

Comparative study on the removal technologies of 2-methylisoborneol (MIB) in drinking water

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Abstract: Removal of 2-methylisoborneol (MIB) in drinking water by ozone, powdered activated carbon (PAC), potassium permanganate and potassium ferrate was investigated. The adsorption kinetics of MIB by both wood-based and coat-based PACs show that main removal of MIB occurs within contact time of 1 h. Compared with the wood-based PAC, the coat-based PAC evidently improved the removal efficiency of MIB. The removal percentage of trace MIB at any given time for a particular carbon dosage was irrelative to the initial concentration of MIB. A series of experiments were performed to determine the effect of pH on the ozonation of MIB. The results show that pH has a significant effect on the ozonation of MIB. It is conclusive that potassium permanganate and potassium ferrate are ineffective in removing the MIB in drinking water.

Keywords: odor; MIB; ozonation; powdered activated carbon; potassium permanganate; potassium ferrate

Introduction

Removing taste and odor compounds from drinking water is a significant challenge for water authorities worldwide. 2-Methylisoborneol(MIB) is an important earthy-musty odorant in drinking water. The odor threshold of MIB is as low as a few ng/L (Pirbazari *et al.*, 1993). The conventional water treatment process (coagulation, chlorination and sand filtration) is not effective to remove MIB (Anselme *et al.*, 1988). The removal of MIB by powdered activated carbon (PAC) and ozone is applied in some water plants (Lin *et al.*, 2002; Cook *et al.*, 2001; Nerenberg *et al.*, 2000). PAC has the flexibility to be applied as needed, but it causes sludge removal and disposal problem, the odor problem caused by MIB cannot be fully resolved by PAC(Ferreira *et al.*, 2003). The concern of disinfection by-products (DBPs) has prompted water plants to consider the use of ozone as alternative disinfectant. The autodecomposition of ozone results in the formation of OH radical. MIB is considered to be susceptible to the attack by OH radical (Suffet *et al.*, 1995). Hence, ozonation will be one of promising processes for the removal of MIB in drinking water, the study of interaction mechanism is of importance.

Drinking water quality in Xicun Water Plant, Guangzhou, has received complaints from customers for a long time for its unpleasant odors, however, no evaluation of odor removal efficiency for possibly applied processes was conducted. MIB with a concentration up to 40 ng/L in raw water was found in Xicun Water Plant. In this study, four kind of removal

technologies of MIB, including PAC adsorption, ozonation, potassium permanganate (KMnO₄) oxidation and potassium ferrate (K₂FeO₄) oxidation, were investigated.

1 Materials and methods

1.1 Reagents and materials

MIB was purchased from Sigma-Aldrich Co., USA, and MIB stock solution of 1 mg/L was obtained by diluting the MIB solution with pure water. PAC A and PAC B (Shanghai Activated Carbon Company, China) were wood-based and coat-based powdered activated carbon, respectively. Potassium indigo trisulfonate employed for determining the aqueous ozone concentration (C_{O_3}) was purchased from Acros Organics, Belgium. Potassium permanganate was of analytical grade. Potassium ferrate(K₂FeO₄) was prepared by hypochlorite oxidation of ferric nitrate according to the method of Delaude and Laszlo (Delaude and Laszlo, 1996), giving a purity over 90% for the recrystallized product. The purity was determined by the chromite titration method(Schreyer *et al.*, 1950). The characteristics of the raw water employed in the experiments are shown in Table 1.

1.2 Experimental methods

1.2.1 PAC adsorption

A carbon slurry of 10 mg/ml prepared by mixing 10 g of the oven-dried PAC in 1 L pure water was used in these experiments. The adsorption experiments were carried in a shaker. In 500 ml bottles, raw water was spiked with stock solution to the desired initial concentration. Carbon was added by

Table 1 Characteristic of raw water

pH	Alkalinity, mg/L CaCO ₃	Hardness, mg/L CaCO ₃	Total organic carbon, mg/L	Turbidity, NTU
7.1–7.2	52–60	110–130	4.5–4.9	3.2–3.6

aliquots of carbon slurry. The bottle without the introduction of carbon was used to determine the initial concentration. These bottles were covered with a PTFE-faced silicone septum and a screw cap. Samples were then withdrawn at the predetermined time intervals up to 240 min and were filtered with glass microfiber filters. The remaining concentration of MIB was determined immediately.

