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Enhanced adsorption of quaternary amine using modified activated carbon Devarly Prahastya, M. J. Wang, Suryadi Ismadji and J. C. Liu ABSTRACT This study examined different methodologies to modify activated carbon (AC) for the removal of quaternary amine, tetramethylammonium hydroxide (TMAH), from water. Commercial carbon (WAC) was treated by nitric acid oxidation (NA-WAC), silica impregnation (SM-WAC0.5), and oxygen plasma (P10-WAC), and their characteristics and adsorption capacity were compared. The Langmuir model fitted the equilibrium adsorption data well under different pH. The maximum adsorption capacity of WAC was 27.77 mg/g, while those of NA-WAC, SM-WAC 0.5, and P10-WAC were 37.46, 32.83 and 29.03 mg/g, respectively. Nitric acid oxidation

9 was the most effective method for **enhancing the adsorption** capacity **of** TMAH. Higher pH **was**

favorable for TMAH adsorption. Desorption study revealed that NA-WAC had no considerable reduction in performance even after five cycles of regeneration by 0.1 N hydrochloric acid. It was proposed that electrostatic interaction was the main mechanism of TMAH adsorption on activated carbon. Key words | activated carbon, adsorption, amine, plasma, silica, tetramethylammonium hydroxide (TMAH) Devarly Prahastya M. J. Wang

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INTRODUCTION Many works have been completed on modifying surface properties of activated carbon (AC) for enhanced adsorption (Yin et al. 2007; Rivera-Utrilla et al. 2011). It is known that AC can change surface charge and surface functional groups either by conventional acidic treatment using oxidizing agents (Chen & Wu 2004) or plasma treatment (Domingo-García et al. 2000). Acid treatment is used to increase the acidic surface functional groups of AC, which results in a dramatic shift of the point of zero charge to a more acidic range (Rivera-Utrilla et al. 2011). Different plasma reactor types and experimental conditions could give different results. Advantages and disadvantages of different methods are discussed in a review by Rivera-Utrilla et al. (2011) Tetramethylammonium hydroxide (TMAH) is a quaternary amine commonly used in semiconductor, optoelectronic, and light emitting diode manufacturing. It is corrosive and highly toxic, and it has caused several occupational accidents, with symptoms of dyspnea and hyperglycemia, and chemical burn, as well as some fatal cases (Lee et al. 2011). Its presence in wastewater is also a problem that needs to be solved. Various treatment technologies have been doi:

10.2166/wst.2014.085 examined for TMAH-containing wastewater, including catalytic oxidation (Hirano et al. 2001), anaerobic biological process (Chang et al. 2008; Hu et al. 2010), aerobic and anoxic/oxic sequencing biological reactor (Lei et al. 2010), and membrane bioreactor (Whang et al. 2008). A cubic mesoporous silicate could remove TMAH and the reaction followed the Langmuir model (Kelleher et al. 2001). The ion exchange process is effective in removing TMAH from wastewater (Citraningrum et al. 2013). Separation and recovery of TMAH can be conducted by hexagonal mesoporous silica (Nishihama et al. 2012). AC made from bamboo showed high potential for adsorption of TMAH (Yamaguchi et al. 2008). We have demonstrated in our previous study that commercial activated carbon (WAC) was effective in removing TMAH due to its microporous nature and high concentrations of acidic surface functional groups (Prahas et al. 2012). In this study, WAC was modified by nitric acid treatment, oxygen glow discharge plasma, and sodium metasilicate impregnation. The objective of the study was to investigate whether the modification of WAC by the above methods could enhance its capacity to adsorb TMAH, so that a more effective adsorbent could be developed. MATERIALS AND METHODS Chemicals and reagents Commercial AC was obtained from Wako Pure Chemicals Industries, Ltd (Richmond, VA) and denoted as WAC. Prior to using it, the WAC was washed with ultra-pure water repetitively until the pH of the washing water was constant and the conductivity was below 5 $\mu\text{S}/\text{cm}$. The washed WAC was

