



## Particle properties in granular activated carbon filter during drinking water treatment

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### Abstract

The elemental composition and bacteria attached in particles were investigated during granular activated carbon (GAC) filtration. The experimental results showed that trapped influent particles could form new, larger particles on GAC surface. The sloughing of individuals off GAC surface caused an increase in effluent particles in the size range from 5 to 25  $\mu\text{m}$ . The selectivity for element removal in GAC filters caused an increasing proportion of metallic elements in the effluent particles. The distribution of molar ratio indicated a complicated composition for large particles, involving organic and inorganic substances. The organic proportion accounted for 40% of total carbon attached to the particles. Compared with dissolved carbon, there was potential for the formation of trihalomethanes by organic carbon attached to particles, especially for those with size larger than 10  $\mu\text{m}$ . The pure carbon energy spectrum was found only in the GAC effluent and the size distribution of carbon fines was mainly above 10  $\mu\text{m}$ . The larger carbon fines provided more space for bacterial colonization and stronger protection for attached bacteria against disinfection. The residual attached bacteria after chlorine disinfection was increased to  $10^2$ – $10^3$  CFU/mL within 24 hours at 25°C.

**Key words:** drinking water treatment; GAC filters; bacterial attachment to carbon

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### Introduction

Granular activated carbon (GAC) filters, as an advanced treatment process, are used for drinking water purification (Dussert, 1994; Zhang, 2009). During the filtration, microbial degradation of pollutants is found in GAC filter systems (Lambert et al., 1996; Schreiber et al., 1997), and bacterial colonization causes the occurrence of biotic particles in water filtered by GAC filters (Castaldelli et al., 2005; Weeks et al., 2007). In recent years, waterborne protozoan outbreaks have occurred in the United States and other countries, indicating that use of turbidity as a control index is insufficient for drinking water security (Hatukai and Ben, 1997). The probability of occurrence of pathogenic protozoa is closely related to the amount of particles ( $> 2 \mu\text{m}$ ) in the product water (Hargesheimer et al., 1998). The number of particles, especially those with a size above 2  $\mu\text{m}$ , is increased by GAC filtration (Wang et al., 2008; Zhu et al., 2009). In addition, microorganisms associated with particles are released from GAC filters and bacteria attached to GAC fines are resistant to disinfection by chlorination (Pierre and Anne, 1997; Uhl and Schaule, 2004; Lin et al., 2006). Therefore, the presence of particles raises concerns regarding the quality of product water.

The chemical or bacteriological properties of particles may influence the treated water quality.

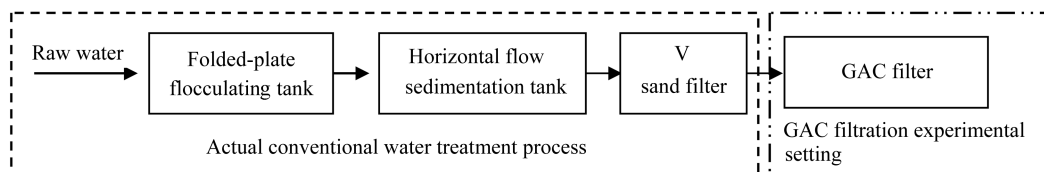
Previous studies focused on the removal of micro-polluted matter and few have reported on the particle properties during GAC water purification (Dussert, 1994; Zhang, 2009). In the present article, the particle size distribution, element composition and bacteria attached to carbon fines were investigated in a pilot-scale experiment.

### 1 Materials and methods

#### 1.1 Sample sites

Water samples were collected from a pilot GAC facility at the water treatment plant in Nanjing, China. Raw water from the Yangtze River was treated by coagulation, sedimentation and sand filtration. A glass column was used for GAC absorption, installed immediately following sand filtration and prior to final chlorination. The experimental schematic is illustrated in Fig. 1. The design parameters of the granular activated carbon absorber are given in Table 1. The backwashing procedure, as shown in Table 1, was designed as follows: an initial air-water backwash step, followed by a water wash. The physicochemical index of adopted coal GAC is listed in Table 2.

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**Fig. 1** Experimental schematic of the granular activated carbon (GAC) facility.

**Table 1** Design parameters for the granular activated carbon filtration column

Parameter	Value
EBCT (min)	20
Diameter (mm)	200
Depth (mm)	1100
<b>Air-water backwashing</b>	
Air backwashing rate (L/(m <sup>2</sup> ·sec))	10
Water backwashing rate (L/(m <sup>2</sup> ·sec))	3
Time (min)	3
<b>Single water backwashing</b>	
Rate (L/(m <sup>2</sup> ·sec))	4
Time (min)	6

EBCT: empty bed contact time.

**Table 2** Main physicochemical average index of GAC

Size (mm)	Weight (%)	Rigidity (%)	Specific area (m <sup>2</sup> /g)	Iodine sorption value (mg/g)
< 1.5	0.4	≥ 90	950–995	910–1020
1.5–2.75	99.4			
> 2.75	0.4			

## 1.2 Experimental methods

### 1.2.1 Particle characteristics

Water samples were collected from GAC effluent to evaluate the number and size distribution of particles. Three parallel samples, each with a volume of 50 mL, were measured by the particle calculating instrument (WHB1-IBR-B1, Interbasic Resources, USA). The instrument was selected to measure particles in the size range from 2 to 200 μm and numbering from 1 to 18,000 count number total (CNT)/mL. The GAC surface functional group was determined by Fourier Transform Infrared Spectroscopy (FT-IR, AVATAR330, Thermo Nicolet Corp., USA) and acid-base titrations. Specific surface area and the porous structure were determined using a surface area and pore size analyzer (ASAP 2020, Micromeritics, USA).