1.2.2 Ozonation of MIB

A series of experiments were performed to determine the effect of pH on the ozonation of MIB in a stainless-steel reactor (Fig. 1). Ozonizer with a variable work voltage was purchased from Mitsubishi Electric Corporation, Japan. Transformation ratio of oxygen to ozone could be adjusted by controlling the work voltage of ozonizer. Thus, ozone partial pressure in the gas phase and the aqueous ozone concentration (C_{O_3} , mg/L) was able to be maintained at desirable range. The feedwater was pure water buffered with a 50 mmol/L sodium phosphate solution. Hydrochloric acid and sodium hydroxide was used to adjust the pH. The reactor temperature was constant at 20°C. After steady-state conditions were obtained, MIB stock solution was injected into the reactor to keep the initial concentration of MIB to 400 ng/L. When sample was removed from the reactor, the ozone and other oxidants in solution were at once quenched by sodium sulfite.

Ozonation of MIB at the concentrations of 100 ng/L spiked in raw water, settled water and pure water was performed in a 1000 ml glass bottle, water samples were stirred by a PTFE-coated stirring bar. Settled water was obtained by flocculating the raw

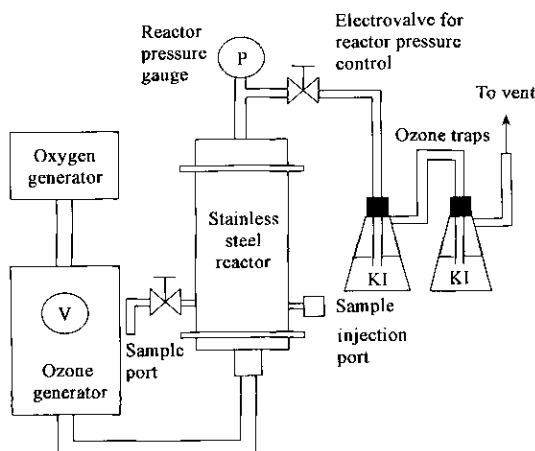


Fig.1 Schematic diagram of ozonation reactor

water with 2.5 mg/L polyaluminum chloride (PAC) as Al_2O_3 . TOC of raw water and settled water was 4.61 and 2.87 mg/L, respectively. Ozone stock solution was first obtained by bubbling ozone gas into pure water. Ozone was introduced by adding aliquots of the ozone stock solution to obtain the desired ozone doses. Experiments were conducted at 20°C and pH 7. The pH was stabilized with 50 mmol/L sodium phosphate buffer. After a 10-min O_3 contact time, a part of sample was quenched with Indigo reagent for the measurement of the O_3 residual and the other sample was quenched by sodium sulfite for MIB analysis.

1.2.3 Potassium permanganate oxidation

A stock solution of $KMnO_4$ was prepared by dissolving crystal permanganate in pure water. Appropriate quantities of MIB spiked into 1000 ml glass bottle to prepare solutions of 100 ng/L. Different amounts of $KMnO_4$ were added to the glass bottles, and the solutions were agitated by magnetic stirring bar. Samples were withdrawn after an hour contact and the remaining MIB concentration was analyzed.

1.2.4 Potassium ferrate oxidation

K_2FeO_4 stock solution at the concentration of 1000 mg/L as FeO_4^{2-} was freshly prepared just before the addition to the raw water. The experiments of removal of MIB by K_2FeO_4 in raw water were performed at the pH value of 7.1, 7.5 and 7.9, respectively. Hydrochloric acid and sodium hydroxide was employed to adjust the pH of raw water. The concentrations of MIB in samples were analyzed after one hour contact.

