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Mechanisms of trichloramine removal with activated carbon: Stoichiometric analysis with isotopically labeled trichloramine and theoretical analysis with a diffusion-reaction model

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ABSTRACT

This study investigated the mechanism by which activated carbon removes trichloramine, a byproduct of water treatment that has a strongly offensive chlorinous odor. A stoichiometrical mass balance for ^{15}N before and after activated carbon treatment of laboratory-prepared ^{15}N-labeled trichloramine solutions clearly revealed that the mechanism of trichloramine removal with activated carbon was not adsorption but rather reductive decomposition to nitrogen gas. There was a weak positive correlation between the surface decomposition rate constant of trichloramine and the concentration of basic functional groups on the surface of the carbon particles, the suggestion being that the trichloramine may have been reduced by sulfhydryl groups (−SH) on the activated carbon surface. Efficient decomposition of trichloramine was achieved with super powdered activated carbon (SPAC), which was prepared by pulverization of commercially available PAC into very fine particles less than 1 μm in diameter. SPAC could decompose trichloramine selectively, even when trichloramine and free chlorine were present simultaneously in water, the indication being that the strong disinfection capability of residual free chlorine could be retained even after trichloramine was effectively decomposed. The residual ratio of trichloramine after carbon contact increased somewhat at low water temperatures of 1–5 °C. At these low temperatures, biological treatment, the traditional method for control of a major trichloramine precursor (ammonium nitrogen), is inefficient. Even at these low temperatures, SPAC could reduce the trichloramine concentration to an acceptable level. A theoretical analysis with a diffusion-reaction model developed in the present study revealed that the increase in the trichloramine residual with decreasing water temperature was attributable to the temperature dependence of the rate of the reductive reaction rather than to the temperature dependence of the diffusive mass transfer rate.

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Nomenclature

$c_I(t,R)$	liquid phase concentration on the outer surface of an adsorbent particle (μg/L)
$C(t)$	adsorbate concentration in bulk water phase as a function of time, t (μg/L)
Cc	adsorbent concentration in bulk water (g/L)
D_p	pore diffusion coefficient (cm^2/s)
$f(R)$	normalized particle size distribution function of adsorbent (cm^{-1})
k_F	liquid film mass transfer coefficient (cm/s)
k_{NCl3}	surface decomposition rate constant of trichloramine (cm/s)
$c(t,r,R)$	liquid phase concentration in pore of an adsorbent having radius R, at radial distance r, and time t (μg/L)
r	radial distance from the center of an adsorbent particle (cm)
R	adsorbent particle radius (cm)
t	time (s)
ρ	adsorbent particle density (g/L)
ε	porosity of adsorbent (dimensionless)
a_P	surface area of pores per apparent volume of adsorbent (1/cm)

1. Introduction

Handling customers' complaints and dissatisfaction regarding the taste and odor of tap water are important issues that practitioners in drinking water treatment plants sometimes face. Chlorinous odor is the leading cause of dissatisfaction among persons who drink water in regions where chlorination or chloramination is employed for disinfection of drinking water (Piriou et al., 2004). Trichloramine (NCl_3) and dichloramine ($NHCl_2$) are recognized as the compounds that cause the chlorinous odor in tap water; trichloramine causes a much stronger chlorinous odor than dichloramine (Kranser and Barret, 1984). Trichloramine is formed mainly by the reaction between ammonium ions, which are present in raw sources of drinking water, and the chlorine used for disinfection. The removal of ammonium ions before the chlorination process is one strategy for mitigating the problem of trichloramine formation. Water treatment involving slow sand filtration (Štembal et al., 2005) or activated carbon (Andersson et al., 2001) are examples of biological methods used to remove ammonium ions. However, the activity of nitrifying microorganisms is reduced by low water temperatures, and in cold regions or during the winter nitrification becomes small to remove ammonium ions efficiently. To solve the trichloramine formation problem when the water temperature is low, treatment technologies that are independent of biological activity are required.

Treatment with activated carbon is the traditional method used to remove dichloramine and monochloramine (NH_2Cl) in water treatment (Bauer and Snoeyink, 1973; Snoeyink and Suidan, 1975). However, sufficient removal requires a very long contact time with the carbon. For example, almost 2 d (45 h) is required to remove dichloramine by using powdered activated carbon (PAC) with diameters of 149–177 μm (Bauer and Snoeyink, 1973; Snoeyink and Suidan, 1975). Therefore, although PAC treatment is a simple process, its slow removal rate detracts from its application as a technology for drinking water treatment. Decreasing the size of the activated carbon particles generally enhances the removal rate achieved with activated carbon, because size reduction increases the specific surface area (surface area per unit weight of activated carbon). However, the technology of pulverizing activated carbon particles has typically produced particles no smaller than 5 μm in diameter (Matsui et al., 2008). Recently, our research group developed a way to produce super fine activated carbon particles (SPAC) with diameters less than 1 μm by pulverizing conventionally sized PAC. We have reported highly improved adsorptive uptake rates of natural organic matter (NOM) (Matsui et al., 2005) and of compounds that produce earthy-musty odors (Matsui et al., 2007, 2009). We hypothesized that treatment with SPAC may also be an effective way to remove trichloramine efficiently. A preliminarily study conducted by our research group actually found that SPAC was superior to PAC for removal of trichloramine and dichloramine (Matsui et al., 2008). However, sufficient studies have not been conducted on the effects of water temperature and SPAC characteristics on trichloramine and dichloramine removal.

In general, an important characteristic of activated carbon is its high adsorption affinity and high capacity to adsorb various target compounds to be removed from raw drinking water sources. Activated carbon has therefore been widely used in drinking water treatment plants for a long time to reduce contaminant levels of NOM (Çapar and Yetiş, 2002), earthy-musty odor compounds (Herzing et al., 1977), and pesticides (Robeck et al., 1965). In contrast to the adsorptive removal of these compounds, the removal of dichloramine and monochloramine by activated carbon has been reported to be due to reductive decomposition of these compounds on the surface of the carbon (Bauer and Snoeyink, 1973; Snoeyink and Suidan, 1975). It has been speculated that dichloramine reacts with functional groups located on the internal surfaces of activated carbon particles and is then reduced to nitrogen gas (Bauer and Snoeyink, 1973; Snoeyink and Suidan, 1975). However, no direct evidence for the reductive decomposition of dichloramine has been presented so far. The mechanism of trichloramine removal by activated carbon is also unclear.

The objectives of this study were 1) to provide direct evidence of the trichloramine removal mechanism involving reductive decomposition of trichloramine to nitrogen gas by activated carbon and 2) to model the effect of water temperature on trichloramine removal. The removal mechanism was investigated by 1) comparing the masses of ^{15}N before and after treatment of laboratory-prepared, ^{15}N-labeled trichloramine solutions, 2) comparing the trichloramine removal performances of activated carbon substrates with various surface characteristics, and 3) modeling the process of trichloramine removal at different temperatures in a diffusion-reaction system. Simulating the effect of water temperature enabled us to judge whether SPAC treatment could be a practical way to control chlorinous odors at low water temperatures.