### 1.2.2 SEM/EDS examinations

One liter of water sample was filtered through a 0.45-μm membrane filter (Millipore) to trap particles in the filtered water. The filter membrane, together with trapped particles, was then dried under naturally aseptis condition (25±1)°C. The semi-quantitative elemental compositions of trapped particles were determined with scanning electron microscope (JSM-5610LV, JEOL Ltd., Japan) coupled with an energy dispersive spectroscope (NORAN System Six, Thermo Electron, USA). All membrane samples were previously metalized with gold and a selected section with a surface area of about 1 cm<sup>2</sup> was examined by SEM/EDS. All measurements were made with a 20-kV accelerating

voltage and a micrometer-sized electron beam randomly scanned over the surface of the selected section. Fifty spot measurements were carried out to avoid problems with the random presence of particles (Mavrocordatos et al., 2004; Kaegi et al., 2008). The sample element contents were then recorded from the experimental results of these spot measurements. For accuracy of analysis, each sample was measured in triplicates and the examinations were carried out six times during a 6-day interval. Therefore, a total of eighteen samples were measured to attain nine hundred valid data points, fifty points from each sample. The probability of a single element was attained by statistic analysis of variance. The elemental composition of the particles was analyzed by the molar ratio of carbon and oxygen to all metallic elements (Oberdorster, 2001; Inoue et al., 2004).

### 1.2.3 Bacteria attached to activated carbon fines

Separate autoclaving gauze filter was used to trap activated carbon fines from the GAC effluent, which was prepared by previously described methods (Camper et al., 1986). Ten liter of water was filtered through the gauze filter and each sample was measured in triplicates. The filter was then aseptically cut in half and placed in a vessel containing 300 mL of cold, sterile, reagent-grade water (Milli-Q system; Millipore Corp., USA). Each vessel was vigorously hand shaken to dislodge particles from the filter. The gauze was removed and the suspended particles were chlorinated with 2.0 mg/L of sodium hypochlorite for 30 min at 4.0°C (pH 6.5 to 7.0) in the dark. This chlorination procedure effectively eliminated bacteria not attached to activated carbon fines. A homogenization technique was used to quantitatively desorb microorganisms from GAC fines, as previously described (Camper et al., 1985). The desorbed bacteria were incubated in an R2A culture medium for 3 days at 25°C. In addition, the morphology of the bacteria was examined with a high resolution scanning electron microscope (JSM-5410LV, JEOL Ltd., Japan). Scanning electron microscopy was carried out in the Laboratory for Electron Microscopy, at the Scientific and Technological Research Equipment Center, Nanjing University, China. The samples were pretreated by fixing with 2.5% glutaraldehyde in a 0.1 mol/L phosphate buffer. Subsequently, the samples were washed and dehydrated in a graded series of ethanol solution (30%, 50%, 70%, 90% and 100%). The samples were dried by the critical point method and coated with platinum.

### 1.2.4 Water quality analysis

The product water quality was determined in five replicate samples. Carbonate (mg/L, calculated as CO<sub>3</sub><sup>2-</sup>)

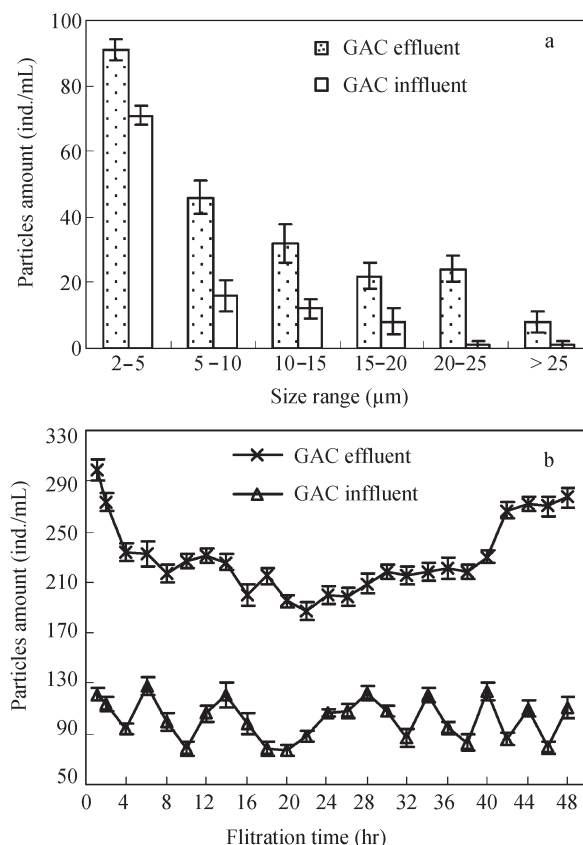
was analyzed by acid-base titration, while sulfate (mg/L, calculated as  $\text{SO}_4^{2-}$ ), chlorite (mg/L, calculated as  $\text{Cl}^-$ ) and nitrate (mg/L, calculated as  $\text{NO}_3^-$ ) were analyzed by ion chromatography (DX-500, Dionex, USA, ED 50 electrochemical detector, suitable analytical columns of dimensions 4 mm  $\times$  250 mm and an Anion Suppressor-ULTRA of length 4 mm). ICP-OES (ICPS-Optima 2100 DV, PerkinElmer, USA) was used for determining the concentration of metal elements, including potassium, calcium, aluminum and silicon. Total carbon (TC) concentration was measured using a total carbon analyzer (Ionics Sievers 800, Boulder Crop., USA). The dissolved organic matter (DOM) in product water was isolated using XAD-8 and XAD-4 resins (Supelco Bellefonte, USA). The water samples were passed through the XAD-8/XAD-4 resin columns, containing approximately 2 L of resin slurry, at a rate of two bed volumes per hour (4 L/hr). Natural organic matter was separated into fractions: hydrophilic substances (HIS), hydrophobic neutrals (HON) and hydrophobic substances (HOM). Trihalomethane formation potential (THMFP) measurements were performed using standard method 5710B (APHA, 1987). All samples were adjusted to a pH of  $7.0 \pm 0.2$ , buffered with a phosphate solution, and chlorinated with an adequate excess amount of concentrated sodium hypochlorite. The residue concentration of free chlorine was controlled at about 3–5 mg/L at the end of the reaction period (requiring 7 days at  $(25 \pm 2)^\circ\text{C}$ ). At the end of this reaction period, the residual chlorine was immediately quenched with  $\text{Na}_2\text{SO}_3$  and the determination of trihalomethanes (THMs) was conducted immediately.

