

Submicron-sized activated carbon particles for the rapid removal of chlorinous and earthy-musty compounds

Yoshihiko Matsui, Kenji Murai, Hiroshi Sasaki, Koichi Ohno and Taku Matsushita

ABSTRACT

Submicron-sized powdered activated carbon (PAC) was produced from a commercially available normal PAC by a bead mill. The submicron PAC decomposed dichloramine and nitrogen trichloride, impairing aesthetic quality with chlorinous odor, at a much faster rate than did normal PAC. Moreover, decomposition rates were faster for dichloramine and nitrogen trichloride than for monochloramine and free chlorine. Selective removal of chlorinous odors among chlorine compounds in a short time was thereby possible. The earthy–musty compound geosmin was also much more rapidly removed by adsorption on submicron PAC than on normal PAC. The increased removal rate was partly due to the adsorption capacity increase owing to the particle size reduction of PAC to submicron range, which accounted for 40% of the improvement of geosmin removal at a PAC contact time of 10 min.

Key words | adsorption, drinking water, flavor, particles

Yoshihiko Matsui (corresponding author)
Kenji Murai
Hiroshi Sasaki
Koichi Ohno
Taku Matsushita
Division of Built Environment,
Graduate School of Engineering,
Hokkaido University,
N13W8, Sapporo 060-8628,
Japan
Tel.: & Fax: +81-11-706-7280
E-mail: matsui@eng.hokudai.ac.jp

INTRODUCTION

Adverse tastes and odors at the tap are the leading causes of consumer complaints and dissatisfaction with drinking water. Some of these tastes and odors are caused by chemical agents used for water treatment, such as chlorine (White 1999). Chlorine is sometimes added as a prechlorination agent to decompose ammonia, oxidize iron and manganese, and prevent algal growth in water treatment facilities. However, it often produces dichloramine and nitrogen trichloride, which have much greater chlorinous odors than does free chlorine. Naturally occurring compounds, such as geosmin, also impair aesthetic quality. These compounds are produced by cyanobacteria and add earthy and musty odors to water.

Adsorption by powdered activated carbon (PAC) is regarded as one of the best available technologies for removing dissolved contaminants such as taste-and-odor compounds from raw water in drinking water production. However, the adsorption capacity of PAC is not fully utilized because of slow uptake of adsorbates (slow adsorption kinetics). Although activated carbon

decomposes dichloramine and nitrogen trichloride (Sontheimer *et al.* 1988), its application in removing these compounds has been limited. This could be also due to the slow decomposition kinetics, which previously rendered this use of activated carbon impractical.

Although PAC particles of smaller sizes would overcome the problems of slow adsorption and decomposition kinetics, the particle size of available PAC was previously limited to about 5 μm . However, recent advancements in nanotechnology enable pulverization of particles down to submicron and nanometre size ranges with reasonable costs. Membrane filtration technology should take advantage of the improved adsorption and decomposition capabilities of such fine particles in water and wastewater treatment (Matsui *et al.* 2005, 2006). In this study, we ground manufacturer-supplied PAC in a bead mill to produce submicron-sized PAC particles (less than 1.0 μm median diameter). We investigated the ability of the submicron PAC particles to decompose dichloramine and nitrogen trichloride and to adsorb geosmin.

METHODS

A thermally activated wood-based PAC (Shirasagi, Japan EnviroChemicals, Ltd., Osaka, Japan) was obtained from its manufacturers. Submicron PACs were obtained by grinding this normal PACs in a bead mill. Particle-size distributions of PACs were determined using laser-light-scattering instruments (LMS-30; Seishin Enterprise Co., Ltd., Tokyo, Japan; Microtrac HRA; Nikkiso Co., Ltd., Tokyo, Japan), and nitrogen gas adsorption and mercury intrusion porosimetry were used to measure pore size distributions in the PAC particles (Prosorp VAS-3000, Seishin Enterprise Co., Ltd., Tokyo, Japan; Porosimeter 200; Carlo Erba, Milan, Italy).

