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Activated carbon adsorption for removal of the nitrogenous disinfection byproduct phenylacetonitrile from drinking water

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ABSTRACT

Nitrogenous disinfection by-products (N-DBPs) are more genotoxic and cytotoxic than the currently regulated carbonaceous DBPs (i.e., C-DBPs), and it has become a frontier issue of drinking water safety research. In this paper, the effect of granular activated carbon (GAC) on adsorption and its influencing factors was investigated for a typical N-DBP phenylacetonitrile, which is produced during chlorination of phenylalanine precursor during water treatment. The results showed that GAC had a high adsorption capacity (q_{max} = 22.92 mg/g) for phenylacetonitrile, and the adsorption isotherm was fitted to the Langmuir isotherm model. Pseudo-second-order equation can well describe the behavior of phenylacetonitrile adsorption on activated carbon ($R^2 > 0.990$), and the adsorption rate constant k_2 = 0.7780–14.12 g/(mg h). Analysis of the influencing factors showed that higher phenylacetonitrile concentration improved the adsorption equilibrium capacity and the adsorption rate. Water temperature and pH had little effect on the capacity or rate of adsorption.

Keywords: Drinking water treatment; Nitrogenous disinfection by-products; Phenylacetonitrile; Activated carbon; Adsorption

1. Introduction

Trihalomethanes (THMs) were the first group of carbonaceous disinfection by-products (C-DBPs) to be detected in chlorinated drinking water in 1974 [1]. Since then, more than 600–800 DBPs have been identified [2–5]. Because of their adverse health effects including cytotoxicity [6], guidance for concentrations of both THMs and haloacetic acids (HAAs) in drinking water have been issued by many agencies, including the U.S. Environmental Protection Agency [7], WHO [8], China [9], EU [10].

Besides regulated C-DBPs such as THMs and HAAs, nitrogenous DBPs (N-DBPs), such as N-nitrosodimethylamine, haloacetonitriles (HANs), halonitromethanes (HNMs) and haloacetamides (HAcAms) [11–13] can also pose adverse health effects in drinking water. NOM contains nitrogen including proteins, polypeptides and amino acids, which can produce halogenated and non-halogenated organic products such as nitriles when chlorinated [14–16]. Phenylalanine, an amino acid found in source water, can produce phenylacetonitrile during chlorine disinfection, and also other DBPs such as phenyl acetaldehyde and

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N-chloramines [16–19]. When investigated in tap water from full-scale drinking water treatment plants (DWTPs), phenylacetonitrile was found in all chlorination DWTPs studied, in part because it is stable in chlorinated drinking water for up to 31 d [19]. Phenylacetonitrile is toxic, has a moderate K_{ow} of 1.56, and possesses a strong unpleasant odor with descriptors of chlorine, sulfur and acidic with an odor threshold in the range of 6 μg/L in air (Table 1). Therefore, it is important to apply technologies to control phenylacetonitrile in treated and distributed drinking water.

There are generally three strategies for DBPs controlling, including precursor removal, alternative disinfectants and direct removal of DBPs. Technologies which can efficiently control DBPs include adsorption [21–23], oxidation and reduction [24–30] and biodegradation [31,32]. Among the above technologies, activated carbon adsorption is more extensively employed for DBPs precursor removal [23,33–38] than for direct DBPs controlling. Actually, NOM in raw water as the common precursor has complicated structure and their removal efficiency by GAC was limited. It is difficult to diffuse into micropores of GAC for the main component of NOM, humic substances with high molecular weight [39]. Comparably, DBPs formed in lower molecular may access easily to the adsorption sites of GAC. Therefore, GAC adsorption may be more suitable to direct DBPs control. Phenylacetonitrile is one kind of nonhalogenated DBPs in smaller size. Moreover, phenylacetonitrile with aromatic ring structure is usually hydrophobic and have high affinity to GAC [40]. Therefore, it was supposed to be treated well by GAC. In this study, activated carbon adsorption was investigated to remove phenylacetonitrile and the specific objectives were: (1) to investigate the kinetics and capacity of GAC and PAC to remove phenylacetonitrile from water; (2) to investigate the impact of influencing factors – pH, temperature, water quality – on removal of phenylacetonitrile by GAC.

2. Materials and methods

2.1. Materials

The GAC and powdered activated carbon (PAC) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai), and their properties are given in Table 2. GAC was washed with reagent water several times, and then dried at 105°C for 24 h before use. Phenylacetonitrile (99% pure) was purchased from Aladdin (Shanghai). N-hexane, sodium chloride, magnesium chloride, potassium chloride, sodium hydroxide, and hydrochloric acid were of analytical grade. Reagent water (18 MΩ) produced by an ultra water purifier (UPHW1-90T, Europtronic, Shanghai) was used for experiments.

