Adsorption characteristics of N-nitrosodimethylamine from aqueous solution on surface-modified activated carbons

Xiaodong Dai [b,c], Linda Zou [a,*], Zifeng Yan [b], Mary Millikan [c]

[a] SA Water Centre for Water Management and Reuse, University of South Australia, Adelaide, SA5095 Australia
[b] Chemistry and Chemical Engineering School, China University of Petroleum, Dongying 257061, Shandong, China
[c] Institute for Sustainability and Innovation, Victoria University, Melbourne, VIC 8001, Australia

ABSTRACT

This study investigated the removal of N-nitrosodimethylamine (NDMA) by an adsorption mechanism using commercially available activated carbons and surface-modified activated carbons. The effects of the modification on the properties of the activated carbon were studied by N_2 adsorption/desorption, Diffuse Reflectance Infrared Fourier Transmission (DRIFT) analysis and X-Ray Photoelectron Spectroscopy (XPS). Adsorption experiments revealed that the activated carbons demonstrated a greater capacity for NDMA adsorption capacity than can be achieved using zeolite. The equilibrium data was fitted to the Freundlich equation and it was found that the adsorption capacity was significantly influenced by the micropore size, relative pore volume and surface characteristics. Adsorption experiments were conducted using unmodified and modified activated carbons. The results indicated that the adsorption capacity of NDMA can be significantly improved by heat treatment and doping of TiO_2 particles. This was because the surface treatments yielded more hydrophobic sites and fewer oxygen-containing surface functional groups, and consequently an increased capacity for NDMA adsorption.

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1. Introduction

Recent research found that low-level N-nitrosodimethylamine (NDMA) can be formed as a by-product of disinfection processes using chlorine or chloramines because of the reaction with organic nitrate in the water and wastewater [1–3]. The US Environmental Protection Agency classified NDMA as a probable human carcinogen [4]. The most common way to treat NDMA is through photolysis. NDMA will break down under UV light irradiation with a wavelength of 175–275 nm [5]. The UV treatment of NDMA required a much higher dosage than is typically used for disinfection. For example, cryptosporidium destruction requires a dose of about 8–12 mJ/cm^2, but NDMA destruction may require 600–800 mJ/cm^2 [1]. Membrane technologies such as reverse osmosis can efficiently remove a broad range of dissolved organics; however, this process shows poor rejection of small, polar, uncharged molecules such as NDMA (which achieved a rejection rate of only 50–65% or less). There is clearly a need to conduct research on alternative treatment technologies. Among them, adsorption is considered as a promising method, as it has the advantages of low cost and easy operation [5–8].

Porous materials such as zeolites, activated carbons (AC) and silica gel are widely used for water treatment because of their porous characteristics. However, it is quite difficult to remove NDMA due to its small molecular size, high molecular polarity and high solubility in water. It has recently been reported that NDMA can be removed from gaseous and aqueous phases by porous adsorbents, especially by zeolites, but these processes achieve only limited adsorption capacity [9–11]. Compared with other porous materials, activated carbons are unique and versatile adsorbents, characterized by a large surface area, wide pore size distribution from micropore to macropore, and other significant surface properties [12,13]. They are used extensively in gas separation, water treatment, chemical engineering processes and so on, and have the potential to become an alternative technology for the removal of NDMA from water. Until now, the adsorption of NDMA by activated carbon in the aqueous phase has not been studied systematically.

For a better understanding of the adsorption mechanism and an investigation of the potential for using activated carbon to remove NDMA, three types of activated carbons made from different raw materials were selected to adsorb NDMA from water for this study. Studies were focused on establishing the relationship between the porous structure of adsorbents and their adsorption capacity, and the effects of surface modification on the adsorptive properties of activated carbons.

* Corresponding author. Tel.: +61 8 8302 5489; fax: +61 8 8302 3386.
E-mail address: linda.zou@unisa.edu.au (L. Zou).

