

Nitrosodiethylamine removal performance of modified activated carbon

Jiangang Lu ^{a,b}, Haisheng Cai ^{a,*}, Yanmei Fu ^c and Xianluo Shi^{a,b}

^a Key Laboratory of Po-yang Lake Watershed Agricultural Resources and Ecology of Jiangxi Province/Development Research Center of Selenium-rich Agricultural Industry, Jiangxi Agricultural University, Nanchang 330045, China

^b Jiangxi Water Resources Institute, Nanchang 330013, China

^c Yuzhang Normal University, Nanchang 330103, China

*Corresponding author. E-mail: caihs1972@163.com

 JL, 0000-0001-7628-8918; HC, 0000-0002-6707-7999; YF, 0000-0001-7063-6571

ABSTRACT

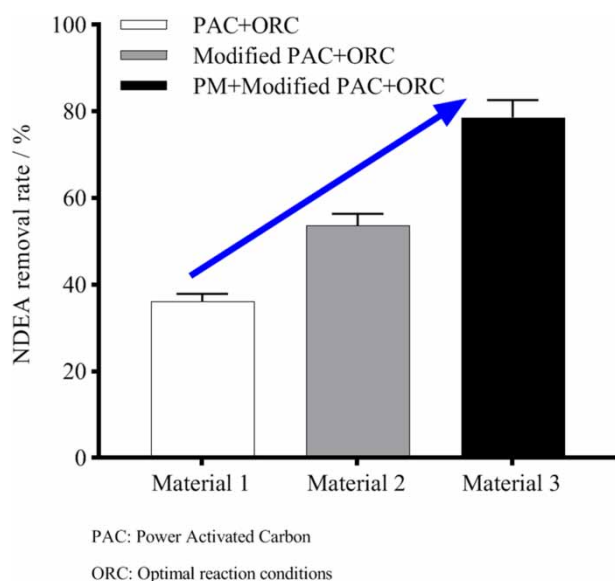
This paper discusses the preparation of modified activated carbon (PAC-1) and its adsorption performance for nitrosodiethylamine (NDEA). The PAC-1 was characterized by SMS and X-ray diffractometer, and its NDEA removal mechanism was investigated. The results showed that, compared with unmodified activated carbon, PAC-1 had a better adsorption effect for NDEA after pre-soaking with 0.8 mol/L permanganate (PM) for 24 hours and calcination at 400 °C for 7 hours. Under the conditions of 8 g/L PAC-1 dosage, pH = 6, and adsorption time of 6 h, the adsorption rate of NDEA with an initial concentration of 50 mg/L reached 78.66%, the maximum equilibrium adsorption capacity was 4.916 mg·g⁻¹, and the adsorption rate of unmodified activated carbon to NDEA was increased by 42.5%. The number of oxygen-containing surface functional groups of activated carbon was increased after permanganate prepreg, which can enhance the NDEA adsorption rate. The adsorption process of NDEA on modified activated carbon conforms to pseudo-second-order kinetics, and the adsorption isotherm corresponds to the Freundlich model.

Key words: adsorption isotherm, adsorption kinetics, adsorption mechanism, modified activated carbon, NDEA, removal rate

HIGHLIGHTS

- A new method for removing NDEA by permanganate and AC is proposed.
- Under optimal conditions, the adsorption effect of NDEA reaches 78.66%.
- Increasing the pore volume of AC can improve the adsorption effect of NDEA.
- The adsorption conforms to the pseudo-second-order adsorption kinetic equation.

GRAPHICAL ABSTRACT



INTRODUCTION

Since the conception of the chlorination disinfection process, the risk of human infections by pathogenic microorganisms in drinking water has been greatly reduced. However, the presence of disinfection byproducts from the reaction of chlorine disinfectant and organic matters in the water have gradually emerged as a new problem affecting human health. Traditional chloride disinfection byproducts are trihalomethanes (THMs) and haloacetic acid (HAAs), with mass concentrations usually reaching 50–100 µg/L in drinking water. (Zhong *et al.* 2019) Studies have shown that chloramine disinfection can reduce the mass concentration of THMs (carbon disinfection by-products, carcinogenesis) and HAAs (carbon disinfection by-products, carcinogenesis) to 1×10^{-6} – 3×10^{-6} %. (Zhong *et al.* 2019) However, chloramine disinfection produces new types of nitrosamine (NAs), which are more carcinogenic than the targeted byproducts. (McCurry *et al.* 2015) Nitrosodimethylamine (NDMA) was first found in drinking water in Lake Ontario, Canada, in 1989 (Taguchi *et al.* 1994). N-nitrosamines have been detected in drinking water on many occasions in China, with mass concentrations usually reaching 12–25 ng/L, and their concentration was higher than that in European and American countries (The mass concentration of NDEA in drinking water in European and American countries is between 1 and 9 ng/L (Wang *et al.* 2011, 2016). Thus far, nine N-nitrosamines, including NDMA, NDEA and NMEA, have been detected in drinking water (Yoon *et al.* 2012). Of these, NDMA and NDEA were classified as class 2A carcinogens by the International Agency for Cancer Research (IARC), but NDEA has shown stronger genotoxicity than NDMA (Liviach *et al.* 2011; Zheng *et al.* 2018).

Scholars have carried out a large number of studies on the control and removal of nitrogen disinfection byproducts (N-DBPs) from drinking water in order to ensure its safety for human consumption (Farre *et al.* 2011). Research on the control and removal of N-DBPs can be divided into three main aspects (Simpson 2008; Reungoat *et al.* 2011; Liao *et al.* 2020): (1) source control, mainly regulating precursors of N-DBPs, dissolved organic nitrogen (DON); (2) process control including methods of controlling the amount of disinfectant, disinfectant replacement, and the optimization of disinfection process combination; (3) terminal control, i.e. the removal of N-DBPs themselves. Although both source control and process control have certain regulation effects on N-DBPs in water, some N-DBPs still remain in solution after the whole water purification and disinfection process. Therefore, it is highly important to study the direct removal of N-DBPs. Direct N-DBP removal is performed mainly through physical, chemical, and biological methods (Shi *et al.* 2018). The physical method essentially aims to remove N-DBPs directly through adsorption materials or filter membranes. For example, activated carbon (AC) can effectively bind various organic compounds in water due to its complex pore structure and large specific surface area (Summers *et al.* 2013; Kennedy *et al.* 2015; Grant *et al.* 2019), therefore, the US Environmental Protection Agency (USEPA) has listed activated carbon adsorption as one of the best treatment processes to remove organic matter in water (Wong *et al.* 2018). The