Instruments and equipments included a gas chromatography (GC2010Plus, Shimadzu, Japan) with an Rtx-5 column (30 m × 0.25 mm × 0.25 μm, Shimadzu, Japan), a quadruple magnetic stirrer (HJ-4, Meixiang, Shanghai), a constant temperature shaker (HYG- II, Hualida, Jiangsu), a pH meter (SX751, Sanxin, Shanghai), an electronic balance (BS124S, Sartorius, Beijing), and an automatic surface area analyzer (JW-BK112, microscopic Triglobal, Beijing).

2.2. Experimental methods

2.2.1. Determination of phenylacetonitrile

Liquid–liquid extraction was used for preconcentration and extraction of phenylacetonitrile from water. A 100 mL sample was placed in a 100 mL volumetric flask and 2 mL hexane was added. The mixture was stirred for 15 min after settlement, the hexane solvent was separated and dried by anhydrous sodium sulfate. The hexane extract was injected into a gas chromatography coupled with electron capture detector (GC-ECD) for phenylacetonitrile determination. GC condition includes that nitrogen carrier gas with flow rate of 41.8 mL/min; splitless injection model. The temperature program was initially 40°C for 5 min, then increased by 10°C/min to 150°C and held for 2 min. The injector temperature was 150°C and the detector temperature was 300°C. Calibration curve was linear ($R^2 = 0.997$). The quantification limits for phenylacetonitrile with GC-ECD was 25 μg/L.

2.2.2. Characterization and adsorption of phenylacetonitrile to AC

The adsorption performance of phenylacetonitrile by GAC or PAC was evaluated by residual concentration and adsorption capacity. A series of batch experiments were designed to explore adsorption performance.

Accurately weighed GAC or PAC amounts, in the range of 0.7–20 mg/L, were placed in individual 250 mL conical flasks with taps, then 100 mL of 500 μg/L phenylacetonitrile in reagent water was added. AC samples and blanks containing 500 μg/L phenylacetonitrile were agitated at 200 rpm for 24 h at 25°C to achieve equilibrium. The residual concentration of phenylacetonitrile at equilibrium was determined after filtering water through a 0.45 μm membrane filter, then extracting with *n*-hexane.

The influencing factors that include pH, temperature, phenylacetonitrile concentration, water matrix and

Table 1
Characteristics of odor DBPs phenylacetonitrile

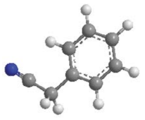
Name	CAS#	K_{ow}	Toxicity	Odor characteristics	Solubility	Chemical structure
Phenylacetonitrile	140-29-4	1.56	High toxicity	Bitter almond, spicy and floral; chlorinous, sulfur, acidic; odor threshold in air is 6 μg/L-air [19,20].	Water soluble <0.1 g/100 mL at 17°C	

Table 2
Properties of the activated carbons

Species	GAC	PAC
Aperture, nm	3.309	2.980
Pore volume, cm^3/g	0.440	0.464
Specific surface area, m^2/g	1,242.6	1,291.4
Relative density	1.9–2.1	1.9–2
Chloride, %	≤0.025	≤0.025
Methylene blue, mg/g	Qualified	Qualified

co-existing cations were investigated. And also the adsorption of phenylacetonitrile in reagent water was compared with that in pH 7.11 drinking water with 8.7 mg/L dissolved oxygen, 0.0086 UV254 (cm^{-1}), 1 NTU and 110 μs/cm conductivity.

Adsorption isotherm data were simulated by Langmuir and Freundlich adsorption models [35,36,41,42]. The phenylacetonitrile uptake at equilibrium, q_e (mg/g), was computed by:

Langmuir adsorption isotherm model as shown in Eqs. (1) and (2).

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{1}$$

$$\frac{1}{q_e} = \frac{1}{q_m b} \times \frac{1}{C_e} + \frac{1}{q_m} \tag{2}$$

Freundlich adsorption isotherm model as shown in Eqs. (3) and (4).

$$q_e = K_f C_e^{1/n} \tag{3}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where C_e (mg/L) is the concentration of phenylacetonitrile at equilibrium; q_e (mg/g) is the mass of phenylacetonitrile sorbed per g of AC; q_m (mg/g) is the maximum sorption capacity; b (L/mg) is affinity coefficient; K_f is the Freundlich adsorption coefficient; n is a constant.