## 2 Results and discussion

### 2.1 Change of particles in filter cycle

As shown in Fig. 2, the amount of particles ( $> 2 \mu\text{m}$ ) in GAC effluent was more than that in GAC influent from the sand filter product water. The effluent particles reached a level of 223 ind./mL, with significant increases in the size range from 5 to 25  $\mu\text{m}$  (Fig. 2a). In addition, the experimental results in Fig. 2b showed that there was low correlation between the influent and the effluent particles during GAC filtration, with  $R$  value being only 0.22.

The increase in effluent particles was a result of the accumulation of biotic and abiotic substances in the GAC filter (Lin et al., 2006). The variety of particles is determined by the interaction of capture and deviation on the GAC surface. Most influent particles are first caught and even attached to the GAC surface by adsorption on functional groups. The porous surface of carbon provides particles with a positive protection for accumulation on the GAC surface and even with in the pores. Subsequently, the deposited particles will form new granular substances by mutual combination with organic compounds, bacteria and ectoenzymes (Schorer and Eisele, 1997). During this process, small sized particles ( $< 2 \mu\text{m}$ ) can aggregate to larger particles ( $> 2 \mu\text{m}$ ), which enriches the presence of elements and ingredients. The retention of particles on the



**Fig. 2** Varieties in size distribution (a) and number (b) of particles ( $> 2 \mu\text{m}$ ) during GAC filtration.

GAC surface depends mainly on Van De Waal's forces and the affinity for chemical bonding (Chen et al., 2007). The particle size gradually enlarges on the GAC surface to form rather diffuse structures, especially in the external layer of the particles. The exterior portion of particles is then easily sloughed or sheared off the intact particles to create further small granular individuals. This different behavior of slough individuals causes an increase in the number of particles ( $> 2 \mu\text{m}$ ) of the effluent during GAC filtration. In addition, it indicates that effluent particles are discharged along with product water, which is mutually determined by the formation on and release of particles from the GAC surface. The particle amount in the effluent was independent of that in the influent.

### 2.2 Elemental composition of particles

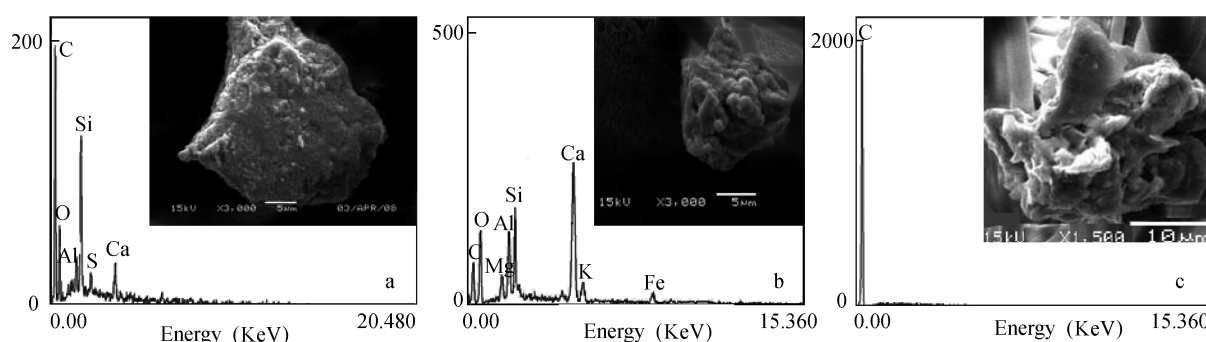
The elemental compositions of particles were investigated by energy spectrum determination and statistic analysis of variance. The experimental results are shown in Table 3 and Fig. 3. The elements in the particles were mainly composed of calcium, iron, aluminum, silicon, carbon and oxygen. The proportion of metallic element in the effluent particle, accounting for 55%, was more than that of the influent (about 27%). As shown in Fig. 3, the effluent particle had more porous and loose surface structure compared with influent particle.