chemical method basically achieves the purpose of removing pollutants by adding oxidants, with the widely used oxidants being permanganate (PM) (Chu *et al.* 2015) and sulfate (Li *et al.* 2019). At present, there are many studies on the removal effect of individual methods on N-DBPs, however, few studies exist on the combined use of different methods. Since David Hanigan *et al.* (2012) proposed that activated carbon can adsorb NDMA, its application in the removal of N-DBPs began to be favored by scholars (Dai *et al.* 2012). At present, the more widely studied activated carbons are biological activated carbon (BAC) (Farre *et al.* 2011; de Vera *et al.* 2016), powder activated carbon (PAC) (Chu *et al.* 2015) and granular activated carbon (GAC) (Velten *et al.* 2011a; Hanigan *et al.* 2012; Cuthbertson *et al.* 2019), and all of these three materials have a certain adsorption effect for N-DBPs. Studies have shown that the contact time between activated carbon and water (Beita-Sandi *et al.* 2016), the dosage (Kristiana *et al.* 2013) and porosity of activated carbon (Grant *et al.* 2019), water temperature (Liang & Singer 2003) and pH (Selbes *et al.* 2014; Yang *et al.* 2015) are all crucial factors affecting the adsorption effect of activated carbon for N-DBPs. Therefore, it is necessary to study the adsorption characteristics of N-DBPs on activated carbon under the combined action of chemical and physical methods.

Currently, most of the research concerns the adsorption of nitrosamine NDMA (Fujioka *et al.* 2013; Beita-Sandi *et al.* 2016; Kadmi *et al.* 2017). In this paper, NDEA was selected as the research object, powder activated carbon (PAC) was chosen as the adsorption material, and the three factors of permanganate concentration, calcination temperature and calcination time were considered for single-factor influence analysis. The best modified activated carbon for NDEA adsorption was selected by orthogonal test, and the adsorption experiments of modified activated carbon for NDEA were subsequently carried out under different reaction times, PAC dosages and pH conditions. The conclusions provide a theoretical reference for further revealing the NDEA adsorption mechanism on activated carbon.

MATERIALS AND METHODS

Materials and instruments

List of materials: Chlorine dioxide (ClO_2): pesticide residue level, methanol (CH_3OH): pesticide residue level, acetone ($\text{C}_3\text{H}_6\text{O}$): pesticide residue level, ether [$(\text{C}_2\text{H}_5)_2\text{O}$]: pesticide residue level, sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), anhydrous sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sulfuric acid (H_2SO_4) $\rho = 1.84 \text{ g/mL}$, sodium hydroxide (NaOH), NDEA ($\text{C}_4\text{H}_{10}\text{N}_2\text{O}$, 99.9%), potassium permanganate (KMnO_4), basic alumina (Alumina): 100–200 mesh, nitrogen (purity > 99.999%), hydrogen (purity > 99.99%), powder activated carbon (PAC). Unless otherwise specified, all chemicals were pure premium grade.

List of instruments and equipment: meteorological chromatograph (GC9790II, Zhejiang Fuli Analytical Instruments Co., Ltd), rotary evaporator (XDSY-3000A, Shanghai Xiande Experimental Instrument Co., Ltd), nitrogen blowing concentrator (NAI-DCY-12Z, Shanghai Naai Experimental Instrument Co., Ltd), muffle furnace (SX2-20-10B, Zhengzhou Xinhan Instrument Equipment Co., Ltd), scanning electron microscope (FlexSEM1000, Hitachi), specific surface area analyzer (BSD-PS1/2/4, BEST Instrument Technology (Beijing) Co., Ltd), quartz capillary column (column length 30 m \times inner diameter 0.25 mm, film thickness 0.25 μm), chromatography column (300 mm length \times 10 mm inner diameter), 500-mL separation funnel, common laboratory instruments and equipment.

Adsorbent screening

PAC was selected as the adsorbent matrix, of which a certain amount was washed and dried by deionized water, and then weighed. Basically, the effects of permanganate concentration, calcination temperature and calcination time on the adsorption performance were considered by conducting a total of 18 groups of adsorbent screening tests. At pH = 7, three groups of single factor level tests were set by the single factor control method. The PAC was pre-soaked in six concentrations of permanganate solution, namely, 0.05, 0.1, 0.2, 0.3, 0.5 and 0.8 mol/L. Given these, a total of six groups of tests were set with calcination temperatures of 200, 300, 400, 500, 600 and 800 $^\circ\text{C}$, respectively, and six further groups of tests were set with calcination times of 1, 4, 5 and 7 h, respectively. All combinations of the above factors resulted in the preparation of 18 modified activated carbon (PAC) sets.

Taking the above PAC sets prepared from 0.5 g amounts of AC, 50 mL of NDEA was treated with an initial concentration of 50 mg/L, shaken at a constant temperature for 24 hours, and the concentration of the remaining NDEA was measured after the entire reaction reached equilibrium.

According to the results of the above tests, under each factor, three groups of materials with the best NDEA adsorption effect were screened out (a total of nine activated carbons were obtained), and a three-factor three-level orthogonal analysis

was performed. In this manner, it was possible to select the optimal combination of activated carbon conditions for NDEA adsorption.

Adsorbent preparation

For each set, 50 g of washed PAC was weighed, activated carbon was added to 50 mL of the permanganate concentration solution of the corresponding concentration, and the solution was shaken for 24 h according to the analysis results in the previous section. After filtering, drying, washing, and molecular sieve screening, the material was calcined at the corresponding temperature and for the corresponding length of time to obtain the modified activated carbon with the best NDEA adsorption performance (abbreviated as PAC-1).

Adsorption experiment

The PAC-1 was used for the follow-up tests, and the effects of adsorption time, pH and dosage on the adsorption effect were mainly considered during the trial. According to the test results, three levels with enhanced removal effect were selected among the three factors of reaction time, dosage and pH value to perform orthogonal experiments, and the reaction conditions with the best adsorption effect were determined.

Material characterization

An SEM test was performed by emission scanning electron microscope (JEOL, JSM6701F), the specific surface area was tested by a specific surface area tester (Beijing JingweiGaobo, JW-BK132F), and an XRD test was performed by X-ray diffractometer (BRUKER, D8 ADVANCE).