2.2.3. Adsorption kinetics

For the adsorption kinetics investigation, residual phenylacetonitrile concentrations were determined in samples taken at specified intervals (0–3 h) until the 24 h equilibrium was reached. Initial concentrations of 100, 200 and 500 μg/L were used in the kinetic experiments, while dosages of AC were 0.1 g/L. Three kinetic models were used to fit the sorption process, which were pseudo-first-order, pseudo-second-order and intraparticle diffusion models according to Eqs. (5)–(9).

Pseudo-first-order kinetic model [42]:

$$\frac{dq_t}{d_t} = k_1 \left(q_e - q_t \right) \tag{5}$$

$$\ln\left(q_e - q_t \right) = \ln q_e - k_1 t \tag{6}$$

Pseudo-second-order kinetic model [41]:

$$\frac{dq_t}{d_t} = k_2 \left(q_e - q_t \right)^2 \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

Intraparticle diffusion models [36]:

$$q_t = k_p t^{0.5} \tag{9}$$

where q_e and q_t (mg/g) are phenylacetonitrile uptakes at equilibrium and time t, respectively; k_1 (min^{-1}) and k_2 (g/mg/min) are rate constants of pseudo-first-order and pseudo-second-order adsorption model. k_p is the equilibrium rate constant of intraparticle diffusion adsorption.

3. Results and discussion

3.1. Characteristics of phenylacetonitrile adsorption by activated carbon

3.1.1. Adsorption isotherm

Equilibrium was reached after 24 h indicated by residual phenylacetonitrile concentration which showed little variation. Isotherm data of phenylacetonitrile at the adsorption equilibrium were analyzed by Langmuir and Freundlich to evaluate the maximum adsorption capacity. Regression analysis was applied and the results are shown in Fig. 1. It can be concluded that the adsorption procedure of phenylacetonitrile on GAC follows Langmuir model (R^2 = 0.9277) better than Freundlich (R^2 = 0.8782). The results revealed the monolayer coverage of phenylacetonitrile on the activated carbon surface. Based on Langmuir model, the maximum adsorption capacity is determined as 22.92 mg/g at 25°C. As reported in the literature, the Langmuir model has good fitting results for activated carbon adsorption of many organic pollutants in aqueous environment [43–45].

3.1.2. Adsorption kinetics

The experimental data for the adsorption rate of phenylacetonitrile were analyzed using three different kinetic models. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were applied in Table 3 and Fig. 2.

It can be deduced that the pseudo-second-order equation has a better fit for the adsorption behavior of phenylacetonitrile (R^2> 0.99), although the pseudo-first-order equation and intraparticle diffusion equation are also acceptable. Similar results were observed by other researchers for the adsorption of aromatic phenols [46]. Along with the increase of initial concentration from 100 to 500 μg/L, the predicted phenylacetonitrile uptake increased from 0.263 to 2.856 mg/g and 0.819 to 4.806 mg/g at 3 h contact and 25°C for pseudo-first and second-order models, respectively. With some

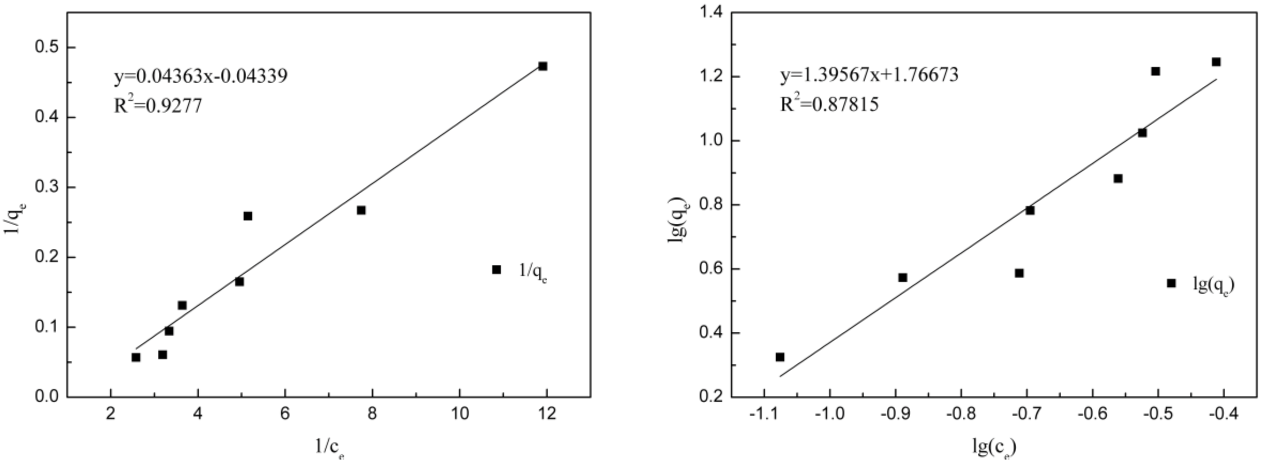


Fig. 1. Comparison of Langmuir and Freundlich model for phenylacetonitrile adsorption onto GAC.