The experimental results indicated that there was selectivity for element removal by adsorption and biodegradation in the GAC filter. The variety mechanism of a typical

**Table 3** Energy spectrum analysis of elements in particles during GAC filtration

Element	Frequency of influent particle (%)				Frequency of effluent particle (%)			
	< 3 $\mu\text{m}$	3–10 $\mu\text{m}$	$\geq 10 \mu\text{m}$	Sum	< 3 $\mu\text{m}$	3–10 $\mu\text{m}$	$\geq 10 \mu\text{m}$	Sum
Si	$4.1 \pm 0.2$	$6.6 \pm 0.7$	$10.4 \pm 1.1$	$21.0 \pm 1.2$	$4.3 \pm 0.3$	$3.3 \pm 0.1$	$2.2 \pm 0.1$	$9.8 \pm 0.4$
C	$11.5 \pm 0.9$	$8.4 \pm 0.5$	$5.9 \pm 0.6$	$25.8 \pm 1.3$	$7.7 \pm 0.3$	$6.1 \pm 0.2$	$3.5 \pm 0.2$	$17.3 \pm 1.2$
O	$9.4 \pm 0.7$	$8.1 \pm 0.8$	$7.3 \pm 0.7$	$24.8 \pm 0.9$	$6.5 \pm 0.4$	$6.7 \pm 0.2$	$2.7 \pm 0.1$	$15.8 \pm 1.3$
S	$0.3 \pm 0.04$	$0.2 \pm 0.03$	$0.2 \pm 0.01$	$0.7 \pm 0.1$	$0.2 \pm 0.01$	$0.2 \pm 0.02$	$0.5 \pm 0.02$	$0.9 \pm 0.1$
Cl	$0.4 \pm 0.07$	$0.1 \pm 0.03$	$0.1 \pm 0.02$	$0.6 \pm 0.06$	$0.3 \pm 0.01$	$0.4 \pm 0.01$	$0.2 \pm 0.01$	$0.8 \pm 0.1$
Ca	$1.9 \pm 0.2$	$1.8 \pm 0.1$	$1.1 \pm 0.1$	$4.8 \pm 0.1$	$3.3 \pm 0.1$	$5.5 \pm 0.3$	$6.5 \pm 0.3$	$15.3 \pm 1.2$
Fe	$0.4 \pm 0.05$	$0.1 \pm 0.01$	$1.0 \pm 0.2$	$1.6 \pm 0.2$	$4.3 \pm 0.1$	$6.2 \pm 0.5$	$8.0 \pm 0.4$	$18.4 \pm 1.5$
Al	$4.2 \pm 0.09$	$5.1 \pm 0.6$	$5.0 \pm 0.3$	$14.4 \pm 0.4$	$6.1 \pm 0.3$	$4.3 \pm 0.1$	$5.8 \pm 0.6$	$16.1 \pm 1.4$
Mg	$0.3 \pm 0.05$	$0.1 \pm 0.03$	$0.7 \pm 0.2$	$1.2 \pm 0.1$	$0.3 \pm 0.01$	$0.2 \pm 0.03$	$0.2 \pm 0.01$	$0.7 \pm 0.08$
K	$0.2 \pm 0.04$	$0.5 \pm 0.02$	$1.3 \pm 0.1$	$2.0 \pm 0.2$	$0.3 \pm 0.01$	$0.1 \pm 0.01$	$0.4 \pm 0.02$	$0.9 \pm 0.1$
Others	$0.7 \pm 0.03$	$2.2 \pm 0.1$	$0.3 \pm 0.02$	$3.2 \pm 0.2$	$0.2 \pm 0.01$	$0.4 \pm 0.02$	$3.4 \pm 0.1$	$4.0 \pm 0.2$
Total	33.4	33.3	33.3	100	33.4	33.3	33.3	100

Data are expressed as mean  $\pm$  SD,  $n = 18$ .

**Fig. 3** Typical energy spectra of influent particle (a), effluent particle (b), and sole carbon fine (c).

element is explained as follows (Flores and Cabassud, 1999; Inoue et al., 2004; Yean et al., 2005): silicon as an important nonmetallic element exists in natural water environments and is also released from quartz media during sand filtration; the crystal lattice substitute occurs during particle formation on the GAC surface, in which the silicon element is replaced by metallic elements such as calcium, aluminum and iron; for other nonmetallic elements, such as carbon and oxygen, the adsorption and biodegradation for organic substance happens in the particle, which decreases the elemental proportion of carbon and oxygen. The metallic elements, including aluminum and iron, can couple or coordinate with organic functional groups of carbon to enhance the proportion of metallic elements. The accumulation of metallic elements and the removal of nonmetallics is gradually reinforced during particle formation as the size increasing. The variety of substances is reflected by the elemental compositions of slough particles from GAC effluent. The metallic elements are obviously increased in particles with size above 3  $\mu\text{m}$ , which indicates the possibility of heavy metal poisoning occurring in the larger particles. Therefore, it is feasible

to decrease the potential danger from metallic compounds by controlling the amount of particles present with sizes above 3  $\mu\text{m}$  in GAC product water.

The varieties of anion and metal elements in product water were investigated to further confirm the above analysis of particle element composition. As shown in Table 4, the concentration of anion, such as  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ , was increased in GAC effluent compared with GAC influent. But there was the decreasing tendency for metal elements, such as Si, Ca, Al and K in GAC effluent.

The increasing concentration of anions is the result of biodegradation of organic substances during GAC purification. The influent substances can be caught by the GAC surface due to the adsorption on carbon surface functional groups. Subsequently, the biodegradation of organic substances is performed by the abundant microorganisms colonizing the GAC particles. During this work, the variety of influent substances was analyzed as follows: The organic carbon is turned by heterotrophic bacteria into inorganic carbon, including carbonate and carbon dioxide. Sulfate radical concentration is increased due to the conversion of sulfide to sulfate by Thiobacteria biodegradation.