Adsorption kinetics and isotherms

Nowadays, the commonly used adsorption kinetic models include pseudo-first-order kinetics and pseudo-second-order kinetics. The relevant equations are as follows (Guo & Wang 2019; Wang & Guo 2020):

$$\text{Pseudo-first-order dynamics: } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\text{Pseudo-second-order dynamics: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

For solutions containing a single component, the common adsorption isotherms are Langmuir and Freundlich isotherms (Burhan *et al.* 2018; Chang *et al.* 2020), and the corresponding equations are as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_0^b} + \frac{C_e}{q_0} \quad (3)$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (4)$$

In the above formulae, q_e represents the equilibrium adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), q_t represents the adsorption capacity at time t ($\text{mg}\cdot\text{g}^{-1}$), q_0 represents the saturated adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$), C_e represents the equilibrium concentration ($\text{mg}\cdot\text{L}^{-1}$), t represents the adsorption time (min), k_1 represents the first-order adsorption rate constant (min^{-1}), k_2 represents the second-order adsorption rate constant ($\text{g}\cdot(\text{mg}\cdot\text{min})^{-1}$), b represents the Langmuir adsorption coefficient ($\text{L}\cdot\text{mg}^{-1}$), k_f represents the Freundlich constant ($\text{mg}\cdot\text{g}^{-1}$), and $1/n$ is the multiphase factor.

Analytical method

The NDEA content was measured by meteorological chromatography, and the sample processing method, instrument reference conditions, as well as standard curve drawing were referred to the relevant standards (China 2016) (see supplementary information for standard curve and regression equation, Table 1). The removal rate and adsorption capacity of NDEA were

calculated according to Formulae (5) and (6), respectively (Gao *et al.* 2010):

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (5)$$

$$q_e = \frac{V(C_0 - C_t)}{W} \quad (6)$$

where C_0 represents initial NDEA concentration (mg/L); C_e represents NDEA equilibrium concentration (mg/L); q_e represents adsorption capacity (mg/g), C_t represents NDEA concentration in the solution at time t (mg/L); V represents solution volume (L); and W represents the amount of adsorbent (g). The data analysis in this paper was performed by SPSS Stastics 21.0, and the graphs were drawn on GraphPad Prism 8.

RESULTS

Adsorbent screening

When the original activated carbon was subjected to 0.1, 0.5, and 0.8 mol/L permanganate, the calcination temperature was 400, 500 and 800 °C, and the calcination time was 2 and 7 h, it had a better adsorption effect for NDEA. The optimal combination of modified activated carbon was screened through three-factor, three-level orthogonal test and range analysis, and the ideal concentration of permanganate was determined as 0.8 mol/L, the calcination temperature as 400 °C, and the calcination time as 7 h. The table for the orthogonal test and range analysis is shown in the supplementary information (Table 2).

Material characterization

A significant change in AC surface morphology was observed after modification, as shown in Figure 1(b), respectively. Before modification, the AC surface had large agglomerated particles, and there was no obvious pore structure on the surface. After modification, the surface turned rough with irregular raised thorn-like granular structure and a developed pore structure. The XRD pattern of AC before and after modification is shown in Figure 1(c). The peak shape was similar before and after AC modification, while some peaks appeared and others disappeared. Figure 1(d) and 1(e) respectively present the adsorption and desorption isotherms before and after PAC modification. They show an overall increasing trend with P/P0, the adsorption volume increases, but in the same case, the PAC-1 adsorption capacity is stronger. Figure 1(f) shows the pore volume-pore size distribution of PAC before and after modification; the pore volume of PAC-1 is larger. The specific surface area of PAC-1 is twice that of PAC, and the cumulative adsorption total pore volume (pore size 1.7–50 nm) is 1.72 times that of PAC.

Effect of reaction time on NDEA removal effect

Figure 2(a) displays the NDEA adsorption performance of the two materials at different time periods when 0.5 g PAC and PAC-1 were added to the NDEA solution (pH = 7). The adsorption of NDEA on PAC-1 reached equilibrium at 120 min (the adsorption capacity was 3.37 mg/g), and the adsorption capacity decreased at 240 min and then tended to equilibrium. The adsorption of NDEA on PAC reached equilibrium within 180 min (the adsorption capacity was 1.25 mg/g). The adsorption rate of NDEA by PAC was higher than that by PAC-1 in the first 30 min, but the adsorption rate of PAC-1 was higher after 30 min.

Effect of pH on NDEA removal effect

Figure 2(b) shows the removal efficiency of NDEA by PAC-1 at different pH values when 0.4 g PAC-1 was added at 25 °C and left to react for 180 min. When the pH was from 3 to 6, the NDEA removal rate gradually increased. When the pH was 8, the removal rate of NDEA reached the maximum of 57.54%.

Effect of dosage on NDEA removal effect

Figure 2(c) depicts the NDEA removal effect for different dosages of PAC-1. The results show that, when the dosage of PAC-1 is increased from 1 to 4 g/L, the NDEA removal rate rapidly increases. At a dosage of 6 g/L, the NDEA removal rate reaches the maximum. When the dosage continues to increase, the NDEA removal rate tends to balance after fluctuating within a small range, which is because a small amount of desorption occurs when PAC-1 adsorbs NDEA. When the dosage is 1 g/L, the adsorption amount is at its minimum, and when the dosage is 2 g/L, the adsorption amount is at its