Table 3
Phenylacetonitrile adsorption rate constants for three kinetic models at 25°C and pH 7.0

	Pseudo-first-order adsorption rate equation			Pseudo-second-order adsorption rate equation			Intraparticle diffusion equation	
Conc. μg/L	q_e mg/g	K_1 h^{-1}	R^2	q_e mg/g	K_2 g/(mg h)	R^2	K_p mg/(g h$^{1/2}$)	R^2
100	0.2632	0.5770	0.9736	0.8194	14.12	0.9979	0.1574	0.9416
250	0.9933	0.6673	0.8402	1.874	2.850	0.9977	0.7064	0.8196
500	2.856	0.8173	0.9203	4.806	0.7780	0.9903	1.923	0.9521

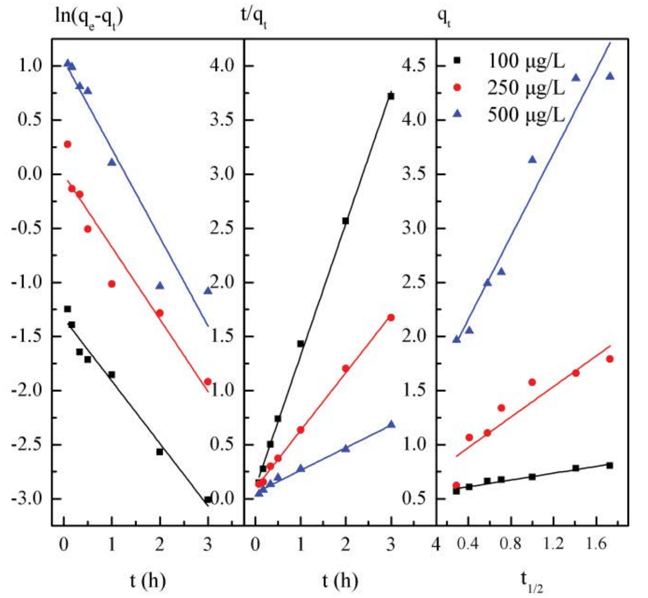


Fig. 2. Pseudo-first-order kinetics model, pseudo-second-order kinetics model, internal diffusion kinetic model fitting curve of GAC adsorption of phenylacetonitrile.

limitations, pseudo-first-order kinetics is usually used to describe the initial stage of adsorption kinetics instead of the long-term process of adsorption accurately. Comparing the magnitude of pseudo-first-order adsorption rate constant h ($h = K_2q_e^2$, mg/(g h)) ($h_{100\ \mu g/L} < h_{250\ \mu g/L} < h_{500\ \mu g/L}$) (Fig. 2), it is more suitable for fitting low concentration adsorption. The pseudo-second-order reaction model contains all the processes of adsorption, such as diffusion of external liquid membrane, surface adsorption and intraparticle diffusion, and more truly and comprehensively describe the adsorption mechanism of phenylacetonitrile on GAC. At 25°C, the q_e values calculated by the pseudo-second-order model were 0.8194, 1.874 and 4.806 mg/g, which were very similar to the actual values (0.856, 1.939 and 4.738 mg/g), and the relative error is lower than 5%.

3.1.3. Adsorption thermodynamics

The physical or chemical nature of phenylacetonitrile adsorption on activated carbon is further demonstrated by evaluation of changes in Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) as follows:

$$\ln\left(K_d\right) = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{10}$$

$$\Delta G° = -RT\ln\left(K_d\right) \tag{11}$$

where R represents the gas constant (8.314 J/mol K), T (°K) is adsorption temperature, and K_d is the distribution coefficient for adsorption. The thermodynamic constants are evaluated by plotting ln (K_d) vs. 1/T. The negative value of $\Delta H°$ indicated the inhibitory effect of heating on adsorption. The adsorption process includes chemisorption process.