13then dried in an oven at 105 WC 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). Nitric acid treatment For nitric acid pretreatment, 20 g ($\pm 1\%$) of activated carbon (WAC) was placed in a custom-built thimble made from wire-mesh. The modification was then conducted using the soxhlet extraction technique by refluxing 500 mL of 5N- HNO_3 at its boiling temperature (± 120 WC) for 6 hours. It was then followed by subsequent washing by refluxing and changing of ultra-pure water until the pH of the water after washing was constant and the conductivity was below 5 $\mu\text{S}/\text{cm}$. The washed WAC

13was dried in an oven at 105 WC overnight and sieved until the

particles were below 100 mesh. Sieved AC was stored in tightly capped clean plastic bottles and was labeled NA-WAC. Plasma treatment In plasma treatment, 0.2 g of WAC was placed in a custom-built glass container having a cap that allowed plasma to flow into the container, enabling the carbon's surface to be

treated. This container was then placed on a 15-cm diameter cylindrical anode inside a plasma reactor with the dimensions 30 cm × 30 cm × 30 cm equipped with a 13.56-MHz radio frequency (RF) plasma generator (PFG-300RF). Prior to plasma treatment, the chamber was evacuated to a base pressure of 10 mTorr by a vacuum pump (Woosung, TRP- 60). After appropriate degassing had been achieved, glow discharge oxygen plasma was introduced into the chamber via a spray-type cathode, which was located just above the container and the anode. At this point, the oxygen flow rate was set to 10 standard cubic centimeters per minute (cm³/min) using a mass flow controller (KD-4000) under the power of 20 or 100 watt, with total reaction pressure of 100 mTorr. After the desired treatment time of 10 min, nitrogen gas was directed into the chamber to permit collection of the container at atmospheric condition. The AC treated by plasma was then stored in a tightly capped plastic bottle inside a dehumidifier cabinet and labeled P10-WAC. Impregnation of sodium metasilicate on WAC was carried out based on earlier published procedures (Karanfil & Kilduff 1999). The latter procedure for impregnation of carbon was modified to avoid the possible effect of sulfuric acid. A typical impregnation method with a quick rinsing by acid in the washing step was used in this study. Twenty grams (±1%) of AC was immersed into sodium metasilicate (Acros, Na₂SiO₃·9H₂O) solution with respect to the impregnation ratio (IR). The IR is defined as the weight of impregnant per unit weight of AC. An IR of 0.5 was obtained by diluting 23.26 g (±1%) of sodium metasilicate into 100 mL of pure water to produce a silicate solution of 0.82 M. The AC was added into the silicate solution

15 **and the slurry was then stirred for 24 hours at room temperature.**

The slurry was

14 **then dried in an oven at 105 °C overnight.** The carbon **was**

then quickly rinsed with 0.01 N HCl (Acros) once, followed by subsequent washing with ultra-pure water several times. Washing was done until the pH of the water after washing was constant and the conductivity was below 5 μS/cm. Washed carbon was dried again at 105 °C overnight and sieved until the particles were below 100 mesh. The sieved AC was stored in tightly capped clean plastic bottles and was labeled SM-WAC0.5. Characterization Brunauer–Emmett–Teller (BET)

16 **surface area (SBET) was determined from N₂ adsorption–desorption isotherms**

at 196 °C by a Quantachrome

20 **Autosorb-1** instrument. **Prior to the measurements, the ACs were degassed at 200 °C in a vacuum condition for at least**

24 h.