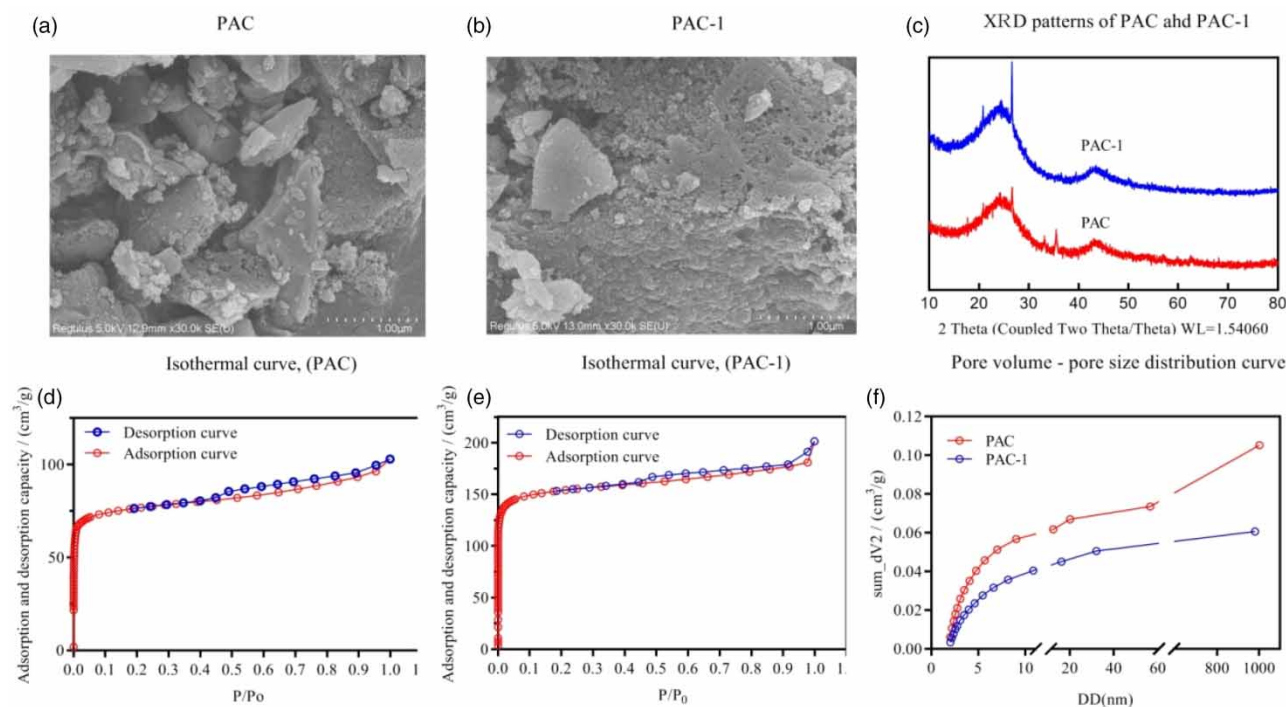


Figure 1 | Material properties before and after AC modification.

maximum. Therefore, under the condition that the total concentration of NDEA in the solution remains unchanged, the removal rate will rise with the increase of dosage, while the adsorption capacity of PAC-1 per unit mass for NDEA will decrease.

Orthogonal results for NDEA adsorption by PAC-1

The experiment established that the adsorption effect for NDEA is enhanced when the dosage of PAC-1 is 6 or 10 g/L, the reaction time is 2 or 6 h, and the pH of the solution is 6, 8 or 9. Based on three-factor and three-level orthogonal test and range analysis the optimal combination was selected as 8 g/L PAC-1 dosage, solution pH of 6, and 6 hours of reaction. The order of pros and cons of the three factors was determined as dosage > pH > reaction time. The orthogonal experimental design and range analysis table is included in the supplementary information (Table 3). Under the optimal conditions, it was found that the adsorption rate of NDEA by PAC-1 reached 78.66%. Under the same conditions, the NDEA adsorption rate on unmodified activated carbon was 36.1%, and the NDEA adsorption rate on modified AC without PM prepreg was 53.7%.

Adsorption kinetics

According to the kinetic equation, when the temperature is 25 °C and PAC-1 dosage is 8 g/L, the pseudo-first-order kinetics and pseudo-second-order kinetics are used for fitting, respectively. It is found that the fitting effect of the second-order kinetic equation is better, with the results shown in Figure 3.

Adsorption isotherm

The equilibrium concentration of NDEA and the equilibrium adsorption capacity of PAC-1 at different initial concentrations are obtained when the reaction temperature is 25 °C and the dosage is 8 g/L. The Langmuir and Freundlich thermodynamic equations are used to fit the data, and the results are shown in Figure 4. It can be seen in the figure that the adsorption process does not conform to the Langmuir isotherm equation, and the Freundlich adsorption isotherm equation fits well. When the initial concentration reaches a certain value, the adsorption tends to equilibrium and reaches saturation.

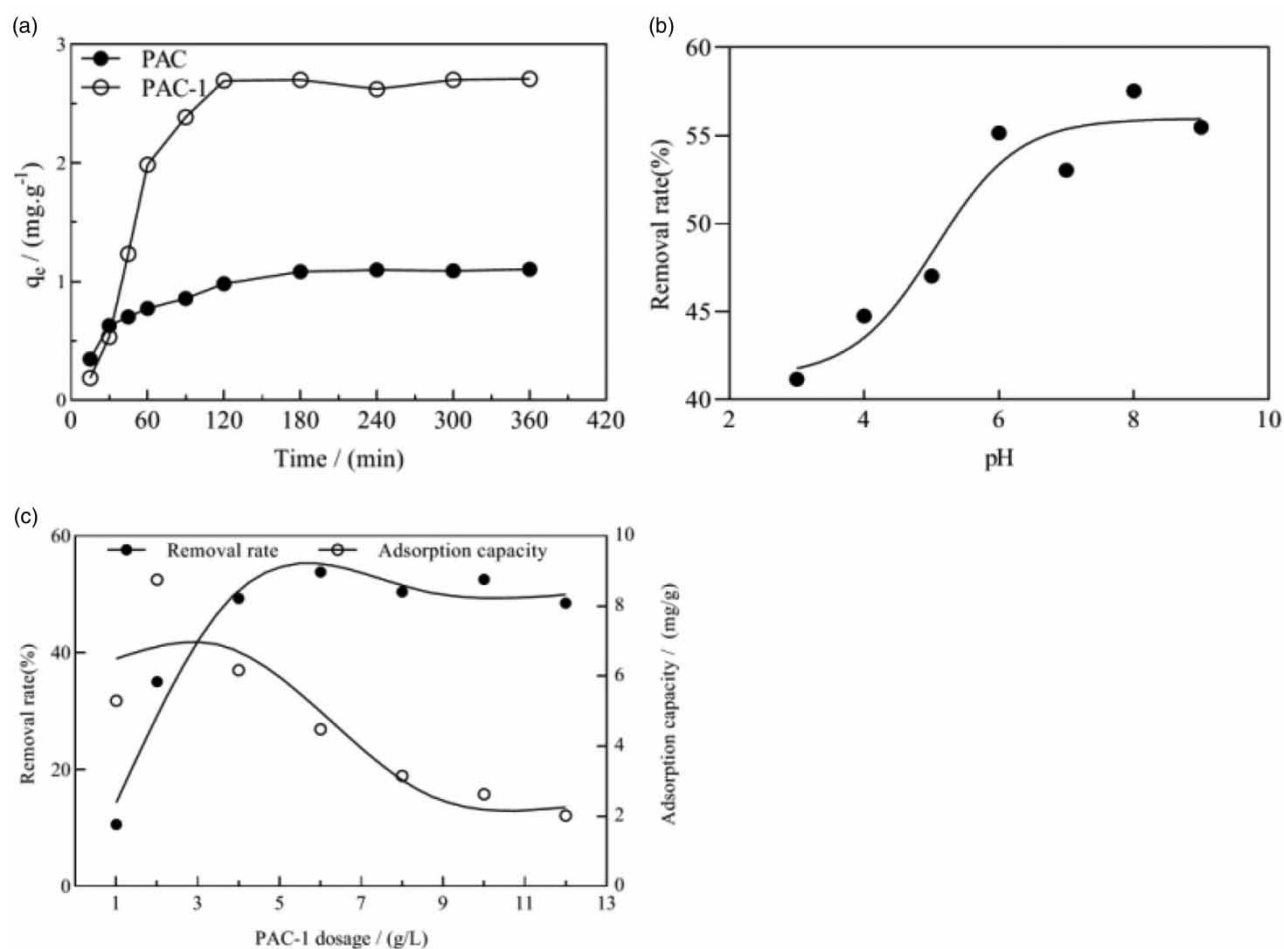


Figure 2 | Comparison of the adsorption performance of PAC and PAC-1 for NDEA under different conditions.