During adsorption, the rate of phenylacetonitrile uptake mainly depends on the rate of adsorbate transported from the exterior to the interior sites of the adsorbent [47]. The initial stage of activated carbon adsorption contributes to physisorption. With increasing contact time, chemical adsorption occurs between phenylacetonitrile and functional groups on the surface of GAC through covalent or chemical bonds, which controlled the rate of adsorption during the process. So the functional groups play an important role in phenylacetonitrile adsorption. The ability of GAC to adsorb phenylacetonitrile is attributed to the presence of the various polar functional groups, mainly oxygen-containing functionalities such as carboxyls, lactones, hydroxyls (or phenols) and carbonyls. Cyano (CN) is a strongly polar group, the electronegativity of the sp hybrid nitrogen atoms is large, pi-bond is easily polarized, so the molecular polarity of phenylacetonitrile is large [48]. Electron donating and withdrawing act as important factors between phenylacetonitrile and oxygen-containing functionalities on the surface of GAC. Benzene contains electron-withdrawing group together with cyano can increase the adsorption capacity [49,50], and phenylacetonitrile is electron withdrawing conjugated system formed by cyano and benzene. Therefore, the chemical adsorption process is dominant; hydrophobic and electrostatic repulsion are the main mechanisms.

3.2. Influencing factors of adsorption of phenylacetonitrile on activated carbon

Physical and chemical water quality conditions may affect adsorption capacity and rate of organic pollutants on ACs. The following figures demonstrated the adsorption data measured at conditions with different kinds of activated carbon, solution pH, temperature and level of phenylacetonitrile, etc.

3.2.1. Activated carbon species

The physical properties of activated carbon affect the adsorption process of pollutants. Phenylacetonitrile adsorption on GAC and PAC are compared in Fig. 3.

For both GAC and PAC, more than 92% of the phenylacetonitrile could be adsorbed at equilibrium, indicating good removal of phenylacetonitrile from aqueous system (Figs. 3a and b). For PAC, sorption was fairly rapid with 87.8% of the phenylacetonitrile removed during the first 5 h, and only an additional 5% removed during the next 5 h for a total removal of 93% at a 10 h contact time. For GAC, the removal was 92.6% after 10 h of adsorption, which is approximately the same removal as PAC in half the contact time. The equilibrium adsorption capacity of GAC (q_e = 4.68 mg/g) is similar to that of PAC (q_e = 4.82 mg/g). The adsorption rate constants K_2 were calculated to be 11.02 g/(mg h) for PAC and 0.40 g/(mg h) for GAC according to the slope and intercept of rate fitting curves. Because the phenylacetonitrile is a compound with lower molecular, the pore size of activated carbon molecules does not significantly affect its adsorption capacity [45]. Similar trends with the report of acrylonitrile adsorbed by PAC and GAC, the maximum adsorption capacities were similar at 51.72 and 46.63 mg/g, respectively, and the removals of 93% and 91%, were not much different.

3.2.2. Effect of pH

The solution pH has effect on superficial charge of the adsorbent, ionization degree of the pollutant, and separation of functional groups influencing the active sites of the sorbent in the adsorption process [51]. Phenylacetonitrile does not have an ionizable hydrogen or pK_a [52] so its chemical properties do not change with pH. To determine the optimum pH for phenylacetonitrile removal, the phenylacetonitrile solutions simulated with pure water were adjusted to different pH and the results are shown in Figs. 4a and b. It can be concluded that a pH range of 3.0–11.0 has a slight effect on the adsorption of phenylacetonitrile by GAC. The corresponding adsorption capacities were 4.61, 4.76, 4.78, 5.11 and 5.18 mg/g, respectively, positively associated with the pH values of 3.0, 5.0, 7.0, 9.0 and 11.0, respectively. At pH 11.0, the highest adsorption capacity and adsorption rate were obtained. It was suggested that the chemical functional groups on the surface of the activated carbon may be