9 The isoelectric point (pHIEP) and point of zero charge (pHPZC) of

the ACs were determined by zeta potential measurement and pH drift method, respectively, with 0.01 N NaCl (Acros) as background electrolyte. The pHIEP could be deduced when the pH versus zeta potential line crossed the line at which the zeta potential is equal to zero. The pHPZC could be found when the final pH is equal to the initial pH. The widely used Boehm titration was used to semi-quantitatively address surface acidity and basicity of the ACs (Boehm 1994, 2002). A qualitative analysis of the D. Prahas et al. | Enhanced adsorption of quaternary amine by modified AC Water Science & Technology | 69.10 | 2014 functional groups of the ACs was conducted by obtaining their Fourier transform infrared spectroscopy (FTIR) transmission spectra using KBr technique. Prior to analysis, the KBr powder and samples were dried overnight at 105 °C. The AC sample was mixed with the KBr powder in the ratio of 1:100 and ground with the agate mortar until they became well-mixed fine particles. Analysis was carried out by FTIR instrument (Bio-Rad, Digilab FTS-3500)

8 in the wave number range of 4,000–400 cm⁻¹

and transmittance (%T) mode. Adsorption experiments Total reaction time was 24 hours in the adsorption experiment. To ensure data validity, experiments were carried out in triplicate analysis with relative standard deviation lower than 10% in every adsorption isotherm experiment. Measurement of TMAH concentration was by an ion chromatography system (Dionex ICS-1000) equipped with an autosampler (Spectra System, AS-1000) with the retention time of 20 min. For desorption experiments, loaded carbon 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 hours. The amount of desorbed TMAH was analyzed after samples were diluted and neutralized. Before undergoing any subsequent adsorption experiment, the adsorbent was collected again by filtration and oven-dried at 105 °C overnight. The cycle of such adsorption and desorption was repeated five times in triplicate analysis.

RESULTS AND DISCUSSION

Characteristics of AC

BET surface area

Properties of the original activated carbon (WAC) and modified ones are listed in Table 1. A slight increase of BET surface area was observed for NA-WAC, while a limited decrease was found for those of SM-WAC0.5 and P10-WAC. No significant change in BET surface area of the modified WAC ACs was found, which was in agreement with literature (Rivera-Utrilla et al. 2011). The slight decrease of BET surface area found in SM-WAC0.5 was probably caused by pore blocking during impregnation (Yamamoto et al. 2003).

Surface charge

Both pHPZC and pHIEP of modified WAC were lower than the original pHPZC of 7.4 (Table 1). Surface charge properties of NA-WAC and SM-WAC0.5 were significantly altered, and the pHPZC and pHIEP (pHPZC–pHIEP) were equal for both modified carbons. Generally, the changes in the pHPZC caused by the modifications were more significant than those in pHIEP. This finding suggested that NA-WAC and SM-WAC0.5 had evenly distributed external and internal surface charge (Biniak et al. 1997). The isoelectric point of silica (SiO₂) was reported to be around 1.7 to 3.5 (Kosmulski 2001). Thus, a slight reduction in pHPZC and pHIEP of SM-WAC0.5 to 5.2 was expected. It seemed that the modifications by chemicals were able to induce significant changes not only to the external surface but also to the interior surface of WAC. Regarding oxygen plasma treatment, surface charge properties of WAC were only slightly changed. This was because the plasma species could hardly reach the micropore structure due to the high reactivity of mono-oxygen species during plasma treatment (Domingo-García et al. 2000). Surface functional groups As

confirmed by Boehm titration results (Table 1), NA-WAC showed a dramatic increase of acidic functional groups and simultaneously reduced the basic functional groups, owing to the incorporation of oxygen functional groups via oxidation of aromatic hydrocarbons (Chen & Wu 2004). In Surface functional groups (meq/g) Carboxyl Lactone 0.179 0.134 0.536 0.280 0.168 0.082 0.373 0.088 Phenol Total acid 0.160 0.473 0.355 1.171 0.466 0.716 0.146 0.607 Base 0.459 0.129 0.432 0.612 contrast, modification by plasma seemed to enhance the carboxyl functional groups. The increase in the surface acidity by plasma treatment was due to oxygen chemical addition, as oxygen free radicals reacted aggressively with carbon atoms at the external surface (Qu et al. 2009). However, it was observed that plasma modification incorporated more basic functional groups as well. This simultaneous enhancement was caused by the high temperature during plasma treatment that acted as heat treatment, which eliminates acidic functional groups and gives rise to the basic functional groups (Jia & Thomas 2000).