2. Materials and methods

2.1. Materials

N-Nitrosodimethylamine >99% was obtained from Advanced Industrial Technology (Hong Kong). To prepare the stock solution for the adsorption experiment, 10 ml NDMA was dissolved in a 1000 ml volumetric flask with deionised water to prepare the NDMA standard solution of 10,000 mg/l. Activated carbons from self-synthesis and commercially available products were as follows: AC-1 (from pilot synthesis), AC-2 (from pilot synthesis) and AC-3 (from Activated Carbon Technology, Australia).

2.2. Experimental method

The experiments to adsorb NDMA by activated carbons were conducted using the following procedure: activated carbon powders were first dried at 387 K for 24 h, then 0.25 g of ACs were weighed and placed in each conical flask. Then, 150 ml solutions containing NDMA concentrations of between 10 mg/l and 200 mg/l were poured in to flasks. To achieve adsorption equilibrium, the flasks were kept in a waterbath shake continuously at 298 K for 24 h. After the adsorption process, the residual concentration (C_e) of NDMA solution was measured by HPLC-UV. To determine the NDMA concentrations, a 20 μl solution containing NDMA was injected with a MilliQ water flow (1 ml/min) to HPLC (waters 600E Quaternary Pump with a waters 717 plus autosampler and waters 996 photodiode array detector). After running 12 min in Column (Waters symmetry shield RP18, 3.5 μm, 4.6 mm × 100 mm), the separated NDMA was detected by UV at a wavelength of 230 nm with retention time of 3 min. Based on the residual concentration C_e results, the adsorbed quantities of NDMA by activated carbon (Q_e) were calculated and the isotherms were plotted.

The activated carbon samples were modified by the following two procedures. First, the surface modification was carried out in a horizontal furnace. Activated carbons were placed in a ceramic container and heated at a ramp rate of 10 K/min to 1123 K and held for 2 h. During the heating process, a nitrogen flow was introduced to protect the samples from being oxidized by oxygen in ambient air.

Second, activated carbons were loaded with fine TiO_2 nanoparticles. The TiO_2 nanoparticles were synthesized by hydrolysis to form a uniform sol as follows: 50 ml of titanium butoxide ($Ti(OC_4H_9)_4$, 97%) were dissolved in ethanol (200 ml). The solution was stirred for 30 min at 298 K. A mixture of deinoized water and nitric acid was then added and the solution was vigorously stirred until a clear and transparent sol was obtained. Activated carbons were then impregnated in the solution. Samples coated with TiO_2 gel were then heat treated in the oven at 473 K for 2 hours to form metal oxides on the surface of the activated carbons.

The adsorption isotherm data in the liquid phase in our work can be presented by the Freundlich equation [13], i.e.:

$$Q_e = K_f \times C_e^{1/n}$$

where K_f is the linear partitioning coefficient, as a relative indicator of adsorption capacity. $1/n$ is indicative of the intensity of the energy reaction as well as the favorability and capacity of the adsorbent/adsorbate system. Q_e and C_e are the equilibrium adsorption capacity (mg/g) and concentration (mg/l). The above equation can be transformed in the following form:

$$\log Q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e$$

2.3. Characterization

The N_2 adsorption/desorption isotherms at 77 K were obtained using a 2010 porosity analyzer (Micrometrics). Prior to analysis, samples were degassed at 673 K for 4 h, until the pressure was less than 1 Pa. The specific surface area was deduced by applying a BET equation from isotherm data. The Horvath–Kawazoe slit pore geometry model was used to calculate the micropore volume and pore size distribution. The BJH equation was used to determine the mesopore volume and size distribution.

Diffuse Reflectance Infrared Fourier Transmission (DRIFT) analysis of the activated carbon powder was performed on a Bruker's Vector-22 FT-IR spectraphotometer. Powder samples were first dried for 24 h at 383 K. Dried samples were then mixed with finely ground KBr at a mass ratio of 1/200. DRIFT spectra were recorded at a resolution of 4 cm^{-1}, with 256 scans per sample and an aperture setting of 15.

