Degradation of 2-methylisoborneol in drinking water by bauxite catalyzed ozonation

Fei Qi, Zhonglin Chen, Bingbing Xu and Zhenzhen Xu

ABSTRACT

Raw mineral bauxites with and without thermal treatment were used as catalysts in a catalyzed ozonation process for the degradation of a typical taste and odour compound 2-Methylisoborneol (MIB). Compared with the sole ozonation or catalyst adsorption, raw mineral bauxite without further thermal treatment did not exhibit remarkable catalytic activity. But all bauxite catalysts with further thermal treatment exhibited some catalytic activity. Changing of the crystalline form during the thermal treatment played an important role in enhanced ozonation efficiency. Bauxite calcined at 450°C (Bauxite450), which is composed of γ-Al$_2$O$_3$, exhibited the most remarkable catalytic activity among all the bauxite catalysts with thermal treatment. Catalyzed ozonation with Bauxite450 could remove MIB effectively and reduce MIB concentration to below its taste and odour threshold concentration. The catalyzed ozonation of MIB followed an indirect oxidation mechanism by hydroxyl radical (•OH). This result was confirmed by *tert*-butyl alcohol inhibiting the catalytic activity and R_{ct} value between the sole ozonation and catalyzed ozonation. As a natural mineral catalyst, bauxite with thermal treatment has supplied an economical and feasible choice for the catalyzed ozonation of MIB in drinking water.

Key words | bauxite, catalyzed ozonation, hydroxyl radical, taste and odour, 2-methylisoborneol

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INTRODUCTION

Taste and odour (T&O) problems in drinking water are a major cause of customer complaints for drinking water utilities. Consumers judge the quality of the water at their tap mainly by its aesthetic properties and the public perception that "if the water tastes and smells bad, then it is not safe to drink" has negatively affected the image of the drinking water industry (Juttner 2007). Algal-derived compounds are receiving widespread attention in the water industry as they can compromise the quality of drinking water. Of major concern are secondary algae metabolites which can impart taste and odour problems (Uwins *et al.* 2007). The most prevalent T&O customer complaints are in regard to earthy-musty odours. Microbial by-products, such as alicyclic alcohols 2-methylisoborneol (MIB), geosmin (GSM), isopropyl methoxypyrazine (IPMP), or trichloro-anisole (TCA) are usually sources of the earthy-musty

odours (Peter & Von Gunten 2007). MIB, microbial by-products associated with blue–green algae and aquatic actinomycetes, are the most common odorants (Zaitlin & Watson 2006). This tertiary alcohol can impart earthy-musty T&O problems in drinking water even when its concentration is as low as $10-25 \, \text{ng} \, \text{L}^{-1}$ (Li *et al.* 2007).

MIB has relatively low molecular weights, moderate hydrophobicity and moderate solubility (Pirbazari *et al.* 1992). At the same time, MIB is dissolved in extracellular of actinomycetes (Watson *et al.* 2007). For these properties of MIB described above, it has been shown to be somewhat recalcitrant to conventional water treatment (Burce *et al.* 2002). For low Henry's constants, MIB is not removed effectively by air stripping. Powdered activated carbon (PAC) or granular activated carbon (GAC) can remove most odorants by adsorption, but high doses of activated

carbon were needed. Furthermore, NOM (natural organic matter) presented in raw water may reduce the adsorption capability of activated carbon (Chestnutt *et al.* 2007). Oxidation processes with chemicals, such as ozone, chlorine, chlorine dioxide and potassium permanganate, have been recently investigated for degradation of MIB in water. Chlorine, chlorine dioxide and potassium permanganate have been proved ineffective for the treatment of MIB (Lalezary *et al.* 1986). Ozone, a powerful oxidant, has been found efficient for the degradation of MIB (Liang *et al.* 2007). Unfortunately NOM in raw water can rapidly deplete ozone, resulting in incomplete oxidation of MIB (Ho *et al.* 2002). Furthermore, ozonation can produce hazardous oxidation by-products such as aldehydes which could arouse strong fragrant odours (Bruchet & Duguet 2004). MIB was biodegradable, but information regarding their removal in biological filters used in water treatment plants was limited (Nerenberg *et al.* 2000).