Geosmin solution was prepared by diluting geosmin-MeOH liquid (Supelco, Sigma Aldrich Japan, Tokyo, Japan) with water. The solution was diluted to concentrations of 100 ngL^{-1} before use. Batch kinetic tests were conducted with efficient mixing in a stainless steel rectangular container containing 5 L of the solution. After addition of a certain amount of PAC, samples were withdrawn at intervals and filtered immediately through a $0.22\text{-}\mu\text{m}$ membrane filter for concentration analysis. The bottle-point technique was used to determine adsorption isotherms of geosmin. Sample waters (150 ml) containing PAC were transferred to 160-ml vials from 3-L solution and the vials were agitated on a shaker for 1 week. The liquid-phase concentrations were measured by filtering the water samples through a $0.22\text{-}\mu\text{m}$ membrane filter. The amount of geosmin adsorbed per unit mass of PAC (solid-phase concentration) was determined according to the mass balance equation. The concentrations of geosmin were analyzed with TDS- (Thermal Desorption System-) GC/MS and SBSE (Stir Bar Sorptive Extraction) methods (GERSTEL K.K., Tokyo, Japan; Agilent Technologies Japan, Tokyo, Japan).

Chloramine solutions were prepared by the batch aqueous reaction of sodium hypochlorite and ammonium (reagent grade chemicals, Wako Pure Chemical Industries, Ltd., Osaka, Japan) in a 3-L cylindrical glass beaker and then divided into 1-L solutions for activated carbon experiments. Monochloramine, dichloramine, and nitrogen trichloride were each dominantly formed at a different sodium hypochlorite/ammonium concentration ratio ($\text{Cl}_2/\text{NH}_3\text{-N}$ ratio): concentrations of ammonia and

sodium hypochlorite (as chlorine) and reaction temperature are described in “Results and Discussion” and figures. The concentrations of free chlorine, monochloramine, dichloramine, and nitrogen trichloride were separately analyzed by the diethyl-*p*-phenylenediamine method according to *Standard Methods for the Examination of Water and Wastewater* (2005).

RESULTS AND DISCUSSION

PAC particle-size distribution

The size distributions of the PAC particles revealed that the pulverized PAC had an effective particle size of $0.27 \mu\text{m}$ and a median size of $0.77 \mu\text{m}$; 65% by volume of PAC particles were smaller than $1 \mu\text{m}$ (Figure 1).

Removal of chlorinous compounds

Chlorinous odor is caused by free chlorine and notably chloramine. Among chloramine compounds, nitrogen trichloride causes the strongest chlorinous odor, followed by dichloramine and monochloramine. The chloramine compounds were produced by the oxidation reaction of ammonia with hypochlorous acid, and the type of the prevailing chloramine compound formed was determined depending on reaction conditions including Cl_2/NH_3 ratio, pH, and temperature. In the experiment with dichloramine, which causes strong chlorinous odor, dichloramine was

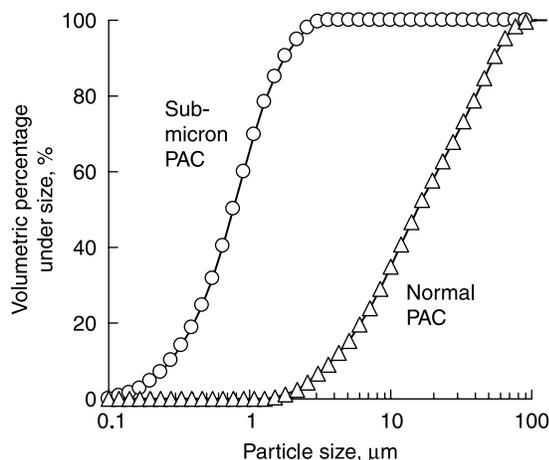


Figure 1 | Size distributions of PAC particles before and after grinding.

formed as the predominant and stable product among chloramines by the reaction condition of $\text{Cl}_2/\text{NH}_3\text{-N}$ ratio of 9.6 at pH 6.7 and 5°C (a small but nonnegligible dichloramine decrease owing to natural decomposition was observed at 20°C , and therefore the dichloramine experiment was conducted at 5°C). After 20 min of the chlorine–ammonia reaction, 5 mg L^{-1} of normal PAC was added to the solution, and the dichloramine concentration decreased gradually over the following 60 min (Figure 2). On the other hand, very fast reduction of dichloramine was observed when 4.9 mg L^{-1} of submicron PAC was added (Figure 3). Even though we used the same dosage of submicron PAC as of normal PAC, the dichloramine concentration dropped by 90% in 10 min and chloramine was not detected 20 min after the PAC addition. Ammonia concentration was $1.0\text{ mg L}^{-1}\text{-N}$ before the chlorine–ammonia reaction, but ammonia was not detected above the detection limit of $0.02\text{ mg L}^{-1}\text{-N}$ when the dichloramine concentration dropped to almost zero after the PAC addition. This result suggests that dichloramine was converted to nitrogen gas and chloride, but not converted back to ammonia (Bauer & Snoeyink 1973). A very small portion of dichloramine could have been converted to free chlorine, as suggested by Figures 3 and 4, which show that free chlorine concentration increased when dichloramine concentration decreased. When dichloramine concentration dropped to zero at 40 min time (Figure 3), free chlorine