1.3 Analytical methods

A gas chromatograph/mass spectrometric detector (GC/MSD) incorporated with solid phase microextraction (SPME) concentration technique was used to determine MIB concentration. The details are described elsewhere (Liang *et al.*, 2005). The indigo Colorimetric method was used to determine aqueous ozone concentration (Eaton *et al.*, 1995).

2 Results and discussion

2.1 PAC adsorption

2.1.1 Adsorption kinetics of MIB by PAC

For the application of PAC in a water treatment plant, the kinetics adsorption is of crucial importance. The effective contact time for PAC in water treatment plants is usually on a scale from minutes to hours, which may not be sufficient to reach adsorption equilibrium. The batch experiments at pH 7.1 for wood-based PAC A and coat-based PAC B were used to evaluate the MIB adsorption kinetics. Experimental data during 4 h batch test with initial concentration of

MIB at 100 ng/L and a 20 mg/L PAC dosage are shown in Fig.2. The main removal of MIB occurred within contact time of 1 h and their removal by PAC A and PAC B in 1 h contact was 53.16% and 74.68%, respectively. PAC B showed better removal than PAC A. The iodine number for PAC A and PAC B was 980 and 950 mg/g, respectively. Difference in the MIB removal for PAC A and PAC B is not due to the iodine number. It may be correlative with carbon elemental composition (Pendleton *et al.*, 1997). The elemental analysis results for the PAC samples are shown in Table 2. MIB adsorption occurs via water displacement. Therefore, the hydrophilic character of the surface is the main parameter influencing adsorption. Although there is one hydroxyl group present in the structure of MIB, MIB is still regarded as hydrophobic compound. Wood-based PAC A contains more oxygen than coat-based PAC B and the former is likely to be more hydrophilic and be more difficult for MIB to displace the adsorbed water molecules. Hence, the PAC B has higher adsorption capacity.

Table 2 Elemental composition

	C, %	H, %	N, %	O, %	S, %	Ash, %
PAC A	88.12	1.19	0.83	5.91	0.29	3.65
PAC B	81.71	1.44	0.55	3.26	0.41	12.61

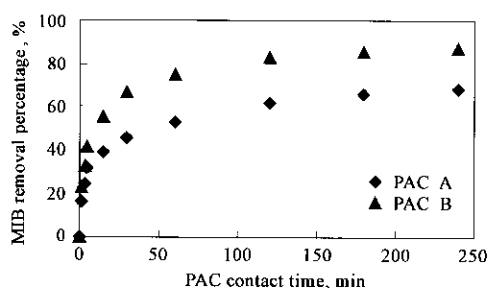


Fig.2 Batch kinetic test data for MIB by PAC A and PAC B

2.1.2 Effect of PAC dosage on removal of odor compounds

The study was primarily aimed towards an investigation of the optimum PAC dosages for the removal of MIB with an initial concentration of 100 ng/L in the simulated water sample. Typically, PAC contact time in water treatment plants is from 30 min to 1 h and main removal of odorants occurs during contact time of 1 h. Thus, the experiments were conducted with a contact time of 1 h and at four different PAC B dosages 5, 10, 15, and 20 mg/L. Fig.3 demonstrates that the removal of MIB increases with the increase of carbon dosage and there is approximately linear correlation between the removal percentage of MIB and the carbon dosage under the

experimental conditions. If PAC dosage exceeds 20 mg/L, PAC will affect the operation of water treatment. So it is difficult to achieve 90% removal of MIB by PAC B.

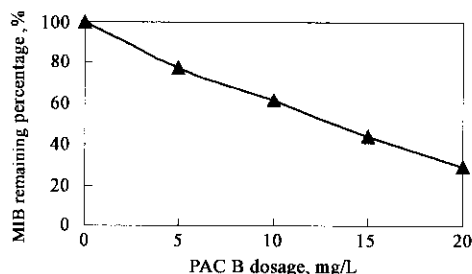


Fig.3 Effect of PAC B dosage on removal of MIB

2.1.3 Effect of initial MIB concentration on removal efficiency

Additional batch kinetic tests were performed with 20 mg/L PAC A to determine the effect of initial concentration of MIB on the removal with time. As shown in Fig.4, the removal percentage of MIB at any given time for a particular carbon dosage is irrelative to the initial concentration of MIB. Therefore, predictions of removal percentage versus time are valid for MIB concentration typical of natural water. According to Fig.3, the amount of PAC B required to reduce various episodes to the threshold odor concentration, given different amounts of contact time in an ideal reactor, may be quickly determined.

