoporous silicate material for the removal of tetramethyl ammonium hydroxide (TMAH) from aqueous solution." J. Chem. Technol. Biotechnol., 76(12), 1216–1222. Kosasih, A. N., Febrianto, J., Sunarso, J., Ju, Y. H., Indraswati, N., and Ismadji, S. (2010). "Sequestering of Cu(II) from aqueous solution using cassava peel (Manihot esculenta)." J. Hazard. Mater., 180(1–3), 366–374. László, K., Tombácz, E., and Josepovits, K. (2001). "Effect of activation on the surface chemistry of carbons from polymer precursors source." Carbon, 39(8), 1217–1228. Lei, C. N., Whang, L. M., and Chen, P. C. (2010). "Biological treatment of thin-film transistor liquid crystal display (TFT-LCD) wastewater using aerobic and anoxic/oxic sequencing batch reactors." Chemosphere, 81(1), 57–64. Lopez-Ramon, M. V., Stoeckli, F., Moreno-Castilla, C., and Marin, F. (1999). "On the characterization of acidic and basic surface sites on carbons by various techniques." Carbon, 37(8), 1215–1221. Menéndez, J. A., Illan-Gomez, M. J., León y León, C. A., and Radovic, L. R. (1995). "On the difference between the isoelectric point and the point of zero charge of carbons." Carbon, 33(11), 1655–1659. Plazinski, W., Rudzinski, W., and Plazinska, A. (2009). "Theoretical models of sorption kinetics including a surface reaction mechanism: A review." Adv. Colloid Interface Sci., 152(1–2), 2–13. Shibata, J., Murayama, N., and Matsumoto, S. (2006). "Recovery of tetra- methyl ammonium hydroxide from waste solution by ion exchange resin." Resour. Process., 53(4), 199–203. Sugawara, H., Tajima, Y., and Ohmi, T. (2002). "A study on reclaimed pho- toresist developer using an electrodialysis method." Jpn. J. Appl. Phys., 41(Part 1, No. 4B), 2374–2379. Thong, J. T. L., Choi, W. K., and Chong, C. W. (1997). "TMAH etching of silicon and the interaction of etching parameters." Sens. Actuators, A, 63(3), 243–249. Tsuzaki, M., and Nakamoto, S. (1990). "Biodegradation of tetramethylam- monium, an ingredient of a positive photoresist developer, by bacteria isolated from activated sludge." NEC Res. Dev., (97), 8–12. Wahab, M. A., Jellali, S., and Jedidi, N. (2010). "Ammonium biosorption onto sawdust: FTIR analysis, kinetics and adsorption isotherms model- ing." Bioresour. Technol., 101(14), 5070–5075. Wibowo, N., Setyadhi, L., Wibowo, D., Setiawan, J., and Ismadji, S. (2007). "Adsorption of benzene and toluene from aqueous solutions onto activated carbon and its acid and heat treated forms: Influence of surface chemistry on adsorption." J. Hazard. Mater., 146(1–2), 237–242. Yalçin, M., Gürses, A., Dogar, C., and Sözbilir, M. (2005). "The adsorption kinetics of cethyltrimethylammonium bromide (CTAB) onto powdered active carbon." Adsorption, 10(4), 339–348. 232 /

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