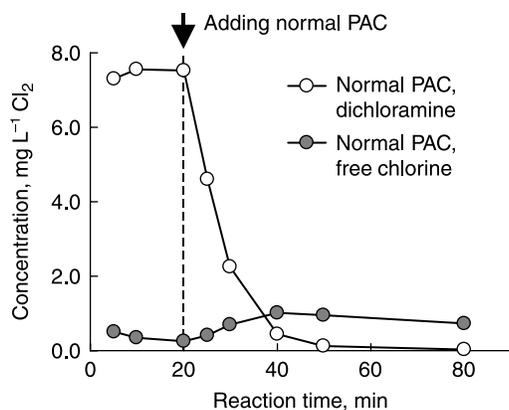


Figure 2 | Dichloramine concentration decay by addition of 5 mg L^{-1} of normal PAC. Dichloramine was formed in the reaction of ammonia (1 mg L^{-1} as N) and sodium hypochlorite (9.6 mg L^{-1} as Cl_2) at 5°C , and the normal PAC was added after 20 minutes of the reaction.

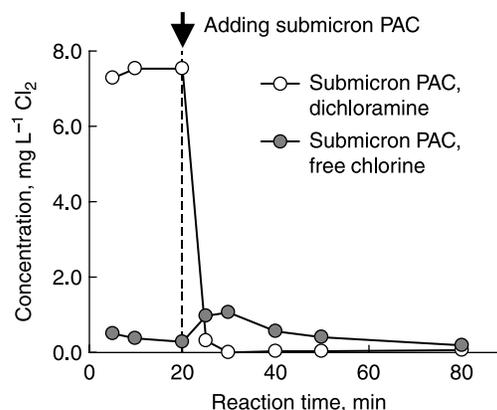


Figure 3 | Dichloramine concentration decay by addition of 4.9 mg L^{-1} of submicron PAC. Dichloramine was formed in the reaction of ammonia (1 mg L^{-1} as N) and sodium hypochlorite (9.6 mg L^{-1} as Cl_2) at 5°C , and the submicron PAC was added after 20 minutes of the reaction.

concentration started to decrease. However, the rate of decrease seems to be slower than that of dichloramine.

Next, monochloramine, which does not strongly impart chlorinous taste and odor, was produced as a dominant chloramine product after liquid sodium hypochlorite was added to ammonia solution (1 mg-N L^{-1}) at a $\text{Cl}_2/\text{NH}_3\text{-N}$ ratio of 5, pH 7, and room temperature (20°C). After 30 min of the reaction, during which the stability of monochloramine concentration was confirmed, submicron PAC was added to the monochloramine solution, but the monochloramine concentration did not change (Figure 4).

Next, we conducted a decomposition experiment of nitrogen trichloride, the most chlorinous-odor-causing

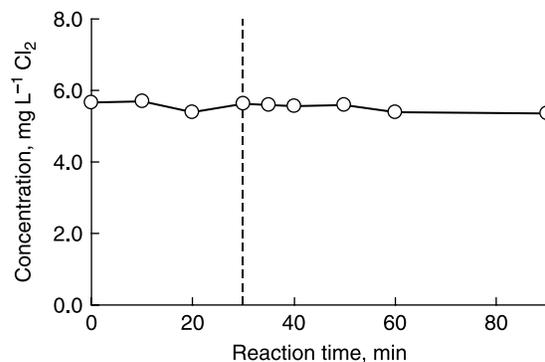


Figure 4 | Change of monochloramine concentration. Submicron PAC was added at 30 min time for a final concentration of 5.1 mg L^{-1} . Monochloramine was formed in the reaction of ammonia (1 mg L^{-1} as N) and sodium hypochlorite (5 mg L^{-1} as Cl_2) at a room temperature (about 20°C), and the submicron PAC was added after 30 minutes of the reaction.