DISCUSSION

Properties of modified materials

The observed structural changes after material modification indicated that the addition of PM formed more adsorption sites on the AC surface (Figure 1(a) and 1(b)), and the adsorption performance of AC was considerably improved. This is similar to the conclusions of existing studies (Luan *et al.* 2020), which have shown that the addition of ferrous sulfate can also improve the adsorption performance. The change of XRD patterns before and after AC modification shows that a new phase formation took place, and AC characteristic diffraction peaks appeared at $2\theta = 28.3^\circ$. Compared with the JCPDS card PDF21-44-0268, it is found that the XRD pattern of PAC-1 covers the characteristic peaks of the β -Mn range, and the characteristic peaks at $2\theta = 22.8^\circ$ are significantly enhanced. Compared with PDF standard card, these peaks are characteristic peaks of manganese oxide, indicating that the content of manganese oxide attached to the surface of alumina increases after AC modification, the crystallinity of modified materials is greater, and the crystal form is more stable. The analysis of Figure 1(f) reveals that the activated carbon both before and after the modification belongs to the middle pore.

Effect of reaction conditions on NDEA removal effect

With the increase of reaction time, the NDEA adsorption capacity on the two materials first increased and then tended to be balanced (Figure 2(a)), indicating that the adsorption was mainly surface adsorption at the initial stage of the reaction (Chen *et al.* 2020), which conforms to the general adsorption law. After reaching the adsorption equilibrium, the adsorption amount fluctuated within a small range because a desorption phenomenon occurred during NDEA adsorption on PAC-1, indicating that there was physical adsorption in the process (Sun *et al.* 2014). At the adsorption equilibrium, the adsorption capacity of

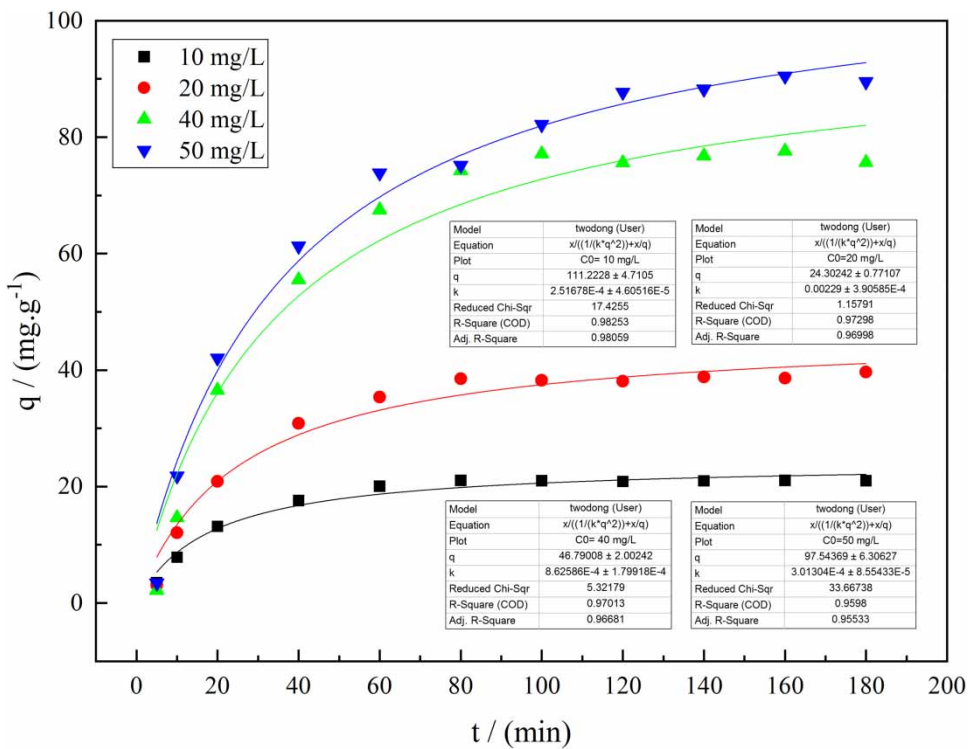


Figure 3 | Pseudo-second-order dynamics.

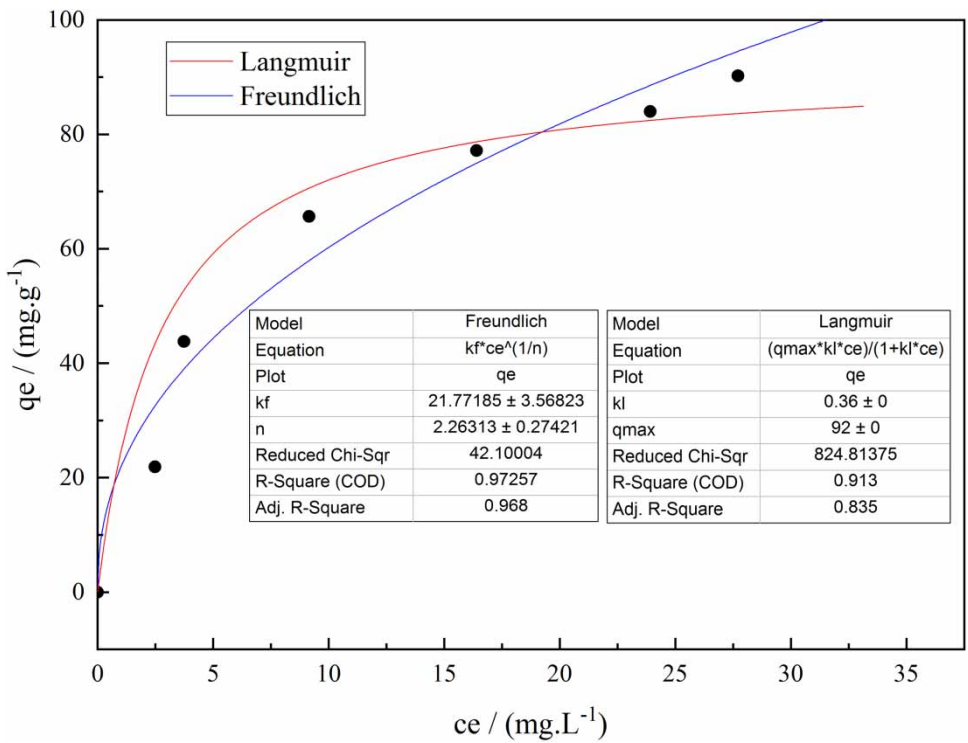


Figure 4 | Adsorption isotherm.