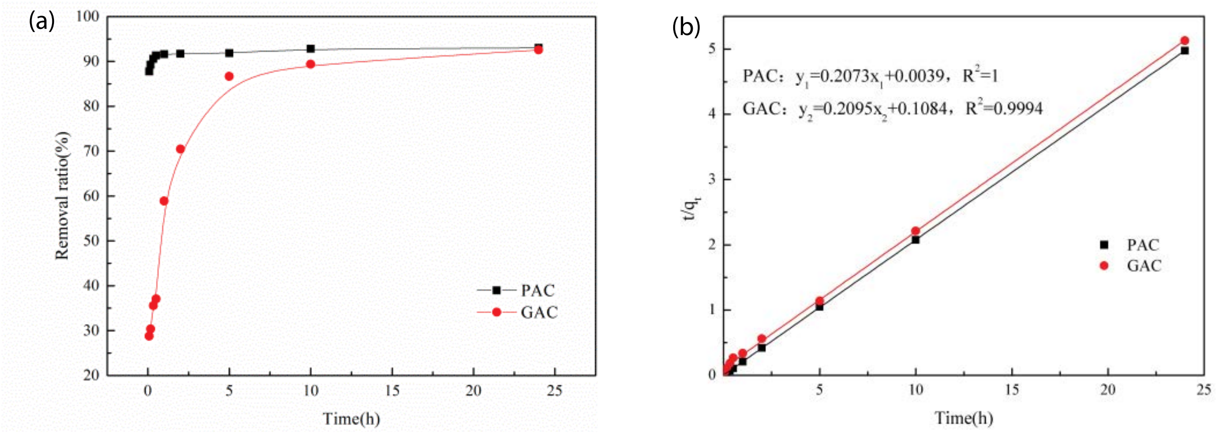


Fig. 3. Influence of activated carbon type on adsorption process: (a) percentage removal and (b) kinetics of removal (experimental conditions: 500 µg/L in reagent water initial phenylacetonitrile concentration, 0.01 g GAC dosage, 0.01 g PAC dosage, 100 mL volume, 25°C).

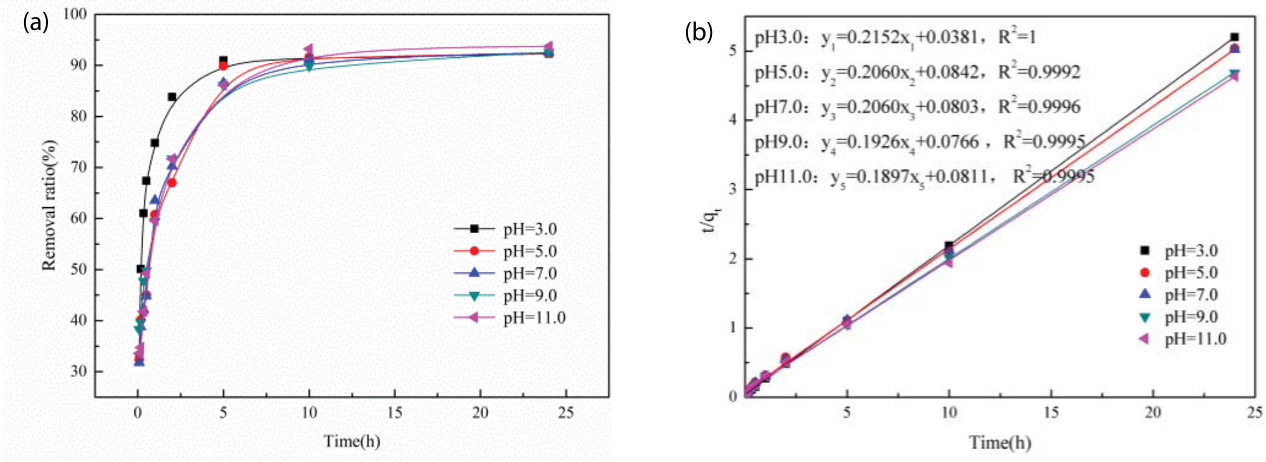


Fig. 4. Influence of different pH on the adsorption process: (a) percentage removal and (b) kinetics of removal (experimental conditions: 500 μg/L in reagent water initial phenylacetonitrile concentration, 0.01 g GAC dose, 100 mL volume, 25°C).

affected by pH. At low pH, the activated carbon is positively charged, H$^+$ and phenylacetonitrile molecules compete for the adsorption sites on the surface of the adsorbent. The hydroxyl groups on the surface of the activated carbon combine with the acid so the binding ability with phenylacetonitrile was reduced, resulting in the adsorption capacity of activated carbon correspondingly decreased under acidic conditions.

3.2.3. Effect of temperature

The temperature can affect pollutant adsorption to activated carbon since most of the adsorption processes were exothermic.

The effect of temperature (15°C, 25°C, 35°C and 40°C) is shown in Figs. 5a and b. For the phenylacetonitrile, the adsorption ratio decreased with temperature increment, though slightly. The adsorption capacity decrease may be attributed to the chemical interaction between the active sites on the adsorbent surface and the phenylacetonitrile. Temperature increase usually leading to higher thermal movement of molecules, and higher collision probability; on the other hand, activated carbon pores may have a thermal expansion and contraction effect. In selected conditions, the difference of adsorption can be ignored, for the little heat effect.