compound. Nitrogen trichloride was formed at a high $\text{Cl}_2/\text{NH}_3\text{-N}$ ratio, but the concentration of nitrogen trichloride at a neutral pH was very low and the concentration was unstable owing to natural decomposition (in practice, nitrogen trichloride causes perceptible chlorinous odor even at such low concentration). Therefore, in the experiment, nitrogen trichloride was formed as a dominant chloramine species with a stable form with reaction conditions of pH 3, 5°C, and a $\text{Cl}_2/\text{NH}_3\text{-N}$ ratio of 12. Nitrogen trichloride was formed at the concentration of 1.44 mg L^{-1} , while free chlorine beyond the stoichiometric quantities of $\text{Cl}_2/\text{NH}_3\text{-N}$ ratio remained at the concentration of 1.14 mg L^{-1} . After the submicron PAC addition, nitrogen trichloride decreased faster than free chlorine (Figure 5). It disappeared by 10 min. Nitrogen trichloride decrease was faster after submicron PAC addition than after normal PAC addition (Figure 6).

Figure 7 shows the concentration decay of free chloramine (hypochlorous acid) at pH 6.7 and pH 3.0; the nitrogen trichloride experiment was conducted at these low pH values. Free chloramine concentration also decreased after the S-PAC addition at a faster rate than after normal PAC addition. However, the concentration did not reach close to zero even after 90 min of contact time both for normal and submicron PACs.

In order to compare the concentration decay rate briefly but quantitatively, we described the decay curves by the first order reaction. Table 1 summarizes the decomposition

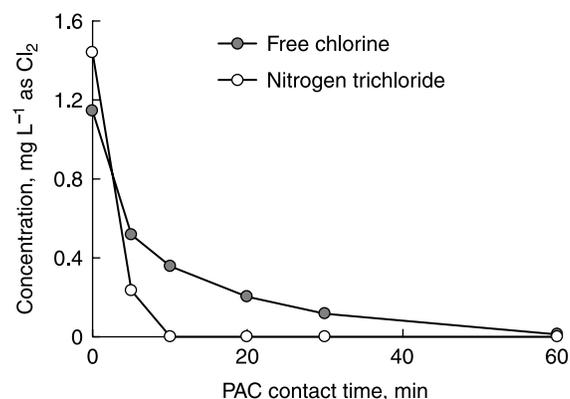


Figure 5 | Concentration changes of free chlorine and nitrogen trichloride after submicron PAC dose (PACs were dosed at zero time). Nitrogen trichloride was formed in the reaction of ammonia (3 mg L^{-1} as N) and sodium hypochlorite (36 mg L^{-1} as Cl_2) at 5°C, and the normal PAC was added after 100 minutes of the reaction (zero time in the x-axis) for a final concentration of 5.0 mg L^{-1} .

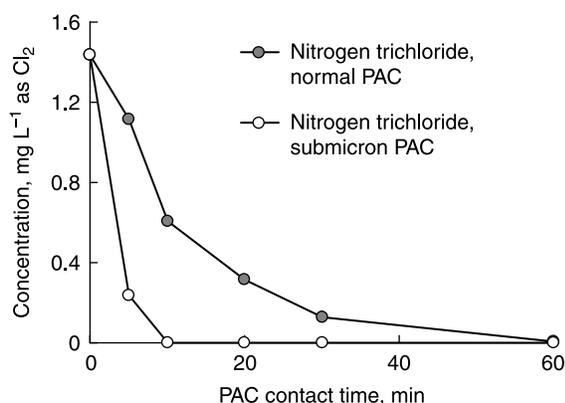
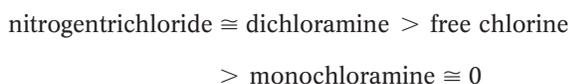


Figure 6 | Concentration change of nitrogen trichloride after PAC dose (PACs were dosed at zero time). Nitrogen trichloride was formed in the reaction of ammonia (3 mg L^{-1} as N) and sodium hypochlorite (36 mg L^{-1} as Cl_2) at 5°C, and the normal and submicron PACs were added after 100 minutes of the reaction (zero time in the x-axis) for final concentrations of 5.2 and 5.0 mg L^{-1} , respectively.

rate constants. For chlorine and chloramines, decay rate constants were in the following order:



This order is similar to one previously reported (dichloramine > hypochlorous acid > hypochlorous ion > monochloramine; Snoeyink & Suidan 1975).