PAC-1 for NDEA was 2.7 times that of PAC, which was due to the fact that PAC-1 had a larger specific surface area and more adsorption sites, which was consistent with the above conclusions on the properties of modified materials. Figure 2(b) shows that, when the solution is alkaline, the removal rate of NDEA is higher than that under acidic conditions. This may be due to the increase in the chemical adsorption of PAC-1 and NDEA under alkaline conditions, which is similar to the conclusion for NDMA adsorption on AC under different pH values. (Padhye *et al.* 2010)

Figure 2(c) shows that, when the dosage reaches a certain value, the adsorbed amount of NDEA gradually decreases with the continued increase of PAC-1. This is because there are many active adsorption sites on the surface of PAC-1. When the dosage of PAC-1 is small, the active adsorption sites are fewer (Velten *et al.* 2011b; Grant *et al.* 2019). The small NDEA molecule quickly binds to the active sites on the surface of activated carbon, resulting in a high rate of adsorption (Hanigan *et al.* 2012). With the increase of PAC-1 dosage, the number of adsorption sites provided by PAC-1 also increase (Velten *et al.* 2011b). However, the total amount of adsorbed NDEA changes relatively little, and the adsorbed amount decreases. At the same time, the increased number of PAC-1 particles also enhances their collision probability (Dai *et al.* 2012), making them prone to mutual cohesion and affecting the NDEA adsorption effect.

Adsorption kinetics and isotherms

The pseudo-second-order kinetic equation has a good fit, indicating that the adsorption of NDEA on activated carbon includes both physical adsorption and chemical adsorption (Figure 3) (Padhye *et al.* 2010), and that the adsorption rate of the reaction is proportional to the square of the reactant concentration. It also shows that increasing the mass concentration of NDEA in the solution will promote the driving force of the concentration gradient and accelerate the adsorption rate.

The Freundlich adsorption isotherm equation fits well with our results (Figure 4), which is consistent with the conclusion of Dai *et al.* 2009 on NDMA, indicating that the adsorption of NDEA on PAC-1 belongs to the multi-molecular layer chemisorption type (Burhan *et al.* 2018). With the increase of initial NDEA concentration, the adsorbed amount of NDEA by PAC-1 in equilibrium also increases. This is because when the concentration of NDEA in the solution is large, the concentration gradient of internal and external solutions of PAC-1 is also large, the diffusion ability of molecules is enhanced, and the diffusion rate of NDEA is high, promoting the adsorption of NDEA on PAC-1.

Adsorption mechanism

After modification, the specific surface area and pore volume of activated carbon greatly increased (Velten *et al.* 2011b), and obvious pore structure could be observed, thus increasing the adsorption capacity of activated carbon for NDEA. In the physical adsorption process, there is van der Waals attraction between NDEA and activated carbon molecules (Sun *et al.* 2016), such that NDEA molecules will be adsorbed on the surface of activated carbon until the adsorption equilibrium. In this study, the modified activated carbon exhibited a desorption phenomenon during NDEA adsorption. The reason is that the van der Waals attraction was small and the intermolecular binding force was weak, indicating that the activated carbon had a poor overall physical adsorption effect for NDEA.

Herein, the chemical adsorption of NDEA on modified activated carbon was mainly multi-molecular layer chemical adsorption (Figure 4), which conforms to the Freundlich equation. This is because the hydrophobicity of modified activated carbon is stronger, and the impregnation of permanganate increases the functional groups on the oxygen-containing surface. (Chu *et al.* 2015; De Vera *et al.* 2015; Sun *et al.* 2018)

At present, the research of nitrosamines mainly focuses on NDMA, and NDEA removal has attracted little attention. The experiment in this study only corresponds to the preliminary research stage. In future research, the types of adsorbent should be increased to analyze the adsorption effect of various adsorbents on NDEA. This paper only studied the static adsorption of NDEA with few factors considered. It is necessary to conduct further research on the dynamic adsorption of NDEA by activated carbon and the regeneration of AC. The high concentration of NDEA solution in this article was also artificially configured, which is different from the actual situation; future research also needs to investigate the NDEA adsorption effect of activated carbon in actual drinking water.

CONCLUSIONS

- (1) When the powdered activated carbon was pre-soaked in 0.8 mol/L permanganate for 24 hours and calcined at 400 °C for 7 hours, the adsorption effect of NDEA was enhanced.

- (2) When the dosage of PAC-1 was 8 g/L, the pH of the solution was controlled to 6, and the reaction time was 6 h, and the adsorption rate of NDEA reached 78.66%. The adsorption rate of NDEA on modified AC was 42.5% higher than that on unmodified AC and 24.94% higher than that on modified AC without PM prepreg.
- (3) The adsorption of NDEA on activated carbon mainly occurs in large and medium pores, and the adsorption effect is the best under large pore size.
- (4) The order of significance of factors affecting the adsorption of NDEA on activated carbon is dosage > pH > reaction time.
- (5) The adsorption process of NDEA on activated carbon conforms to the pseudo-second-order kinetic model, and it includes both physical adsorption and chemical adsorption.
- (6) The chemical adsorption type of NDEA on activated carbon is mainly multi-molecular layer chemical adsorption, which conforms to the Freundlich equation. Pre-leaching with permanganate increases the oxygen-containing surface functional groups of activated carbon, which in turn improves the adsorption effect of NDEA.

AUTHOR CONTRIBUTIONS

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Haisheng Cai, Yanmei Fu and Xianluo Shi. The first draft of the manuscript was written by Jiangang Lu and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.'

