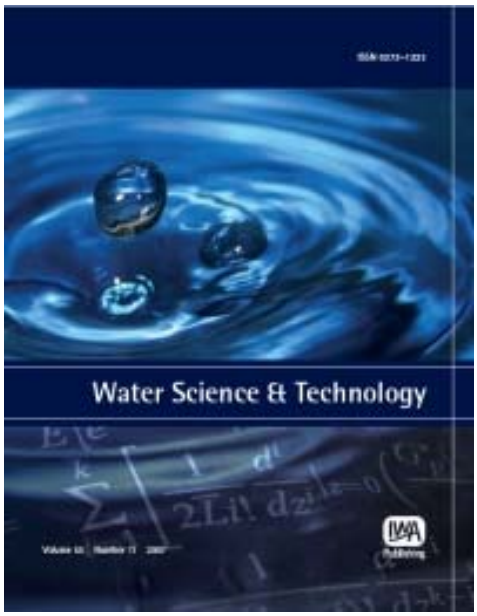

Enhanced adsorption of quaternary amine using modified activated carbon

Devarly Prahas, 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 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)

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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 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.

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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 μS/cm. The washed WAC was 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).

Nitric acid treatment

For nitric acid pretreatment, 20 g (±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 °C) 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 μS/cm. The washed WAC was dried in an oven at 105 °C 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 (cm^3/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

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, $Na_2SiO_3.9H_2O$) 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 and the slurry was then stirred for 24 hours at room temperature. The slurry was 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) surface area (S_{BET}) was determined from N_2 adsorption–desorption isotherms at −196 °C by a Quantachrome Autosorb-1 instrument. Prior to the measurements, the ACs were degassed at 200 °C in a vacuum condition for at least 24 h. The isoelectric point (pH_{IEP}) and point of zero charge (pH_{PZC}) of the ACs were determined by zeta potential measurement and pH drift method, respectively, with 0.01 N NaCl (Acros) as background electrolyte. The pH_{IEP} could be deduced when the pH versus zeta potential line crossed the line at which the zeta potential is equal to zero. The pH_{PZC} 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

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) 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 pH_{PZC} and pH_{IEP} of modified WAC were lower than the original pH_{PZC} of 7.4 (Table 1). Surface charge properties of NA-WAC and SM-WAC0.5 were significantly altered, and the pH_{PZC} and pH_{IEP} (pH_{PZC}–pH_{IEP}) were equal for both modified carbons. Generally, the changes in the pH_{PZC} caused by the modifications were more significant than those in pH_{IEP}. 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 (SiO_2) was reported to be around 1.7 to 3.5 (Kosmulski 2001). Thus, a slight reduction in pH_{PZC} and pH_{IEP} 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

Table 1 | Surface properties of WAC and modified WAC

		Surface charge		Surface functional groups (meq/g)				
Samples	S_{BET} (m^2/g)	pH_{PZC}	pH_{IEP}	Carboxyl	Lactone	Phenol	Total acid	Base
WAC	862.19	7.4	5.3	0.179	0.134	0.160	0.473	0.459
NA-WAC	902.33	4.6	4.6	0.536	0.280	0.355	1.171	0.129
SM-WAC 0.5	834.08	5.2	5.2	0.168	0.082	0.466	0.716	0.432
P10-WAC	839.51	7.1	5.2	0.373	0.088	0.146	0.607	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). Oxygen surface complexes are predominantly of acidic character while surface basic sites of ACs 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 –C = 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 –OH stretching and Si–O–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 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:

$$q_e = K_f.C_e^{1/n} \quad (1)$$

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

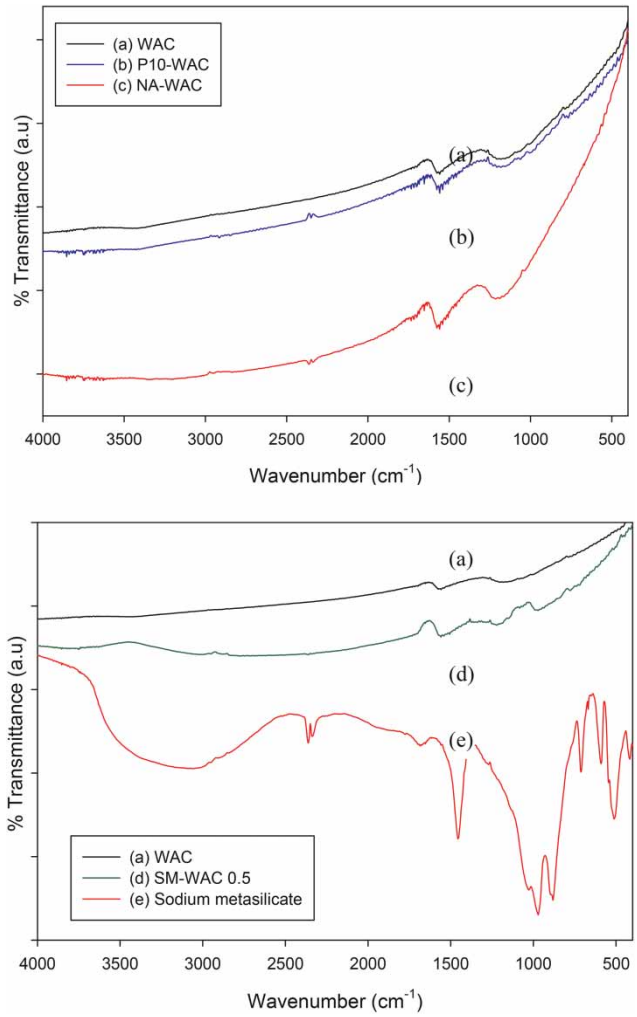

Figure 1 | FTIR spectra of (a) WAC, (b) P10-WAC, (c) NA-WAC, (d) SM-WAC0.5, and (e) pure sodium metasilicate.

being adsorbed, while K_f and n are empirical constants. The Langmuir isotherm can be applied for type I equilibrium adsorption:

$$q_e = q_0 \cdot \frac{b.C_e}{1 + b.C_e} \quad (2)$$

where 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 isotherms, the adsorption isotherms of modified WAC could be better fitted to the Langmuir isotherm than the Freundlich

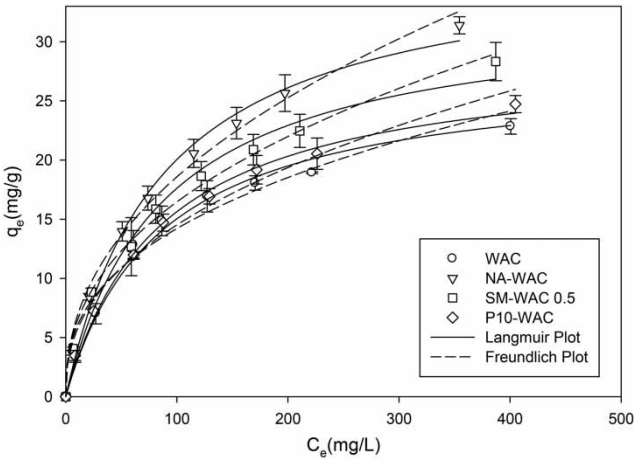

Figure 2 | Langmuir and Freundlich isotherms of TMAH adsorption on original WAC and modified WACs (adsorbent dose: 4 g/L, pH: 11.8 ± 0.2, reaction time: 24 hours).

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):

$$\equiv Si{-}OH + OH^- \rightleftarrows \equiv Si{-}O^- + H_2O \quad (3)$$

$$\equiv Si{-}O{-}Si\equiv + OH^- \rightleftarrows \equiv Si{-}O^- + HO{-}Si\equiv \quad (4)$$

This $\equiv Si{-}O^-$ 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 always 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 pH 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 pH of the solution that determines the surface charge of the ACs. Whenever the pH was lower than the pH_{PZC} 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 pH_{PZC} 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 pH_{PZC} (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 pH_{PZC} to a higher pH, the adsorption density increased dramatically and then eventually reached a plateau when it was far from the pH_{PZC}.