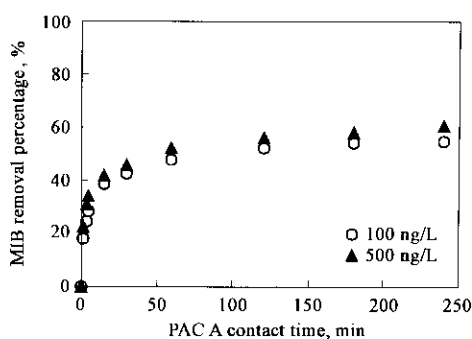


Fig.4 MIB removal percentage as a function of contact time vs. PAC A dose

2.2 Ozonation

2.2.1 Effect of pH on the ozonation of MIB

Three experiments were conducted at an ozone concentration of 0.35 mg/L and pH value of 5, 7 and 9, respectively. The effect of pH on the ozonation of MIB is shown in Fig.5. The removal of MIB within 20 min reaction at pH value of 5, 7 and 9 was 54.16%, 86.03%, 99.65%, respectively. High pH value promoted the formation of OH radical by the autodecomposition of ozone, hence the removal

efficiency of MIB increased as pH value increased. The results show that OH radical plays an important role in the ozonation of MIB.

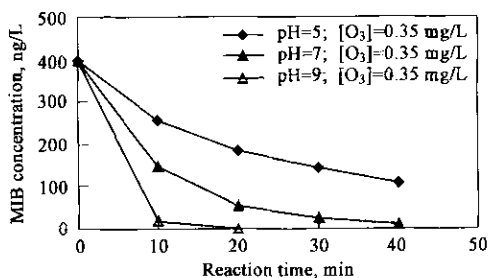


Fig.5 Ozonation of MIB at pH value of 5, 7 and 9 (aqueous ozone concentration, 0.35 mg/L)

2.2.2 Effect of background organics on ozonation of MIB

The raw water, settled water and pure water spiked with 100 ng/L MIB were ozonated at O₃ doses of 1, 2 and 3 mg/L. As shown in Fig.6, the removal of MIB increased with increasing O₃ dose, up to 77% removal at the highest O₃ dose. The order of removal efficiency for MIB was pure water>raw water>settled water. There was an interesting phenomenon that the removal efficiency of MIB in the raw water was higher than that in the settled water. As shown in Fig. 7, the O₃ residual concentration in samples followed the order: pure water > settled water > raw water. Organic matters in water samples did promote the decomposition of O₃ leading to a lower removal of MIB; at the same time, organic matters could initiate the formation of OH radical accelerating MIB removal (McGuire and Gaston, 1988). For ozonation of MIB in raw water, the latter may play a more important role. This may be the reason why ozonation of MIB in raw water is more effective than that in settled water. The removal efficiency for MIB in pure water was improved about 5% compared with raw water; hence the effect of background organics on the ozonation of MIB was not significant at the experimental conditions.

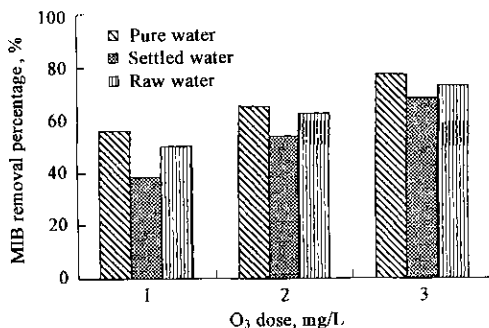


Fig.6 Ozonation of MIB in pure water, settled water and raw water

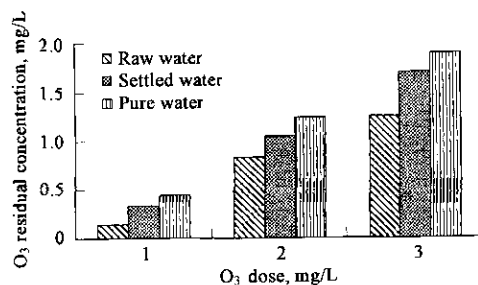


Fig.7 O₃ residual concentration in raw water, settled water and pure water after 10 min contact