Advanced oxidation processes (AOPs) are attractive alternatives to traditional water treatments and have received considerable attention recently. AOPs involve the generation of hydroxyl radical ($\cdot$OH) as the predominant species responsible for the degradation of pollutants. It was reported that TiO_2 photocatalysis, UV/H_2O_2 and ultrasonic irradiation could remove MIB from drinking water and $\cdot$OH was the predominant species responsible for its degradation (Lawton *et al.* 2003; Rosenfeldt *et al.* 2005; Song & O'Shea 2007). Unfortunately, there were some disadvantages of these AOPs in water treatment applications, such as the unsedimentation of TiO_2 powder, the short life of UV lamps and the low penetrating force of ultrasonic irradiation equipment. The combination of ozone and hydrogen peroxide (H_2O_2), known as homogenous catalytic ozonation, appears very simple and easy to carry out, but the residual of H_2O_2 should be taken into account (Beltrán 2004). Solid metal oxides can induce ozone decomposition to generate $\cdot$OH, and solid metal oxides catalyzed ozonation is more convenient for water treatment (Kasprzyk-Hordern *et al.* 2003). So more research was focussed on solid metal oxides catalyzed ozonation for the removal of recalcitrant pollutants. Recently, many catalysts have been developed for improving the efficiency of ozonation, such as α-FeOOH, nano- ZnO and Al_2O_3 (Park *et al.* 2004; Huang *et al.* 2005; Kasprzyk-Hordern

et al. 2006). Chen *et al.* (2006) reported that γ-Al_2O_3 catalyzed ozonation can remove MIB effectively in drinking water. As functional materials with abundant resources, some natural minerals have been used in environmental fields. For instance, natural clay and zeolite can be used as adsorbing materials (Tang & Weber 2006), catalyst support (Barrault *et al.* 2000) and catalyst (Pushpaletha *et al.* 2005). However, the reports of natural minerals used as ozonation catalysts were still rare in water and wastewater treatment to the best of our knowledge.

Natural bauxite is a kind of inexpensive and environmental friendly mineral with a moderate solubility in water. In this paper, raw bauxite and bauxite under thermal treatment were used as catalysts in a catalyzed ozonation process to degrade MIB in water. Experiments were carried out to investigate the catalytic activities of thermal treated bauxites calcined under different temperatures, to speculate on the activity species generated during the catalyzed ozonation process, and to reveal the relationship between the catalytic activities and the texture and crystallographic form changing of bauxites.

MATERIALS AND METHODS

Chemicals

Raw bauxite mineral was purchased from Gongyi of He Nan Province in China. The raw bauxite was crushed and sieved into 0.075–0.3 mm.

MIB was synthesized by the method described by Wood & Snoeyink (1977). The purity of synthesized MIB was above 95.0% confirmed by GC-MS. Stock solution of MIB was prepared by dissolving it in Milli-Q water, and the concentration was $100\,\mu g\,L^{-1}$. *p*-Chlorobenzoic acid (*p*CBA) was purchased from Sigma (USA) and the purity of *p*CBA was 98%. Stock solution of *p*CBA was prepared by dissolving it in Milli-Q water, and the concentration was $3.19\,mmol\,L^{-1}$. *n*-Pentane and methanol was HPLC grade purchased from Aldrich. Other reagents such as *tert*-butyl alcohol (*t*-BuOH), KH_2PO_4, NaCl, Na_2SO_3 and H_3PO_4 were all of analytic grade without further purification. The pure water ($\geq 18.0\,M\Omega\cdot cm$) used in this work was produced with a Millipore Milli-Q system.