3.2.4. Effect of initial phenylacetonitrile concentration on adsorption

Different initial concentrations (200, 500, 750 and 1,000 μg/L) of phenylacetonitrile were prepared for adsorption processes and the results were illustrated in Fig. 6. The adsorption of high concentrations (750 and 1,000 μg/L) was better than those of low concentrations (200 and 500 μg/L). The removal ratio increased along with the initial concentration increased, which was especially obvious at the initial stage of adsorption. The adsorption capacities were 1.94, 4.38, 6.72 and 10.82 mg/g for 200–1,000 μg/L solutions while the adsorption rate constants K_2 were decreased from 1.97,

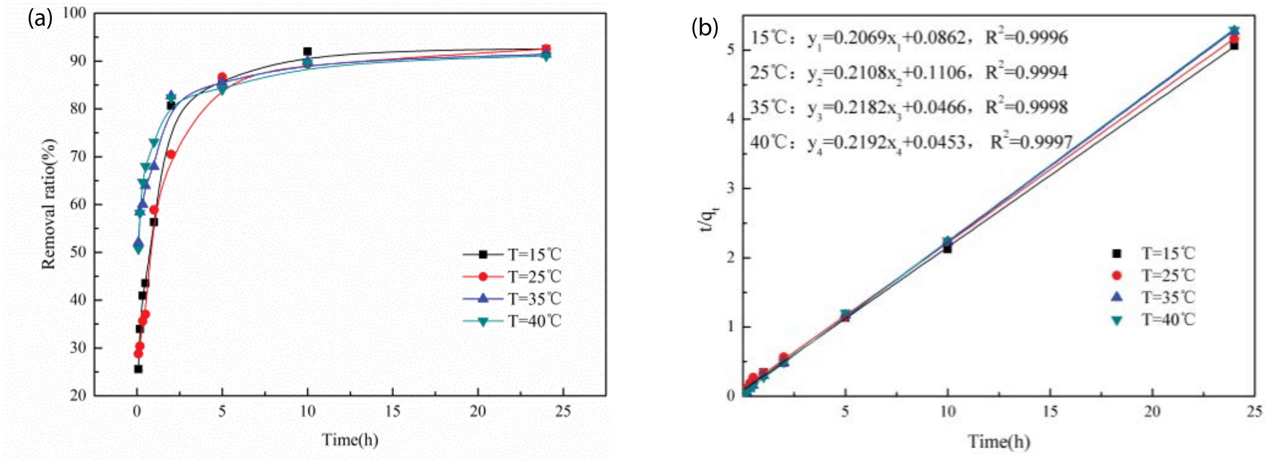


Fig. 5. Influence of different temperature on the adsorption process: (a) percentage removal and (b) kinetics of removal (experimental conditions: 500 μg/L in reagent water initial phenylacetonitrile concentration, 0.01 g GAC dose, 100 mL volume, 25°C. The tap water was at pH 7.1).

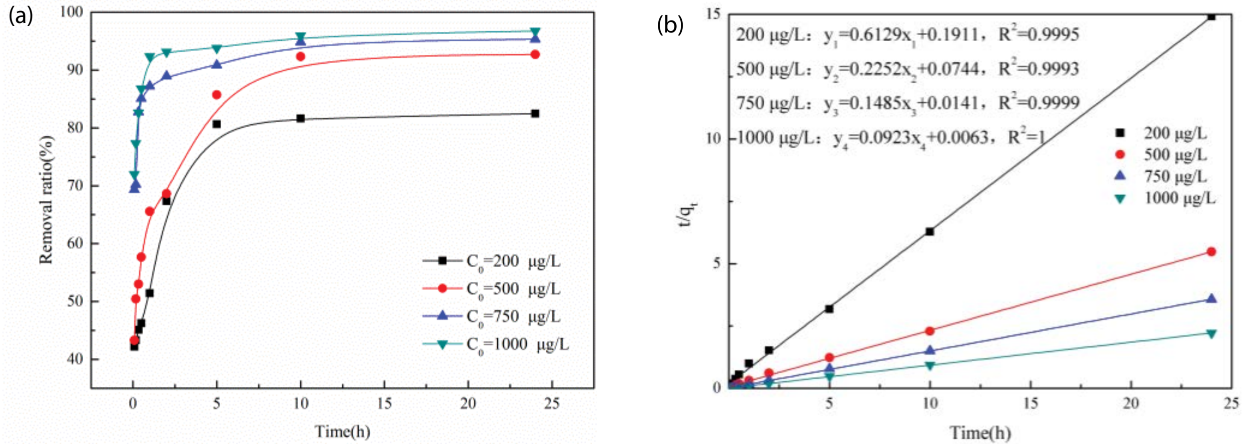


Fig. 6. Influence of different initial solution concentration on the adsorption process: (a) percentage removal and (b) rate of removal (experimental conditions: 0.01 g GAC dose, 100 mL volume, 25°C).