X-ray photoelectron spectroscopy (XPS) spectra were acquired with an Axis Ultra DLD Spectrometer (Kratos Analytical, UK), using a monochromatic Al Kα ($h\nu = 1486.6$ eV) X-ray source operating at 150 W. A pass energy of 160 eV and a resolution for the binding-energy scale of 1 eV per step were used for the sample analysis. During acquisition, surface charging of the samples was compensated by a coaxial low-energy electron source. The relative fractions of the elements detected from the spectra were calculated from the areas under the most intense photoelectron peak for each, weighted by the appropriate relative sensitivity factor.

3. Results and discussion

3.1. Porous structures of activated carbons

Activated carbons are defined by their highly developed porous structure, and the wide range of their pore sizes and shapes. These properties may impose a significant influence on the adsorption capacity and behavior of activated carbons. Depending on the classification of IUPAC, the pores in activated carbons are divided into: micropore (<2 nm), mesopore (2–50 nm), and macropore (>50 nm) [12]. The micropores play an important role in the adsorption capacity. It appears that mesopores and macropores have the capacity to take less adsorbate.

The porous properties derived from nitrogen adsorption/desorption isotherms were outlined in Table 1. As expected, all three types of activated carbons possessed the developed

Table 1
Porous structure of activated carbons.

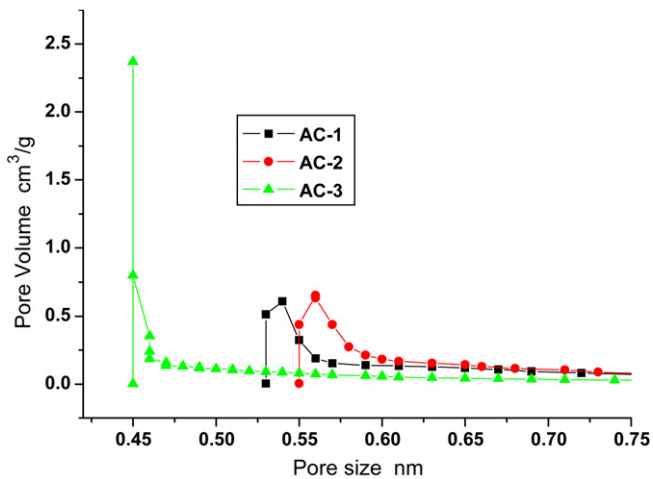| Sample	S_{BET} (m²/g)	S_{micro} (m²/g)	V_{micro} (cm³/g)	S_{meso} (m²/g)	V_{meso} (cm³/g)	D_{meso} (nm)	Average pore width (nm)
AC-1	1466	860	0.39	606	0.38	2.53	2.11
AC-2	1700	985	0.42	715	0.48	2.67	2.12
AC-3	1065	787	0.31	278	0.31	4.47	2.33
AC-1-850	1032	525	0.25	507	0.36	2.85	2.35
AC-3-850	1104	639	0.29	465	0.32	2.73	2.21
AC-1-TiO₂	1128	642	0.40	486	0.33	2.67	2.23
AC-3-TiO₂	962	809	0.39	153	0.13	3.45	2.18

Fig. 1. Micropore size distribution of activated carbons.

porous structures. Both AC-1 and AC-2 are made from petroleum coke, but AC-2 showed a larger surface area and had slightly more micropores and mesopores than AC-1. It was found that AC-3, which originated from coconut shell, possessed the smallest surface area of 1065 m²/g and the smallest micropore and mesopore volume, indicating that it may not be the best adsorbent. However, pore size, especially micropore size distribution, was also an important factor in the adsorption application. Fig. 1 showed the micropore size distribution calculated from HK equations. It was clear that AC-3 had a smaller micropore size of about 0.46 nm, compared with the size of others of 0.55 nm. Due to their different porous structures, these activated carbons appear to demonstrate a significant difference in their capacity for the adsorption of NDMA.

3.2. NDMA adsorption in water

The use of activated carbon to adsorb compounds from solutions has been carried out for centuries, for purification, detoxification and decolourization. The adsorption characteristics depend not only upon the porous characteristics and surface chemistry of the adsorbent, but also on the properties of the contaminants in water, such as molecular structure, polarity and solubility. NDMA is a small organic molecule (molecular dimension 0.45 nm), that is polar ($\log K_{ow} = 0.57$) and highly soluble (100 g/l 293 K) [1].