Also, the decomposition rate constants of submicron PAC for dichloramine, monochloramine, and free chlorine is two times greater than those of normal PAC, respectively. For nitrogen trichloride, the decomposition rate constant of

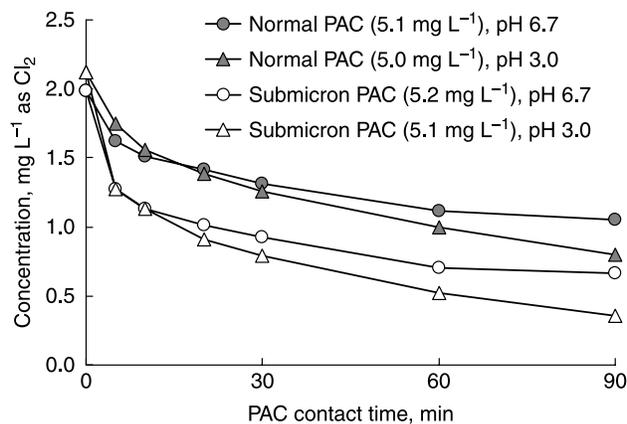


Figure 7 | Concentration change of free chlorine after PAC dose (PACs were dosed at zero time and reaction temperature was 5°C).

Table 1 | Decomposition rate constants

	Normal PAC	Submicron PAC
Nitrogen trichloride, pH 3.0	2.2 h ⁻¹	9.4 h ⁻¹
Dichloramine	2.7 h ⁻¹	5.5 h ⁻¹
Monochloramine	0.0 h ⁻¹	0.0 h ⁻¹
Free chlorine, pH 3.0	0.32 h ⁻¹	0.59 h ⁻¹
Free chlorine, pH 6.7	0.23 h ⁻¹	0.41 h ⁻¹

submicron PAC was almost 4 times greater than that of normal PAC. Finally, submicron PAC can quench chlorinous odor compounds, nitrogen trichloride and dichloramine, selectively among free and combined chlorine, and complete decomposition can be achieved in 10 min contact time with a dosage of only 5 mg L⁻¹.

Removal of earthy-musty compounds

An adsorption kinetic test for geosmin also showed the superiority of submicron PAC particles. The addition of submicron PAC to a geosmin solution decreased the geosmin concentration by more than 95% in 30 min, while normal PAC decreased the concentration by only 20% with the same dosage (Figure 8).

Moreover, an adsorption equilibrium test showed that size reduction of PAC particles by pulverization increased the adsorption capacity of PAC for geosmin. Figure 9 shows

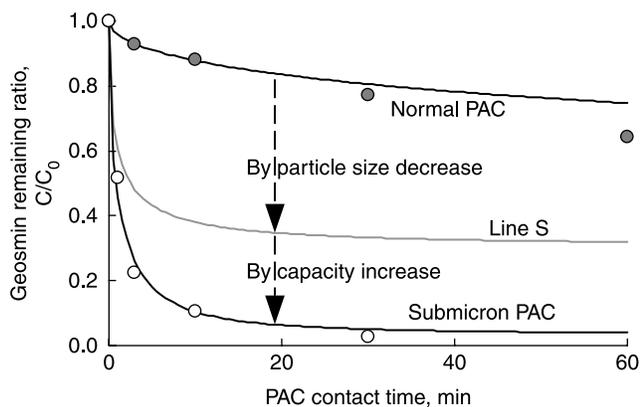


Figure 8 | Effects of particle size on batch adsorption kinetics of geosmin on PAC (initial geosmin concentrations were 104 and 94 ngL⁻¹ for normal and submicron PAC experiments, respectively; PAC dosages were 0.6 mgL⁻¹). Plots are observed data and lines are simulated by the branched pore adsorption model (surface diffusion coefficient = 4.3×10^{-13} cm² s⁻¹, rate coefficient for mass transfer between macropores and micropore = 6.7×10^{-9} s⁻¹, and fraction of adsorptive capacity available in macropore region = 0.46).