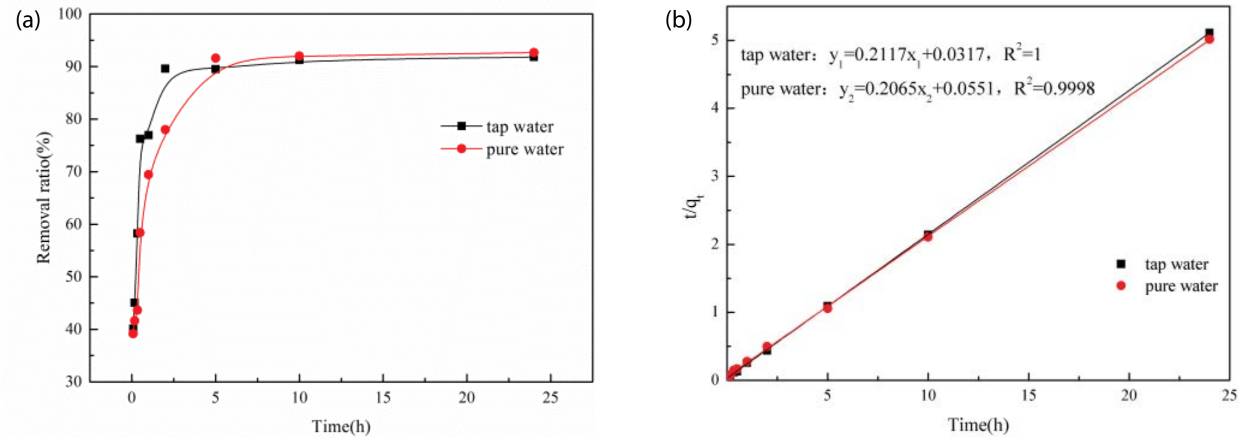


Fig. 7. Different substrate effects on the adsorption process: (a) percentage removal and (b) rate of removal. (Experimental conditions: 500 μg/L in reagent water initial phenylacetonitrile concentration, 0.01 g GAC dose, 100 mL volume, 25°C).

1.68, 1.56 to 1.35 g/(mg h), respectively. Since the higher concentration enhances the interaction between phenylacetonitrile in the aqueous phase and GAC surface, the mass transfer driving force between solid and solution phases would become larger, hence resulting in higher adsorption values. The adsorbate concentrations in the solution can also strongly affect the mechanism controlling the overall kinetic coefficient [51].

3.2.5. *Effect of water quality*

Phenylacetonitrile removal in tap water and reagent water were quite similar (Figs. 7a and b). The water quality parameters of the tap water were pH 7.11, 8.7 mg/L dissolved oxygen, 0.0086 UV_{254} (cm^{-1}), and 1.0 NTU and conductivity 110 μs/cm. The percentage removal of phenylacetonitrile in the tap water was similar to that of reagent water, 91.6% and 92.7%, respectively. The adsorption capacities were also similar, 4.69 mg/g in tap water and 4.75 mg/g in reagent water. The adsorption rate constants K_2 were 1.41 and 0.77 g/(mg h) for tap and reagent water, respectively, indicating a faster uptake in tap water.

4. Conclusions

Phenylacetonitrile can be removed from aqueous solutions by using activated carbon. (1) The adsorption of phenylacetonitrile by GAC fit Langmuir model best and was proved to be a monolayer adsorption process. (2) The adsorption of phenylacetonitrile is well described by the pseudo-second-order equation ($R^2 > 0.99$). (3) The phenylacetonitrile adsorption was influenced by various factors. Uptake by PAC was faster than with GAC, although their equilibrium concentrations showed minor difference. pH and temperature had little effect on the adsorption kinetics or equilibrium of phenylacetonitrile. The capacity and kinetics confirmed effective removal of phenylacetonitrile by GAC when treating drinking water.

Acknowledgments

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