Fig. 2a showed the NDMA adsorption isotherms at 298 K of three activated carbons. Q_e and C_e were the adsorbed amount and the equilibrium concentration, respectively. It was observed that activated carbons presented good adsorption capacity (24 mg g⁻¹) from water, whereas an adsorption of 17 mg g⁻¹ by zeolites was reported by Zhu et al. under different experimental conditions [9]. All the tested activated carbons (AC-1, AC-2, and AC-3) showed an increase in the amount of adsorption. The increase in C_e in the AC-3 sample exhibited the greatest capacity for the adsorption of NDMA. One possible explanation of these results is that the pore size and structure of the AC-3 is more effective for accommodating the NDMA's molecular, i.e. the pore size distribution of AC-3 peaks at 0.46 nm, which is closer to the NDMA molecular dimension of 0.45 nm, whereas the pore size distribution peaks at 0.53 nm for AC-1 and 0.56 nm for AC-2. Although AC-1 and AC-2 both have a larger surface area and more micropores, they exhibited a lower adsorption capacity due to their relatively unfavorable pore size distributions. Due to the slightly larger surface area and its more developed micropores, AC-2 might possess a higher adsorption capacity than AC-1. Interestingly, similar adsorption isotherms were observed for AC-1 and AC-2, which could be attributed to the difference in chemical functional groups on the surface. This proved that the adsorption of NDMA on activated carbon was not only strongly dependent on the surface physical properties such as surface area and porous
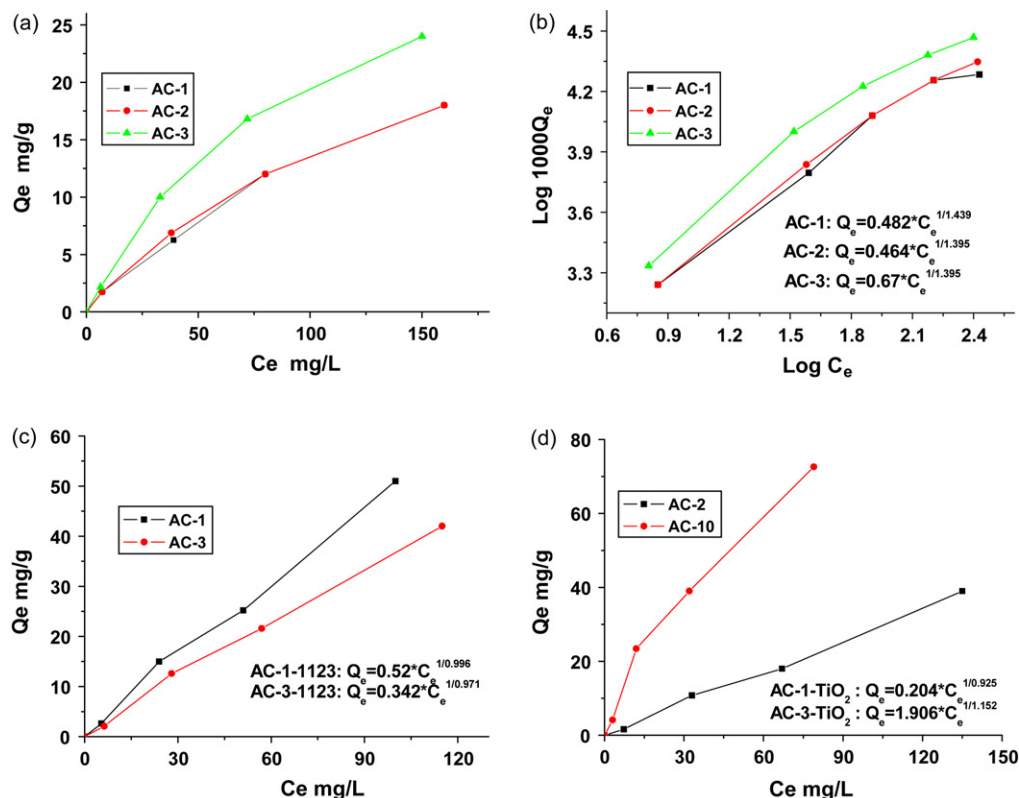

Fig. 2. Adsorption isotherms and Frenudlich analysis of NDMA by activated carbons.

structures, but also on the surface chemical properties of adsorbents, i.e. the hydrophobic and hydrophilic characteristics [14].