**Table 4** Analysis of water quality variety during GAC filtration

	Metal element (mg/L)				Anions (mg/L)				TC (mg/L)	
	Si	Ca	Al	K	$\text{NO}_3^-$	$\text{CO}_3^{2-}$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	TOC	IC
Influent	$0.6 \pm 0.1$	$62.7 \pm 1.2$	$0.08 \pm 0.02$	$2.5 \pm 0.1$	$9.5 \pm 0.6$	$124.2 \pm 3.2$	$38.3 \pm 1.2$	$18.2 \pm 0.7$	$1.9 \pm 0.3$	$23.3 \pm 0.9$
Effluent	$0.4 \pm 0.1$	$53.6 \pm 1.2$	$0.05 \pm 0.01$	$2.6 \pm 0.2$	$11.3 \pm 1.3$	$137.3 \pm 2.1$	$46.1 \pm 1.7$	$17.9 \pm 1.1$	$1.6 \pm 0.2$	$29.3 \pm 1.2$

TC: total carbon, TOC: total organic carbon, IC: inorganic carbon, TC = TOC + IC.

Data are expressed as mean  $\pm$  SD,  $n = 5$ .

The present Nitrobacteria and Nitrosobacteria achieve the conversion of organic nitrogen and ammonia to nitrate. Adsorption on carbon surface functional groups is predominant for the removal of metallic elements during GAC purification. Subsequently, the biodegradation and ion chemical reaction can convert the absorbed metallic elements into a complex compound, which mainly exists as an absorptive particle on the GAC surface. Therefore, there is a tendency for a decrease in the levels of metal elements in GAC product water.

### 2.3 Analysis of elemental composition mode in particles

The molar ratio of elemental composition, i.e., carbon plus oxygen to total metallic elements, was calculated in terms of the energy spectrum determination. As shown in Table 5, there was a broad ratio, ranging from 1 to 40. The particles, with a molar ratio less than 10, accounted about 58% and 41% in the influent and effluent streams, respectively. The low molar ratio value mainly occurred in particles with sizes less than 10  $\mu\text{m}$ . Compared with influent particles, the proportion of molar ratio beyond 15 was increased in the effluent.

The low molar ratio value indicates that the particle is possibly composed of inorganic carbon oxide, such as carbonate, bicarbonate and metal complexes (Okada and

Kai, 2004). At a high molar ratio, the particle is prone to involve organic substances besides inorganic carbon oxide. The accumulation of influent substances on the GAC surface results in a formation of large particles, which easily includes a combination of inorganic and organic matter. Therefore, a high molar ratio occurs readily in larger particle sizes. Smaller sized particles have relatively simple components and possibly even have the same composition as inorganic individuals. The biodegradation of organic substances results in an increase in inorganic ingredients in the total carbon, which is reflected by the predominant proportion of a molar ratio less than 10.

### 2.4 Property of attached carbon to particles

The properties of particles which are attached to carbon and dissolved carbon in product water were investigated. The experimental results are shown in Tables 6 and 7. Inorganic carbon accounted for more than 60% of the total carbon attached to particles. The TOC content and the THMFP value were increased in the large particle, especially with sizes above 10  $\mu\text{m}$ . Compared with attached organic carbon, dissolved organic carbon had a higher THM content. However, for THMFP, the values for dissolved and attached organic carbon were similar.

Hydrophobic organic substances (HOM) can be easily

**Table 5** Element mole ratio of carbon and oxygen to the sum of metallic element

Ratio	Frequency of influent particle (%)				Frequency of effluent particle (%)			
	< 3 $\mu\text{m}$	3–10 $\mu\text{m}$	$\geq 10 \mu\text{m}$	Sum	< 3 $\mu\text{m}$	3–10 $\mu\text{m}$	$\geq 10 \mu\text{m}$	Sum
1–4	7.3 $\pm$ 1.0	6.7 $\pm$ 1.1	6.9 $\pm$ 0.9	20.9 $\pm$ 1.6	5.4 $\pm$ 0.3	4.4 $\pm$ 0.2	3.7 $\pm$ 0.1	13.5 $\pm$ 0.7
5–10	14.3 $\pm$ 1.2	12.4 $\pm$ 1.3	10.5 $\pm$ 1.2	37.2 $\pm$ 1.7	13.6 $\pm$ 1.2	9.2 $\pm$ 0.1	5.1 $\pm$ 0.2	27.9 $\pm$ 1.3
11–15	3.0 $\pm$ 0.5	3.5 $\pm$ 0.9	3.3 $\pm$ 0.4	9.9 $\pm$ 1.1	2.1 $\pm$ 0.1	2.7 $\pm$ 0.1	4.7 $\pm$ 0.1	9.5 $\pm$ 0.4
16–20	2.2 $\pm$ 0.3	2.3 $\pm$ 0.4	1.4 $\pm$ 0.3	5.9 $\pm$ 0.6	1.8 $\pm$ 0.1	2.7 $\pm$ 0.2	3.4 $\pm$ 0.1	7.9 $\pm$ 0.3
21–25	1.9 $\pm$ 0.2	2.9 $\pm$ 0.3	2.8 $\pm$ 0.2	7.5 $\pm$ 0.7	3.4 $\pm$ 0.3	4.5 $\pm$ 0.1	5.2 $\pm$ 0.04	13.0 $\pm$ 0.4
26–30	1.6 $\pm$ 0.1	2.5 $\pm$ 0.2	2.5 $\pm$ 0.3	6.6 $\pm$ 0.2	2.6 $\pm$ 0.1	4.0 $\pm$ 0.2	6.1 $\pm$ 0.4	12.7 $\pm$ 0.5
31–35	1.3 $\pm$ 0.1	1.8 $\pm$ 0.1	2.8 $\pm$ 0.2	5.9 $\pm$ 0.3	1.8 $\pm$ 0.2	2.7 $\pm$ 0.1	2.7 $\pm$ 0.2	7.2 $\pm$ 0.2
36–40	1.8 $\pm$ 0.1	1.0 $\pm$ 0.1	2.8 $\pm$ 0.4	5.5 $\pm$ 0.2	2.3 $\pm$ 0.2	2.4 $\pm$ 0.03	2.0 $\pm$ 0.1	6.7 $\pm$ 0.1
> 40	–	0.2 $\pm$ 0.04	0.3 $\pm$ 0.03	0.5 $\pm$ 0.1	0.5 $\pm$ 0.03	0.7 $\pm$ 0.04	0.4 $\pm$ 0.01	1.6 $\pm$ 0.1
Total (%)	33.4	33.3	33	100	33.4	33.3	33	100