17 Oxygen surface complexes are predominantly of acidic character

while surface basic sites of ACs

17 are essentially of the electron-donating (Lewis) type associated with

exposed basal graphite planes possessing π electron-rich regions (Lopez-Ramon et al. 1999). Therefore, the plasma etching effect could also contribute to the increase of basic functional groups on P10-WAC. FTIR analysis FTIR spectra of WAC and modified carbons are shown in Figure 1. There was no significant difference that could be observed from the spectra of WAC, P10-WAC, and NA-WAC (Figure 1). Only small disturbances near the range of 1,725–1,700 cm^{-1} could be noticed. The disappearance of this peak typical of $-\text{C}=\text{O}$ in ketones, aldehyde, lactone, and carboxyl might be attributed to the overlapping of weak peaks (Pavia et al. 2009). On the other hand, there was a new peak for SM-WAC0.5. As illustrated, sodium metasilicate had characteristic bands of silanol $-\text{OH}$ stretching and $\text{Si}-\text{O}-\text{Si}$ stretching as shown by the broad band at 3,700–2,500 cm^{-1} and strong peaks at 1,450 and 970 cm^{-1} , respectively (Abo-El-Enein et al. 2009). Thus, the

15 appearance of a new peak at 970 cm^{-1}

and higher intensity of the broad band at 3,400–2,400 cm^{-1} of SM-WAC0.5 (Figure 1), compared to its original, confirmed that SM-WAC0.5 contains silica deposit. Adsorption study The empirical Freundlich equation is written in the following form: $q_e = K_f C_e^n$ (1)

12 where q_e is the mass of substance adsorbed per unit mass of adsorbent, C_e is the equilibrium concentration of the solute

Figure 1 | FTIR spectra of (a) WAC, (b) P10-WAC, (c) NA-WAC, (d) SM-WAC0.5, and (e) pure sodium metasilicate. being adsorbed, while K_f and n are empirical constants. The Langmuir isotherm can be applied for type I equilibrium adsorption: $q_e = \frac{q_0 b C_e}{1 + b C_e}$ (2)

2where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g), and q_0 and b are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively.

As shown in Figure 2 as well as Table 2, the TMAH adsorption capacity was in the order NA-WAC > SM-WAC0.5 > P10-WAC > WAC. Similar to adsorption iso-therms, the adsorption isotherms of modified WAC could be

14better fitted to the Langmuir isotherm than the Freundlich

D. Prahas et al. | Enhanced adsorption of quaternary amine by modified AC Water Science & Technology | 69.10 | 2014 Figure 2 | Langmuir and Freundlich isotherms of TMAH adsorption on original WAC and modified WACs (adsorbent dose: 4 g/L, pH: 11.8 ± 0.2 , reaction time: 24 hours). equation (Table 2). The adsorption density was lower than that of ion exchange resin (Citraningrum et al. 2013). The enhancement as shown in the adsorption isotherm was consistent with the incorporation of acidic functional groups resulting from particular modifications. SM-WAC05 possessed more oxygen surface functional groups as shown by Boehm titration results. Yamamoto et al. (2003) observed that the AC impregnated with any dose of sodium silicate showed an enhancement of water vapor adsorption towards a lower relative pressure region than that of raw AC. The following reactions could occur in a high pH condition (Vautier-Giongo & Pastore 2006): $\equiv \text{Si} - 2\text{OH} \rightleftharpoons \text{OH}^- \rightarrow \leftarrow \equiv \text{Si} - 2\text{O}^- \rightleftharpoons \text{H}_2\text{O} \rightleftharpoons \text{Si} - 2\text{O}^- \rightleftharpoons 2\text{Si}^- \rightleftharpoons \text{OH}^- \rightarrow \leftarrow \equiv \text{Si} - 2\text{O}^- \rightleftharpoons \text{HO}^- \rightleftharpoons 2\text{Si}^- \rightleftharpoons \text{Si} - 2\text{O}^-$ sites could contribute to the attraction forces between TMAH and the impregnated AC. Moreover, P10-WAC had better adsorption capacity than WAC despite the decrease in BET surface area, suggesting that the surface chemistry played an important role in the adsorption process. Carboxylic groups on oxidized carbon surfaces contribute most towards cation exchange properties, while carbons