Table 2 | Isotherm parameters of TMAH adsorption on WAC and modified WACs (adsorbent dose = 4 g/L; pH = 11.8 ± 0.2; reaction time = 24 h)

Isotherms	Parameters	WAC	NA-WAC	SM-WAC0.5	P10-WAC
Freundlich	K_f (mg/g)(L/mg)$^{1/n}$	2.44	2.40	2.40	2.13
	n	2.61	2.25	2.39	2.40
	$1/n$	0.383	0.444	0.418	0.416
	R^2	0.9652	0.9617	0.9640	0.9834
Langmuir	q_0 (mg/g)	27.77	37.46	32.83	29.03
	b (L/mg)	0.0118	0.0115	0.0116	0.0117
	R^2	0.9902	0.9916	0.9811	0.9950

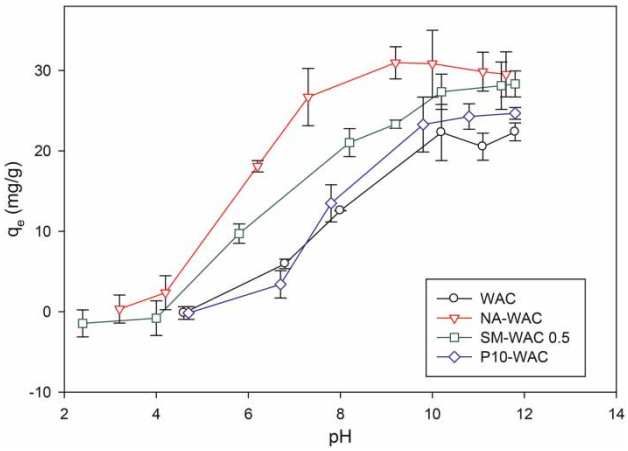

Figure 3 | Effect of equilibrium pH on the adsorption of TMAH on WAC and modified WACs (C_0: 20 ± 2 mg/L (a), C_0: 500 ± 50 mg/L (b), adsorbent dose: 4 g/L, reaction time: 24 hours).

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 (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.

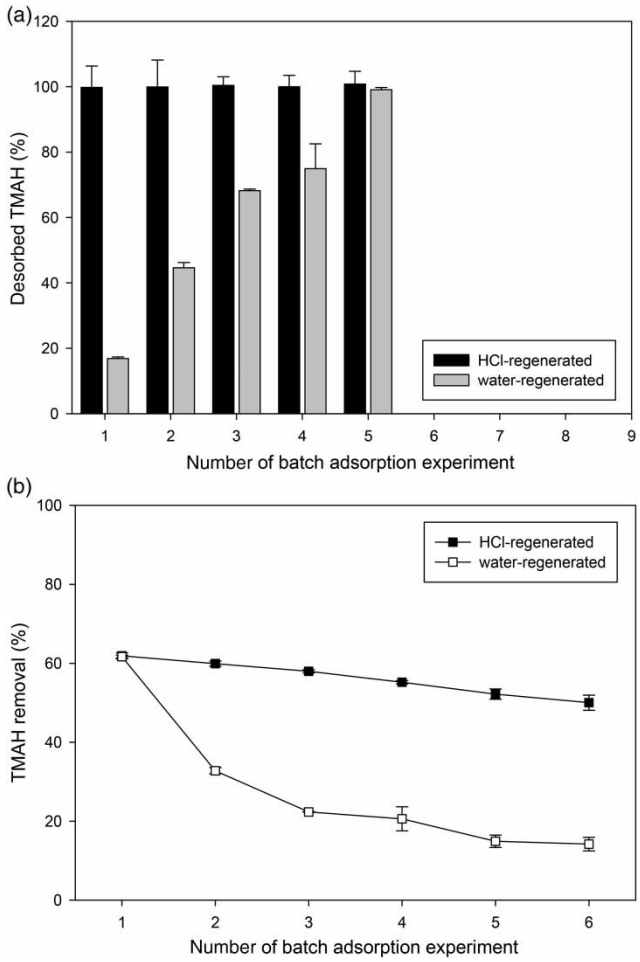

Figure 4 | (a) Regeneration of NA-WAC by 0.1 N HCl and water (C_0: 50 ± 5 mg/L, adsorbent dose: 4 g/L, pH: 11.8 ± 0.2, reaction time: 24 hours). (b) Batch adsorption cycles of NA-WAC (C_0: 50 ± 5 mg/L, adsorbent dose: 4 g/L, pH: 11.8 ± 0.2, reaction time: 24 hours).

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 adsorption of low molecular weight molecules, adsorption energy 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 $Å^3$, 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 surface area rather than volume as revealed in the micropore 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 pH_{PZC} of 7.4 was mainly driven by hydrogen bonding, and hydrophobic and van der Waals interactions. Tamai *et al.* (2004) studied the adsorption 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

Table 3 | Surface area and pore volume of WAC occupied by TMAH

pH	S_{BET} (m^2/g)	Occupied surface area (m^2/g)	Occupied surface area (%)	q_0 (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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