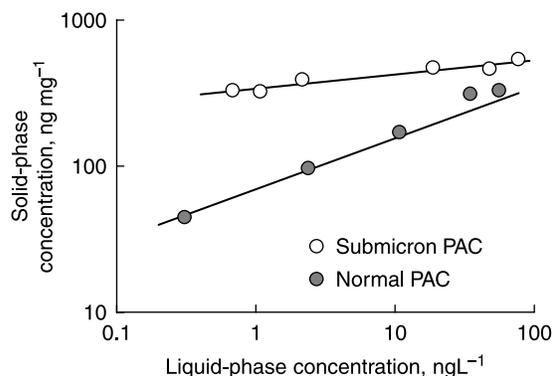


Figure 9 | Effects of particle size on geosmin adsorption isotherm for PAC.

adsorption isotherms of geosmin, in which the adsorption capacity of submicron PAC was higher than that of normal PAC. A similar phenomenon was reported for NOM adsorption on normal and submicron PACs (Matsui *et al.* 2004). Weber *et al.* (1983) reported the particle-size effect of granular activated carbon on NOM adsorption capacity, showing that smaller particles have greater capacity for adsorbing NOM. For low-molecular-weight (-MW) pure chemicals, however, the change of adsorptive capacity owing to carbon particle size has not been reported (Derick & Beckmann 1969; Letterman *et al.* 1974; Peel & Benedek 1980a; Najim *et al.* 1990; Matsui *et al.* 2004). The pore-size distribution data explained the adsorption capacity increase for adsorbates of high MW. The lack of adsorption capacity change for low-MW adsorbates showed that the volume of micro-pores, to which small molecules such as phenol (MW 98) adsorb, was not changed after the PAC pulverization produced submicron PAC, while the meso-pore volume for macro-molecule adsorption did increase (Matsui *et al.* 2004). However, geosmin is rather small molecules with MW 182, and the higher adsorption capacity of submicron PAC for these compounds was not explained by the pore-size distribution data. Although we have not yet determined the reason for the increased adsorption capacity, the experimental data clearly show that geosmin can be removed by submicron PAC at much lower dosages and much shorter PAC–water contact times than by normal PAC.

Besides the effect of the adsorption capacity increase, the particle size reduction of PAC should effectively increase its adsorption kinetics because more outer surface area is exposed to bulk water and because the diffusion pathway

from a particle's surface to its centre decreases in size. Therefore, the improvement of geosmin removal at a given PAC contact time should be due to the two effects caused by PAC particle size reduction: equilibrium and kinetic effects. Adsorption kinetic model analysis was conducted to separately evaluate the equilibrium and kinetic effects. We applied a branched pore adsorption model (Peel & Benedek 1980b), since normal adsorption kinetic models (homogeneous surface diffusion and pore-surface diffusion models) could not describe the adsorption kinetic data. Changing surface diffusivity (or liquid-filled pore diffusivity) was needed, depending on PAC particle size, to describe the adsorption kinetic data of both submicron and normal PACs.

The branched pore model successfully described the kinetic data of both submicron and normal PACs with the same kinetic parameter values; diffusion coefficient and other model parameters did not change with PAC particle size (Figure 7). Upon the successful application of the model, we conducted model simulation to investigate the equilibrium and kinetic effect. Line S in Figure 8 is a simulated result based on the hypothesis that PAC particle size was reduced but adsorption capacity did not increase (the PAC particle size was that of submicron PAC, but the adsorption isotherm parameter values were those of normal PAC). Therefore, the area between the normal PAC line and Line S represents improvement in geosmin removal owing to the adsorption kinetic effect of PAC particle size, whereas the area between Line S and the submicron PAC line represents improvement in geosmin removal owing to the adsorption capacity effect of PAC particle size. The result revealed that the 60% of improvement in removal percentage was due to the kinetic effect by PAC size reduction, while the remaining 40% was due to the increase in adsorption capacity (Figure 8). Therefore, the improved adsorptive removal resulting from the PAC particle size reduction to submicron range was due to increases in both adsorption capacity and kinetics.

CONCLUSIONS

1. Submicron PAC showed a very fast reaction rate in quenching chlorinous odors due to dichloramine and nitrogen trichloride. Dichloramine and nitrogen trichloride

were decomposed, probably to nitrogen gas, in 10 min by submicron PAC at 5 mg L⁻¹ dosage. The rates of decomposition by PAC were in the order of nitrogen trichloride ≅ dichloramine > free chlorine > monochloramine ≅ 0, and selective removal of dichloramine and nitrogen trichloride among free and combined chlorines was possible.

2. Submicron PAC showed a very fast adsorptive removal rate for the earthy-musty compounds geosmin. The improved adsorptive removal owing to PAC particle size reduction to submicron range was due to both kinetic and adsorption capacity increases. The former accounted for 60% and the latter 40% of the improvement, according to the branched pore model analysis.

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