4always exhibit an anion exchange capacity because basic surface oxides are always present when carbons have been exposed to the atmosphere

after activation (Boehm 1994, 2002). Effect of pH Solution pH is always one of the main factors that influence adsorption. Effects of

6pH on the adsorption of TMAH on WAC and

modified WAC ACs are shown in Figure 3. Since TMAH remains permanently ionized over any pH range, its adsorption depended strongly on the

7pH of the solution that determines the surface charge of the

ACs. Whenever the pH was lower than the pHPZC of the ACs, the adsorption capacity dropped significantly. Overall, higher pH was favorable for adsorption of TMAH and no adsorption could occur when the pH was shifted to pH lower than the pHPZC of each AC. The effect of pH on TMAH adsorption suggested that the electrostatic interaction was the main driving force for the adsorption (Prahas et al. 2012). The presence of an acidic functional group is beneficial to TMAH adsorption particularly when the solution pH is higher than the pHPZC (Lopez-Ramon et al. 1999; László et al. 2007). As demonstrated by several surface modification methods in this study, bringing the point of zero charge of the original carbons as low as possible would be advantageous for the adsorption of TMAH. This behavior was well represented by NA-WAC. As the pH shifted from pHPZC to a higher pH, the adsorption density increased dramatically and then eventually reached a plateau when it was far from the pHPZC. Table 2 | Isotherm parameters of TMAH adsorption on WAC and modified WACs (adsorbent dose $\frac{1}{4}$ 4 g/L; pH $\frac{1}{4}$ 11.8 \pm 0.2; reaction time $\frac{1}{4}$ 24 h) Isotherms Parameters WAC NA-WAC SM-WAC0.5 P10-WAC

5 Freundlich K_f (mg/g)(L/mg) $^{1/n}$ n R^2

2.44 2.61 0.383 0.9652 2.40 2.25 0.444 0.9617 2.40 2.39 0.418 0.9640 2.13 2.40 0.416 0.9834

5 Langmuir q_0 (mg/g) b (L/mg) R^2

27.77 0.0118 0.9902 37.46 0.0115 0.9916 32.83 0.0116 0.9811 29.03 0.0117 0.9950 Figure 3 |

6 Effect of equilibrium pH on the adsorption of TMAH on WAC and

modified WACs (C_0 : 20 \pm 2 mg/L (a), C_0 : 500 \pm 50 mg/L (b), adsorbent dose: 4 g/L, reaction time: 24 hours). Desorption study Just as in WAC (Prahas et al. 2012), the results of the NA-WAC desorption study confirmed that the bonding between TMAH and the AC surface was not a strong chemical one and was a reversible type. The regeneration could also be completed by 0.01 N HCl with 100% efficiency

8(Figure 4(a)). There was also no significant decrease in the TMAH removal efficiency

of NA-WAC even after five cycles of regeneration by 0.01 N HCl (Figure 4(b)). Significant reduction in TMAH removal by the regeneration cycles carried out by water was observed, indicating that hot water was not good for desorption. Discussion Physical interactions in adsorption usually include two aspects, i.e. size exclusion and microporosity effects. Since TMAH is a quaternary ammonium compound with substituted methyl groups creating short hydrophobic branches but no chain, steric repulsion as the cause of size exclusion can be neglected. In