Data are expressed as mean  $\pm$  SD,  $n = 18$ .

**Table 6** Attached carbon content and the formation capacity of THMs

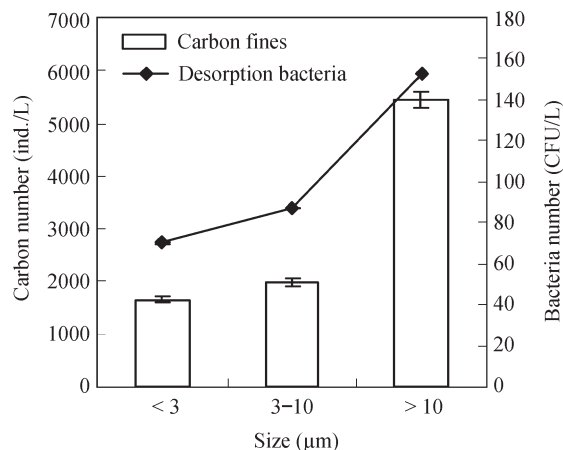
	Influent particle				Effluent particle			
	< 3 $\mu\text{m}$	3–10 $\mu\text{m}$	$\geq 10 \mu\text{m}$	Sum	< 3 $\mu\text{m}$	3–10 $\mu\text{m}$	$\geq 10 \mu\text{m}$	Sum
TC (mg/L)	0.20 $\pm$ 0.02	0.20 $\pm$ 0.04	0.18 $\pm$ 0.02	0.58 $\pm$ 0.04	0.35 $\pm$ 0.02	0.32 $\pm$ 0.01	0.36 $\pm$ 0.02	1.03 $\pm$ 0.07
IC (mg/L)	0.17 $\pm$ 0.03	0.13 $\pm$ 0.01	0.08 $\pm$ 0.02	0.38 $\pm$ 0.03	0.28 $\pm$ 0.02	0.19 $\pm$ 0.02	0.16 $\pm$ 0.01	0.63 $\pm$ 0.04
TOC (mg/L)	0.03 $\pm$ 0.005	0.07 $\pm$ 0.01	0.10 $\pm$ 0.01	0.20 $\pm$ 0.03	0.07 $\pm$ 0.003	0.13 $\pm$ 0.001	0.20 $\pm$ 0.02	0.40 $\pm$ 0.03
THMs ( $\mu\text{g/L}$ )	0.70 $\pm$ 0.10	1.81 $\pm$ 0.42	3.97 $\pm$ 0.72	6.48 $\pm$ 0.40	1.23 $\pm$ 0.31	3.01 $\pm$ 0.44	5.20 $\pm$ 0.52	9.44 $\pm$ 0.52
THMFP	23.3 $\pm$ 1.31	25.8 $\pm$ 1.52	39.7 $\pm$ 0.91	32.4 $\pm$ 1.14	17.6 $\pm$ 1.13	23.2 $\pm$ 0.93	26.0 $\pm$ 1.12	23.6 $\pm$ 1.31

Data are expressed as mean  $\pm$  SD,  $n = 5$ .

**Table 7** Content of dissolved carbon including hydrophobic organic substances (HOM), hydrophilic substances (HIS) and neutral organic substances (HON), and the formation capacity of THMs

	Influent			Effluent		
	Content (mg/L)	THMs ( $\mu\text{g/L}$ )	THMFP	Content (mg/L)	THMs ( $\mu\text{g/L}$ )	THMFP
HIS	1.2 $\pm$ 0.3	73.3 $\pm$ 0.4	61.1 $\pm$ 0.7	0.8 $\pm$ 0.2	43.1 $\pm$ 0.4	53.7 $\pm$ 0.8
HON	0.4 $\pm$ 0.05	8.4 $\pm$ 0.5	21.0 $\pm$ 0.4	0.7 $\pm$ 0.1	12.2 $\pm$ 0.4	17.1 $\pm$ 0.2
HOM	0.3 $\pm$ 0.04	8.3 $\pm$ 0.1	27.6 $\pm$ 0.5	0.1 $\pm$ 0.03	3.2 $\pm$ 0.4	30.0 $\pm$ 0.5
Sum	1.9	89.0 $\pm$ 0.5	46.6 $\pm$ 1.3	1.6 $\pm$ 0.2	58.5 $\pm$ 0.4	34.7 $\pm$ 0.7

Data are expressed as mean  $\pm$  SD,  $n = 5$ .