To further investigate the adsorption of NDMA by activated carbons, the Freundlich model for aqueous adsorption was correlated with the experimental equilibrium data. Three typical Freundlich adsorption plots were observed in Fig. 2b, and three regression equations were established. The corresponding constants K_f and n were obtained as following: AC-1 $K_f = 0.482$, $n = 1.439$, $R = 0.989$; AC-2 $K_f = 0.464$, $n = 1.395$, $R = 0.995$; AC-3 $K_f = 0.670$, $n = 1.395$, $R = 0.986$. NDMA adsorption at lower concentration was fitted perfectly for the Freundlich model, whereas a slight discordance appeared at higher concentration. Simultaneously, the good correlation coefficients R (>0.98) are evidence that the Freundlich adsorption law provided a good explanation for the presented data. The data indicated that the NDMA molecular adsorption process was mostly carried out on a coarse surface based on the hypothesis of the Freundlich equation. As known, activated carbons had a surface structure consisting of aromatic sheets with dislocated, discontinued carbon atoms and some functional groups, which acted as active sites to adsorb NDMA onto the nonpolar layers of sheets of aromatic condensed ring systems. The similarity of the raw materials of petroleum coke might be the reason for the observed similar adsorption properties for AC-1 and AC-2 during the experiments, in addition to their porous structures.

3.3. Effect of surface modification on NDMA adsorption

3.3.1. Surface modification by heat treatment

Different functional groups such as O, N, S, H, and so on that are derived from the raw material and activation procedure are presented on the carbon surface. Among them, carbon–oxygen groups are the most important ones for their influence on the surface hydrophobic and hydrophilic characteristics. When the hydrophilicity decreased, the carbon surface became more and more hydrophobic, a process associated with the decrease in the number of oxygen functional groups. The surface modification of AC-1 and AC-3 was carried out in a nitrogen gas environment. The porous characteristics of post-surface modification were given in Table 1. It was observed that the heat treatment process led to the decrease in both surface area and porosity of AC-1, due to the collapse of some pore walls. By contrast, AC-3 presented a slight increase in surface and porosity, which could be explained as a result of the activation reaction to form new pores. When heated at 1123 K, more heteroatoms from coconut shell originated activated carbon would react as activation agents to eliminate carbon and create new porosity on AC-3 surface.