19 adsorption of low molecular weight molecules,

adsorption

19energy is greater in micropores since **pore width approaches** the **adsorbate**

dimension (Karanfil & Kilduff 1999). According to Kelleher et al. (2001), the arrangement of TMAH at molecular level could be visualized as layers composed of molecules being contained in each cubical molecular space of 107.9 Å³, assuming surface monolayer coverage. By the ratio of volume occupied by TMAH over the pore volume, the values shown in Table 3 could be obtained. However, to address the surface layering mechanism, it is better to use Figure 4 | (bae)nRtedgoesnee:ra4tgio/nL, opfHN:1A1-W.8A±C0b.2y, 0r.e1acNtiHoCnltiamnde: w24atheoru(Crs0):. 5(b0) ±Ba5tcmhga/dL,soardpstoior-n cycles of NA-WAC (C0: 50 ± 5 mg/L, adsorbent dose: 4 g/L, pH: 11.8 ± 0.2, reaction time: 24 hours). surface area rather than volume as revealed in the micro- pore filling mechanism. Still, the fractions of pore volume occupied in WAC were still low. The micropore filling mechanism in WAC was therefore unlikely since the fraction of occupied surface area was not significantly higher than the occupied pore volume. A recent study by Duman & Ayranci (2010) showed that the removal of quaternary ammonium compounds by AC cloth with PHPZC of 7.4 was mainly driven

7by hydrogen bonding, and hydrophobic and van der Waals interactions.

Tamai et al. (2004) studied the

16adsorption of tetraalkylammonium ions onto both **microporous and mesoporous**

ACs and pointed out that the main driving force was hydrophobic interaction. It is obvious that TMAH has no long carbon chain in the structure. If there were hydrophobic interactions, the adsorption at D. Prahas et al. | Enhanced adsorption of quaternary amine by modified AC Water Science & Technology | 69.10 | 2014 Table 3 | Surface area and pore volume of WAC occupied by TMAH pH SBET (m²/g) Occupied

10surface area (m²/g) Occupied surface area (%) q₀ (mg /g) Total pore volume (mL/g) Occupied pore volume (mL/g) Occupied pore volume

(%) 11.8 ± 0.2 862.19 39.14 4.54 27.77 0.3609 0.0170 5.43 7.8 ± 0.2 862.19 20.47 2.37 13.45 0.3609 0.0096 2.66 7.0 ± 0.2 862.19 9.50 1.10 6.24 0.3609 0.0044 1.23 4.7 ± 0.2 862.19 N/A N/A N/A 0.3609 N/A N/A any pH range should always occur since AC contains significant hydrophobic sites. However, the adsorption behavior of TMAH onto AC demonstrated that there was practically no adsorption at a certain point below the point of zero charge. These findings confirm that the main driving force of the adsorption of TMAH on AC was electrostatic interaction. CONCLUSIONS This study examined three different methodologies to modify AC for the enhanced removal of quaternary amine, TMAH, from water. Commercial carbon (WAC) was treated by nitric acid oxidation (NA-WAC), silica impregnation (SM-WAC0.5), and oxygen plasma (P10-WAC), and their characteristics and adsorption capacity were compared. Major findings can be

summarized as follows. • The adsorption capacity of AC could be increased after modification due to more incorporation of acidic functional groups, particularly carboxyl ones. • By Langmuir isotherm, maximum TMAH adsorption capacities of NA-WAC, SM-WAC, and P10-WAC were found to be 37.46, 32.83 and 29.03 mg/g, respectively. • Nitric acid oxidation was the most effective method for enhancing acidic functional groups of the AC to increase the adsorption capacity of TMAH. While significant increase in adsorption capacity was introduced by nitric acid oxidation and sodium metasilicate impregnation, less effect was produced by oxygen plasma treatment due to simultaneous increase in acidic and basic functional groups. • The desorption study showed that NA-WAC had no considerable reduction in performance after five cycles of regeneration by 0.1 N HCl. • It was proposed that electrostatic interaction was the main mechanism of TMAH adsorption on AC.

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