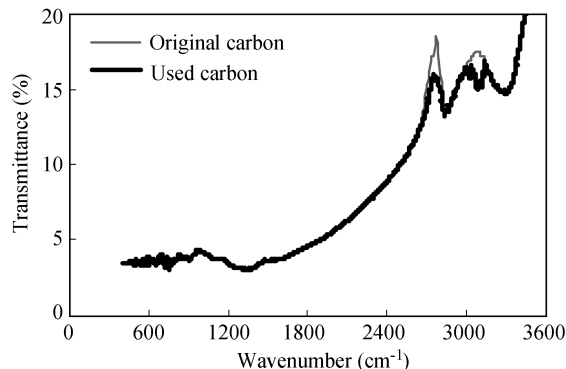
**Fig. 4** Size distribution and number change of desorption bacteria attached to carbon fines.

attached by the basic functional groups on hydrophobic carbon surfaces, and HIS of low molecular weight can be easily biodegraded by the microorganisms colonizing GAC (Guo, 2007). In addition, some large molecular and HON are excreted by exoenzymes of the microorganisms. The biodegradation for organic substance attached to particles results in an increasing proportion of inorganic carbon. The THMs of product water was mainly contributed by HIS, whereas that in effluent particles may be caused by attached HOM and metabolic HON (Edzwald, 1993). There is a worth regarding THMFP value for the attached organic carbon to particle. The number of effluent particles was found to exceed 2000 ind./mL in a spot investigation in various southern China waterworks (He and Xu, 2004; Zhu, 2009). More particles will hold a higher amount of attached organic carbon and thus contribute more to THM products. Therefore, it is necessary to decrease THMs products from attached organic carbon by controlling the GAC effluent particles.

## 2.5 Bacteria attached to activated carbon fines

As shown in Fig. 3c, a pure carbon element energy spectrum was found only in the GAC effluent, which indicates that micro carbon fines sloughing off GAC. The experimental results in Fig. 4 show that carbon fines with size > 10 μm are predominant and the number of carbon fines accounted for less than 5% of the total particles. The physicochemical indexes for varieties of GAC before and after the experiment are shown in Fig. 5 and Table 8. The variety of GAC surface groups by FI-TR (Spectrum 400, PerkinElmer, USA) determination mainly occurred in the characteristic peak with wavenumbers ranging from 2700 to 3100 cm<sup>-1</sup>. The experimental results in Table 8 further confirmed the decrease in acidic groups after carbon was used for water purification.

The accumulation of substances can block pores and cause a drop in the surface area and pore volume of GAC. The adsorption capacity of carbon is decreased by the formation of high boiling compounds from oxidation, decomposition and polymerization reactions. The colonizing bacteria not only biodegrade adsorbed organic matters but decompose the functional groups, especially



**Fig. 5** FI-TR spectra of GAC before and after experiment.

acidic groups with high oxygen content. The biological and chemical actions influence the GAC structure, which results in carbon fines sloughing off GAC by flow shearing force.

The biological security of carbon fines was a serious concern due to the release of bacteria attached to carbon fines with a strong resistance to chlorination disinfection (Pierre and Anne, 1997; Chen et al., 2007). As shown in Fig. 4, the bacteria desorbed from carbon fines, of size above 10 μm, was 10 times higher than that for a carbon size under 3 μm. The SEM images (Fig. 6) show that bacteria were not only attached to the porous surface but were in inner cavities. The large sized carbon fines provide sufficient space for bacterial attachment due to its high surface area, cave-like structures and functional groups. Micro-examination showed that heterotrophic bacillus is the major attached bacterial species, including *Alcaligenes*, *Chromobacterium*, *Pseudomonas* and *Acinetobacter*.

The chlorine disinfection of free and attached bacteria was investigated and the experimental results are shown in Fig. 7 and Table 9. As can be seen, the disinfection rate of free bacteria was more than that of attached bacteria under the same conditions. The large size of carbon fines provided more protection for bacteria against disinfection. Attached bacteria were disinfected with 3 mg/L of chlorine and 30 min of contacting time. The experimental results in Fig. 8 show that residual bacteria on carbon fines increased to 10<sup>2</sup>–10<sup>3</sup> CFU/mL within 24 hours under the culture conditions at 25°C. Extensive bacterial colonization oc-

**Table 8** Varieties in surface area, pore volume and functional groups of GAC before and after experiment

	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Basic group (mmol/g)	Acidic group (mmol/g)
Original carbon	862.06	0.21	0.84	0.45
Used carbon	842.89	0.18	0.81	0.37

**Table 9** Chlorine disinfection rate of attached bacteria with various carbon sizes (%)

Dosage of chlorine	< 3 μm	3–10 μm	≥ 10 μm	Average
1.0 mg/L	47.1 ± 2.2	34.3 ± 1.1	26.3 ± 2.2	35.9 ± 2.1
3.0 mg/L	90.2 ± 2.3	82.4 ± 3.1	63.3 ± 2.3	78.6 ± 3.4

Conditions: pH 7.5; 28°C; contacting time 30 min.