FUNDING

The research is supported by National Natural Science Foundation of China (31660140), National Science and Technology Support Program Project of China (2012BAC11B00), Science and Technology Project of Jiangxi Provincial Water Resources Department (202022YBKT15, 202223YBKT42, 202223YBKT45). Author Haisheng Cai has received research support from the 'National Natural Science Foundation of China' and 'National Science and Technology Support Program Project of China', Author Jiangang Lu and Xianluo Shi has received research support from 'Water Resources Department of Jiangxi Province'.

ETHICS APPROVAL

This study does not involve any animal and human sample.

CONSENT TO PARTICIPATE

Not applicable.

CONSENT FOR PUBLICATION

Not applicable.

COMPETING INTERESTS

The authors declare no competing interests.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Beita-Sandi, W., Ersan, M. S., Uzun, H. & Karanfil, T. 2016 Removal of N-nitrosodimethylamine precursors with powdered activated carbon adsorption. *Water Research* **88**, 711–718.
- Burhan, M., Shahzad, M. W. & Ng, K. C. 2018 Energy distribution function based universal adsorption isotherm model for all types of isotherm. *International Journal of Low-Carbon Technologies* **13** (3), 292–297.
- Chang, C. K., Tun, H. & Chen, C. C. 2020 An activity-based formulation for Langmuir adsorption isotherm. *Adsorption-Journal of the International Adsorption Society* **26** (3), 375–386.

- Chen, J. L., Gao, L., Shi, C. L., Wang, Y.-Z., Qi, D.-W., Hong, Y., Shen, W.-J., Wang, Y. & Zhu, J. H. 2020 New versatile zincic sorbent for tobacco specific nitrosamines and lead ion capture. *Journal of Hazardous Materials* **383**, 121188. DOI: 10.1016/j.jhazmat.2019.121188.
- China, M.o.E.a.E.t.P.s.R.o. 2016 HJ 809-2016. *Water Quality-Determination of Nitrosamine Compounds-Gas Chromatography*.
- Chu, W., Yao, D., Gao, N., Bond, T. & Templeton, M. R. 2015 The enhanced removal of carbonaceous and nitrogenous disinfection by-product precursors using integrated permanganate oxidation and powdered activated carbon adsorption pretreatment. *Chemosphere* **141**, 1–6.
- Cuthbertson, A. A., Kimura, S. Y., Liberatore, H. K., Summers, R. S., Knappe, D. R. U., Stanford, B. D., Maness, J. C., Mulhern, R. E., Selbes, M. & Richardson, S. D. 2019 Does granular activated carbon with chlorination produce safer drinking water? From disinfection byproducts and total organic halogen to calculated toxicity. *Environmental Science & Technology* **53** (10), 5987–5999.
- Dai, X. D., Zou, L., Yan, Z. F. & Millikan, M. 2009 Adsorption characteristics of N-nitrosodimethylamine from aqueous solution on surface-modified activated carbons. *Journal of Hazardous Materials* **168** (1), 51–56.
- Dai, X., Li, G., Zhang, Z., Zou, L. & Yan, Z. 2012 N-nitrosodimethylamine adsorption in aqueous phase by activated carbons with different porous and surface structures. *Asia-Pacific Journal of Chemical Engineering* **7** (2), 266–273.
- De Vera, G. A., Stalter, D., Gernjak, W., Weinberg, H. S., Keller, J. & Farre, M. J. 2015 Towards reducing DBP formation potential of drinking water by favouring direct ozone over hydroxyl radical reactions during ozonation. *Water Research* **87**, 49–58.
- de Vera, G. A., Keller, J., Gernjak, W., Weinberg, H. & Farre, M. J. 2016 Biodegradability of DBP precursors after drinking water ozonation. *Water Research* **106**, 550–561.
- Farre, M. J., Reungoat, J., Argaud, F. X., Rattier, M., Keller, J. & Gernjak, W. 2011 Fate of N-nitrosodimethylamine, trihalomethane and haloacetic acid precursors in tertiary treatment including biofiltration. *Water Research* **45** (17), 5695–5704.
- Fujioka, T., Khan, S. J., McDonald, J. A., Roux, A., Poussade, Y., Drewes, J. E. & Nghiem, L. D. 2013 N-nitrosamine rejection by reverse osmosis membranes: a full-scale study. *Water Research* **47** (16), 6141–6148.
- Gao, J. X., Wang, T. F., Shu, Q., Nawaz, Z., Wen, Q., Wang, D. Z. & Wang, J. F. 2010 An adsorption kinetic model for sulfur dioxide adsorption by ZL50 activated carbon. *Chinese Journal of Chemical Engineering* **18** (2), 223–230.
- Grant, G. A., Fisher, P. R., Barrett, J. E. & Wilson, P. C. 2019 Removal of agrichemicals from water using granular activated carbon filtration. *Water, Air, & Soil Pollution* **230** (1), 1–12. DOI: 10.1007/s11270-018-4056-y.
- Guo, X. & Wang, J. L. 2019 A general kinetic model for adsorption: theoretical analysis and modeling. *Journal of Molecular Liquids* **288**, 111100. DOI: 10.1016/j.molliq.2019.111100.
- Hanigan, D., Zhang, J., Herckes, P., Krasner, S. W., Chen, C. & Westerhoff, P. 2012 Adsorption of N-nitrosodimethylamine precursors by powdered and granular activated carbon. *Environmental Science & Technology* **46** (22), 12630–12639.
- Kadmi, Y., Favier, L., Simion, A. I., Rusu, L., Pacala, M. L. & Wolbert, D. 2017 Measurement of pollution levels of N-nitroso compounds of health concern in water using ultra-performance liquid chromatography–tandem mass spectrometry. *Process Safety and Environmental Protection* **108**, 7–17.
- Kennedy, A. M., Reinert, A. M., Knappe, D. R., Ferrer, I. & Summers, R. S. 2015 Full- and pilot-scale GAC adsorption of organic micropollutants. *Water Research* **68**, 238–248.
- Kristiana, I., Tan, J., Joll, C. A., Heitz, A., von Gunten, U. & Charrois, J. W. 2013 Formation of N-nitrosamines from chlorination and chloramination of molecular weight fractions of natural organic matter. *Water Research* **47** (2), 535–546.
- Li, S., Shi, C. L., Wang, Y.-Z., Sun, X. D., Qi, D.-W., Wu, D., Wang, Y. & Zhu, J. 2019 New efficient selective adsorbent of tobacco specific nitrosamines derived from discarded cigarette filters. *Microporous and Mesoporous Materials* **284**, 393–402.
- Liang, L. & Singer, P. C. 2003 Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. *Environmental Science & Technology* **37** (13), 2920–2928.
- Liao, X. B., Cheng, Y. S., Liu, Z. H., Shen, L. L., Zhao, L., Chen, C., Li, F. & Zhang, X. J. 2020 Performance of BAC for DBPs precursors' removal for one year with micro-polluted lake water in East-China. *Environmental Technology* **41** (27), 3554–3561.
- Liviac, D., Creus, A. & Marcos, R. 2011 Genotoxic evaluation of the non-halogenated disinfection by-products nitrosodimethylamine and nitrosodiethylamine. *Journal of Hazardous Materials* **185** (2–3), 613–618.
- Luan, X. M., Liu, X. Y., Fang, C., Chu, W. H. & Xu, Z. X. 2020 Ecotoxicological effects of disinfected wastewater effluents: a short review of in vivo toxicity bioassays on aquatic organisms. *Environmental Science: Water Research & Technology* **6** (9), 2275–2286.
- McCurry, D. L., Krasner, S. W., von Gunten, U. & Mitch, W. A. 2015 Determinants of disinfectant pretreatment efficacy for nitrosamine control in chloraminated drinking water. *Water Research* **84**, 161–170.
- Padhye, L., Wang, P., Karanfil, T. & Huang, C.-H. 2010 Unexpected role of activated carbon in promoting transformation of secondary amines to N-nitrosamines. *Environmental Science & Technology* **44** (11), 4161–4168.
- Reungoat, J., Escher, B. I., Macova, M. & Keller, J. 2011 Biofiltration of wastewater treatment plant effluent: effective removal of pharmaceuticals and personal care products and reduction of toxicity. *Water Research* **45** (9), 2751–2762.
- Selbes, M., Kim, D. & Karanfil, T. 2014 The effect of pre-oxidation on NDMA formation and the influence of pH. *Water Research* **66**, 169–179.
- Shi, C. L., Li, S. H., Sun, X. D., Wang, Z. P., Wang, Y.-Z., Xiong, J.-W., Gu, W.-B., Wang, W.-M., Yao, H.-M., Wang, Y. & Zhu, J. H. 2018 New activated carbon sorbent with the zeolite-like selectivity to capture tobacco-specific nitrosamines in solution. *Chemical Engineering Journal* **339**, 170–179.
- Simpson, D. R. 2008 Biofilm processes in biologically active carbon water purification. *Water Research* **42** (12), 2839–2848.