The NDMA adsorption isotherms of post-surface modification are shown in Fig. 2c. It was demonstrated that the adsorption capacity had increased after surface treatment. The AC-1 presented greater uptake of NDMA than AC-3, where the highest achieved NDMA adsorption capacity was 54 mg/g. This adsorption capacity result not only closely correlated with porous structure, but also had a significant connection with the hydrophobicity on the carbon surface. This indicated that NDMA adsorption on activated carbon was strongly dependent upon the surface characteristics. Surface modification caused by the heating process appears to have resulted in the removal of the oxygen atoms and the reduced hydrophilicity of carbon, which could be reflected in DRIFT spectra (Fig. 3.) As seen in Fig. 3a for AC-1, the peak at 1415 cm^{-1} pronounced by carboxyl (−COOH) groups shows a decreasing trend. Also, sharp decreases around 1400–1670 cm^{-1} (carboxyl (−COOH, 1415 cm^{-1}), carbonyl (−C=O, 1689 cm^{-1})) appeared in Fig. 3b for AC-3. Both these decreases could be attributed to the removal of oxygen species and some nitrogen species on the carbon surface [15]. Those carbon–oxygen surface groups acted as primary adsorption centres of water through hydrogen bonds [16,17]. With
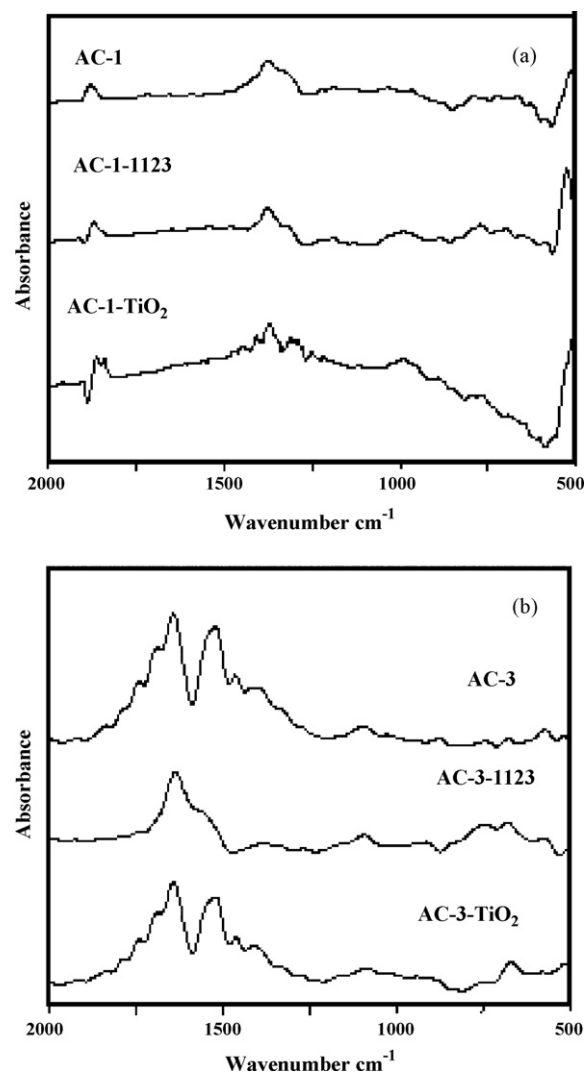
Fig. 3. DRIFT spectra of (a) AC-1 and (b) AC-3 samples.

the decrease in active sites for water molecules, the surface with relative higher hydrophobicity finally promoted the adsorption of NDMA (shown in Fig. 4). Simultaneously, the adsorption isotherms fit the Freundlich equation very well.

3.3.2. Surface treatment by loading TiO₂ particles

Activated carbon impregnated with metals and their oxides as adsorbents or catalysts have been widely used. The loading process on activated carbon surfaces could modify its porous structure and surface characteristics. The porous structures after TiO₂ modification are given in Table 1. It was clear that AC-1 with TiO₂ resulted in
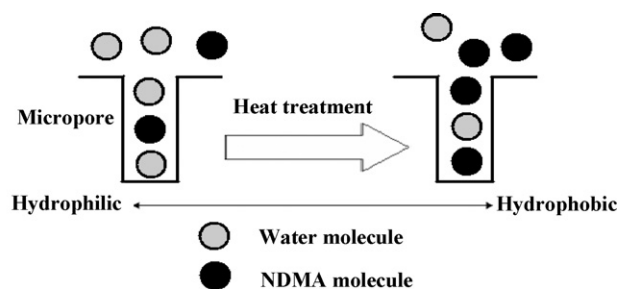
Fig. 4. Possible NDMA adsorption mechanism in micropores.

Table 2
Atomic fractions (%) of activated carbon loading TiO_2.

Sample	Atomic fractions (%)							
	Mg (1s)	O (1s)	Ti (2p)	N (1s)	K (2s)	Ca (2p)	C (1s)	Si (2p)
AC-3	0.1	6.9	<dl[a]	0.4	0.4	<dl	92.2	0.1
AC-3-NDMA	1.1	9.2	<dl	0.4	<dl	0.3	88.8	0.2
AC-3-TiO$_2$	0.2	17.8	4.6	0.3	1.2	0.2	75.6	0.1
AC-3-TiO$_2$-NDMA	0.1	18.9	5.2	0.4	0.5	0.1	74.8	0.1

[a] <dl: less than the detection limit.

a slight decrease in BET surface area and pore volume. The reduction of AC-1 in porosity can be explained as a result of blockage by TiO_2 deposition on pore walls. TiO_2 modification increased microporosity for AC-3 but decreased mesoporosity. This indicated that TiO_2 particles were mostly deposited in mesopores and narrowed them to micropores, due to the surface properties originating from the coconut shell.