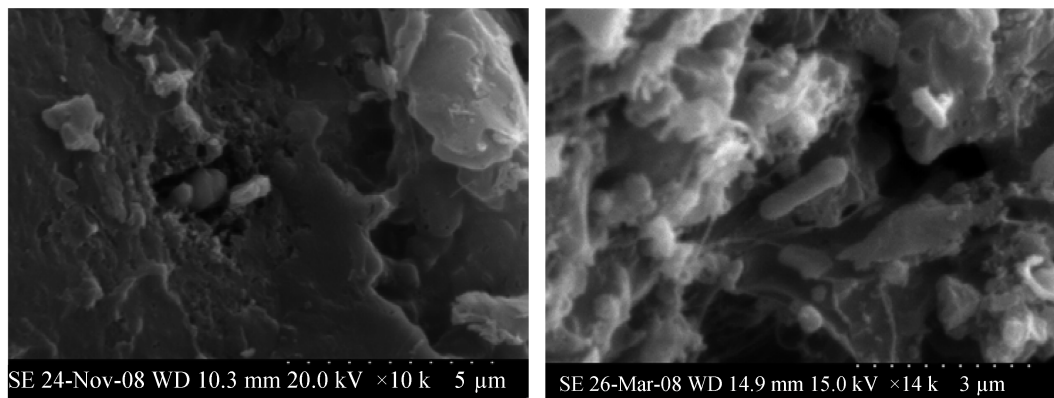


Fig. 6 SEM image of bacteria attached to carbon fines.

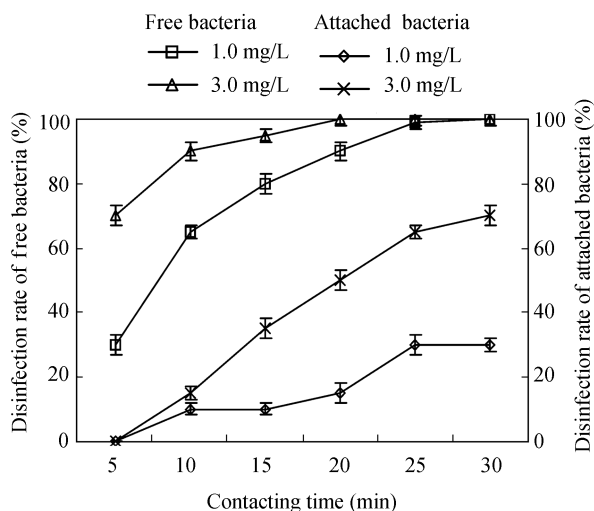


Fig. 7 Disinfection comparison between attached and free bacteria.

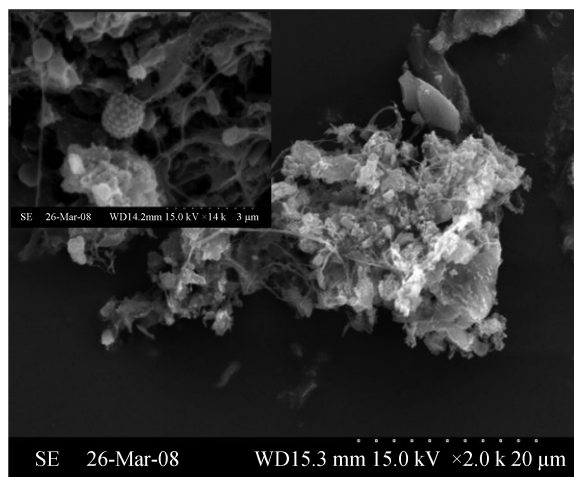


Fig. 8 SEM image of disinfection residual attached bacteria by culturing for 24 hr at 25°C.

curred on carbon fines, including filamentous and spore microorganisms, with strong resistance to disinfection.

The properties of carbon fines provide protection for bacteria against chlorine disinfection. The micron size provides a high specific surface area for bacterial attachment. The larger sized carbon fines can provide more adsorption spots, surface cavities and micron pores for bacterial colonization and resistance to disinfectant. The hydrophobic

surface of carbon hard to the absorption of hydrophilic hypochlorous molecules. The extensive micropores in the carbon structure are unfavorable to the penetration and the diffusion of disinfectant molecules that might inactivate bacteria within the cavities. The reductive characteristic of carbon will react with oxidative disinfectant to decrease the valid dosage for bacterial disinfection. Some studies found that free bacteria in the GAC effluent also had a strong resistance to disinfection (Lechevallier, 1990). The residual bacteria, together with carbon fines, enter the distribution system and cause secondary biotic pollution due to pipe biotic colonization, which is not inactivated with 0.5 mg/L chlorine or 1.0 mg/L chloramines (Pierre and Anne, 1997). Similarly, the residual bacteria was found to increase to  $10^3$ – $10^4$  CFU/mL within 3 days at 20°C (Stewart et al., 1990). The biotic security of attached bacteria is usually resolved by increasing disinfectant dosage, which may result in more disinfection byproducts. Therefore, it is better to decrease the bacteria attached to carbon fines by controlling the amount of particles in the GAC effluent.

### 3 Conclusions

The porous surface of GAC provides a positive environment for new particle formation. The amount of particles in effluent streams is clearly increased by GAC filtration. An increasing proportion of metallic elements occur mainly in large particles ( $> 3 \mu\text{m}$ ) in GAC effluent. The molar ratio value of particle elements has a broad range from 1 to 40, which was enhanced with increasing size. The TOC content and the THMFP value were increased in larger particles, especially those larger than  $10 \mu\text{m}$ . It was useful to consider the potential for the formation of THMs by organic carbon attached to particles. Major carbon fines were bigger than  $10 \mu\text{m}$ . The disinfection rate for free bacteria was higher than that of attached bacteria under the same conditions. Residual attached bacteria could cause secondary biotic pollution.

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