2.3 Potassium permanganate oxidation

As shown in Fig.8, KMnO₄ oxidation appears to be ineffective in removing the MIB. In the pH range of 3 to 11.5, most KMnO₄ oxidation reactions proceed via a three-electron transfer, leading to the formation of several insoluble manganese oxide species. The sorptive properties of manganese dioxide [MnO₂(s)] may cause the limited removal of MIB during the KMnO₄ treatment process.

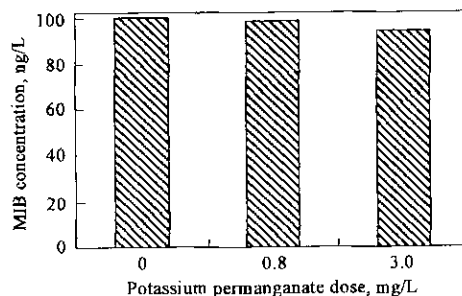


Fig. 8 Removal of MIB by KMnO₄

2.4 Potassium ferrate oxidation

Recent studies have shown that ferrate is an environmentally friendly oxidant and coagulant for water and wastewater treatment (Lee *et al.*, 2003; Qu *et al.*, 2003; Read *et al.*, 2003). Its reduction potentials are 0.72 and 2.20 V (versus NHE) in base and acid, respectively (De Luca *et al.*, 1996). Its oxidizing ability is directly relative to the pH value of solution and ferrate decomposes rapidly in acidic aqueous solution, generating Fe³⁺, hydroxide and molecular oxygen. Whether ferrate is able to oxidize the target compounds in the water and wastewater must be tested in specific pH value of aqueous solution.

Three batch experiments were conducted in the raw water at potassium ferrate concentration of 10 mg/L as FeO₄²⁻ and at the pH value of 7.1, 7.5 and 7.9, respectively. As shown in Fig.9, MIB cannot be removed by potassium ferrate at above conditions. Potassium ferrate at the concentration of 10 mg/L as FeO₄²⁻ in the raw water fully decomposed within 40 s,

7 min, 20 min at the pH value of 7.1, 7.5 and 7.9, respectively. Potassium ferrate is unstable to exist in water at the lower pH of aqueous solution and its oxidizing ability is not sufficient to oxidize MIB at higher pH of aqueous solution. Hence, MIB in drinking water cannot be removed by potassium ferrate.

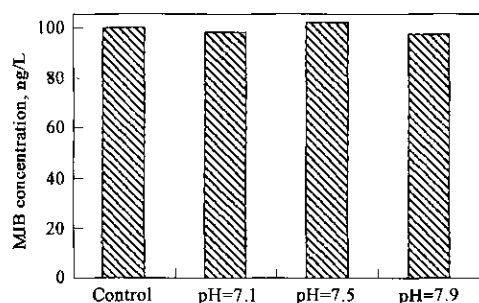


Fig.9 Removal of MIB by potassium ferrate of 10 mg/L as FeO_4^{2-}

3 Conclusions

The coat-based PAC B showed better removal for MIB than wood-based PAC A. The more oxygen in PAC A may cause its low removal efficiency for MIB. The removal percentage of trace MIB at any given time for a particular carbon dosage is irrelative to the initial concentration of MIB. Therefore, predictions of percent removal versus time are possible for MIB concentration typical of natural water.

The results indicate also that pH has a significant effect on the ozonation of MIB, which supports the theory that OH radical plays an important role on the destruction of MIB. The effect of background organics on the ozonation of MIB was not significant at the experimental conditions.

Potassium permanganate and potassium ferrate are ineffective in removing the MIB in drinking water.

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