The NDMA adsorption isotherms on TiO_2 modified activated carbons were shown in Fig. 2d. Both AC-1 and AC-3 presented significant improvement in adsorption of NDMA after modification by TiO_2, with the highest adsorption capacity achieved of 76 mg g^{-1}. This increased capacity could be explained by the increased number of surface adsorption sites. When activated carbon was impregnated with TiO_2 gel, most of the more hydrophobic TiO_2 particles would deposit on the hydrophilic surface, and relatively enhance the hydrophobicity of the active sites for NDMA adsorption. On the other hand, the presence of TiO_2 on the carbon surface might also decompose some of the adsorbed NDMA molecules, providing more sites available for further adsorption. This contributed to the increased adsorption capacity [18,19].

Table 2 presented the elemental atomic fractions (%) calculated from the XPS spectra. It can be seen that the oxygen atomic fractions (O (1s)) showed an increasing trend from the lowest to the highest following the order of unmodified AC-3 (6.9%), unmodified AC-3 adsorbed with NDMA (9.2%), TiO_2 loaded AC-3 (17.8%), and finally TiO_2 loaded AC-3 adsorbed with NDMA (18.9%). These increases were caused by the oxygen atoms contained in the NDMA and TiO_2 molecules. In contrast, the carbon atomic fractions (C (1s)) showed a decreasing trend from the highest to the lowest following the same order, AC-3 (92.2%), unmodified AC-3 adsorbed with NDMA (88.8%), TiO_2 loaded AC-3 (75.6%), and finally TiO_2 loaded AC-3 adsorbed with NDMA (74.8%). These decreases were due to the TiO_2 particles and NDMA molecules both covering some of the carbon surface. In addition, the non-detection of titanium (Ti (2p)) in AC-3 and AC-3 NDMA versus the detection of titanium in sample AC-3-TiO$_2$ (4.6%) and AC-3-NDMA (5.2%) proved the successful loading of TiO_2 on the AC samples. Although nitrogen existed in NDMA, no significant increase was observed on nitrogen atomic fractions (N (1s)) for the samples adsorbed with NDMA. This was probably due to the bulky methyl groups and oxygen in the NDMA masking the nitrogen which was on the detection limit of the XPS instrument. It also appeared that there was background nitrogen found in the activated carbon before the adsorption of NDMA. Some other elements such as Mg (1s), Ca (2p) and Si (2p) were detected at trace level.

4. Conclusion

In this study, commercially available activated carbons were used to adsorb N-nitrosodimethylamine from water. It was found that due to their highly developed porosity, all three types of activated carbons presented higher removal efficiency than zeolites. The adsorption isotherms correlated with the Freundlich equation well. The NDMA adsorption capacity was significantly influenced by

the porous structure of activated carbon as evidenced by micropore size, relative pore volume and surface characteristics.

The effects of surface modification by heating and impregnating with TiO_2 particles were studied. Surface treatment generally resulted in the increase in hydrophobic surface and modification of porous structures, leading to a greatly improved capacity for adsorption. When the oxygen containing functional groups was removed by the heating process, the carbon surface became more hydrophobic, providing more active sites to adsorb NDMA.

When the activated carbon was impregnated with TiO_2 particles, more hydrophobic TiO_2 particles would deposit on the hydrophilic carbon surface, enhancing the hydrophobicity of the active sites for NDMA adsorption. Furthermore, the TiO_2 presented on carbon surfaces appeared to decompose some of the adsorbed NDMA molecules, providing more sites for further adsorption and contributing to the increased adsorption capacity.

Overall, activated carbon with surface modification is a promising alternative technology for removing the disinfection by-product NDMA from water.

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