- Summers, R. S., Kim, S. M., Shimabuku, K., Chae, S. H. & Corwin, C. J. 2013 Granular activated carbon adsorption of MIB in the presence of dissolved organic matter. *Water Research* **47** (10), 3507–3513.
- Sun, X. D., Lin, W. G., Wang, L.-J., Zhou, B., Lv, X. L., Wang, Y., Zheng, S.-J., Wang, W.-M., Tong, Y.-G. & Zhu, J. H. 2014 Liquid adsorption of tobacco specific N-nitrosamines by zeolite and activated carbon. *Microporous and Mesoporous Materials* **200**, 260–268.
- Sun, X. D., Li, Y. Y., Wang, L.-J., Wu, D., Zheng, S.-J., Wang, W.-M., Tong, Y.-G., Wang, Y. & Zhu, J. H. 2016 Capturing tobacco specific N-nitrosamines (TSNA) in industrial tobacco extract solution by ZnO modified activated carbon. *Microporous and Mesoporous Materials* **222**, 160–168.
- Sun, X. D., Shi, C. L., Li, S. H., Wang, Y.-Z., Qi, D.-W., Wang, W.-M., Yao, H.-M., Wang, Y. & Zhu, J. H. 2018 New shape-selectivity discovered on graphene-based materials in catching tobacco specific nitrosamines. *Journal of Hazardous Materials* **358**, 234–242.
- Taguchi, V., Jenkins, S. D. W., Wang, D. T., Palmentier, J. & Reiner, E. J. 1994 Determination of N-nitrosodimethylamine by isotope-dilution, high-resolution mass-spectrometry. *Canadian Journal of Applied Spectroscopy* **39** (3), 87–93.
- Velten, S., Boller, M., Koster, O., Helbing, J., Weilenmann, H. U. & Hammes, F. 2011a Development of biomass in a drinking water granular active carbon (GAC) filter. *Water Research* **45** (19), 6347–6354.
- Velten, S., Knappe, D. R. U., Traber, J., Kaiser, H.-P., von Gunten, U., Boller, M. & Meylan, S. 2011b Characterization of natural organic matter adsorption in granular activated carbon adsorbers. *Water Research* **45** (13), 3951–3959.
- Wang, J. L. & Guo, X. 2020 Adsorption kinetic models: physical meanings, applications, and solving methods. *Journal of Hazardous Materials* **390**, 122156. DOI: 10.1016/j.jhazmat.2020.122156.
- Wang, W., Ren, S., Zhang, H., Yu, J., An, W., Hu, J. & Yang, M. 2011 Occurrence of nine nitrosamines and secondary amines in source water and drinking water: potential of secondary amines as nitrosamine precursors. *Water Research* **45** (16), 4930–4938.
- Wang, W., Yu, J., An, W. & Yang, M. 2016 Occurrence and profiling of multiple nitrosamines in source water and drinking water of China. *Science of the Total Environment* **551**, 489–495.
- Wong, S., Ngadi, N., Inuwa, I. M. & Hassan, O. 2018 Recent advances in applications of activated carbon from biowaste for wastewater treatment: a short review. *Journal of Cleaner Production* **175**, 361–375.
- Yang, X., Gan, W., Zhang, X., Huang, H. & Sharma, V. K. 2015 Effect of pH on the formation of disinfection byproducts in ferrate(VI) pre-oxidation and subsequent chlorination. *Separation and Purification Technology* **156**, 980–986.
- Yoon, S., Nakada, N. & Tanaka, H. 2012 A new method for quantifying N-nitrosamines in wastewater samples by gas chromatography-triple quadrupole mass spectrometry. *Talanta* **97**, 256–261.
- Zheng, J., Lin, T. & Chen, W. 2018 Removal of the precursors of N-nitrosodiethylamine (NDEA), an emerging disinfection byproduct, in drinking water treatment process and its toxicity to adult zebrafish (*Danio rerio*). *Chemosphere* **191**, 1028–1037.
- Zhong, Y., Gan, W., Du, Y., Huang, H., Wu, Q., Xiang, Y., Shang, C. & Yang, X. 2019 Disinfection byproducts and their toxicity in wastewater effluents treated by the mixing oxidant of ClO_2/Cl_2 . *Water Research* **162**, 471–481.

First received 23 December 2021; accepted in revised form 3 March 2022. Available online 15 March 2022