Experiment procedures

The catalyzed ozonation experiments were performed at room temperature ($20 \pm 2°C$) in a cylinder reactor (3L) shown in Figure 1. Ozone was produced by a laboratory ozonizer (DHX-SS-1G, Harbin Jiujiu Electrochemistry Engineering Ltd. China) with a maximum ozone production of $9\,g\,h^{-1}$, using pure oxygen as feed gas. After ozone being introduced into the reactor which contained 3L Milli-Q water, catalysts were dropped into the reactor. And then, the circulation pump was turned on. Samples of 200 ml were collected at the specified time and the residual ozone was quenched by sodium sulfite solution. In terms of changing the flux of oxygen, the time of introducing ozone and the voltage of the ozone producing canal, the dissolved ozone concentration could be controlled. The pH of the solution was adjusted with phosphate buffer solution at the time the experiments took place. To reduce the influence of higher solution pH on ozone decomposition and investigate the hydroxyl radical mechanism of bauxite catalyzed ozonation, most ozonation experiments were carried out under the subacid solution condition (pH = 5.7).

The experiments of R_{ct} measurement were carried out in the reactor above. Ozone was introduced into the reactor described hereinbefore. The catalyst and diluent stock solution of pCBA were added into the reactor instantaneously after the ozone was introduced. Then circulation pump was turned on. Samples were collected at the specified time, and the residual ozone was quenched by sodium sulfite solution. Samples were filtered with cellulose acetate filters and transferred to 25 ml volumetric flasks.
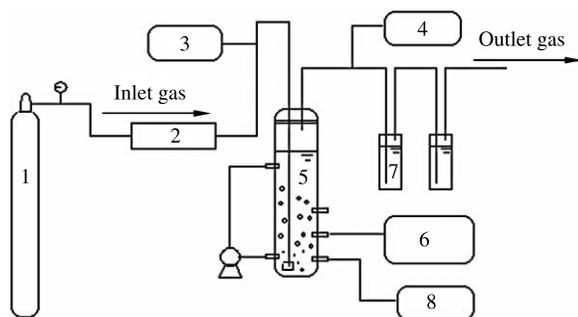
Figure 1 │ Schematic diagram of catalyzed ozonation system. (1) pressure oxygen container, (2) ozonizer, (3) inlet gas ozone analysis, (4) outlet gas ozone analysis, (5) catalyzed ozonation reactor, (6) GC-MS analysis, (7) KI solution, (8) dissolved ozone analysis.

Analysis methods

Characterization of catalysts

The crystallographic form of powder sample was characterized by X-ray powder diffraction (XRD) on an X-ray diffractometer (Rigaku D/MAX-rA, Japan). TG-DTA characterized by Rigaku TAS 100 thermal analysis instrument, and the temperature rate was $10°C\,min^{-1}$.

Aqueous ozone and MIB analysis

The aqueous ozone concentration was measured with the indigo method (Bader & Hoigné 1981). The method of MIB analysis was described by Shin with Agilent GC6890-MS5973 N instrument (Shin & Ahn 2004).

pCBA analysis and R_{ct} determination method

The concentration of pCBA was analyzed by HPLC (LC-10AVP, Shimadzu, Japan) equipped with an UV detection. The chromatograph column is VP-ODS. Samples were analyzed with an eluant (containing 0.5 percent of H_3PO_4 and methanol with the ratio 7:3) at a flow rate of $1\,ml\,min^{-1}$ and detected at 234 nm. The volume of injection was $100\,\mu l$.

RESULTS AND DISCUSSION

The catalytic activity of raw bauxite

Figure 2 shows the removal curve of MIB dissolved in Milli-Q water by raw bauxite adsorption, the sole ozonation and raw bauxite catalyzed ozonation. MIB adsorption efficiency on raw bauxite at the mass of $200\,mg\,L^{-1}$ could be detected at a lower level. Only 10 percent less MIB could be adsorbed within 10 minutes. The adsorption ability of raw bauxite was faint. The MIB removal efficiency of sole ozonation was only 28 percent. MIB could not be removed effectively in short contact time during the ozonation process. When being treated with raw bauxite catalyzed ozonation for 10 minutes, the removal efficiency of MIB could be achieved at 41 percent, only 13 percent higher than that of ozonation alone. The increase in MIB removal of raw bauxite catalyzed ozonation might account for the adsorption of the catalyst. It was concluded that the raw bauxite had no catalytic activity for ozonation of MIB.
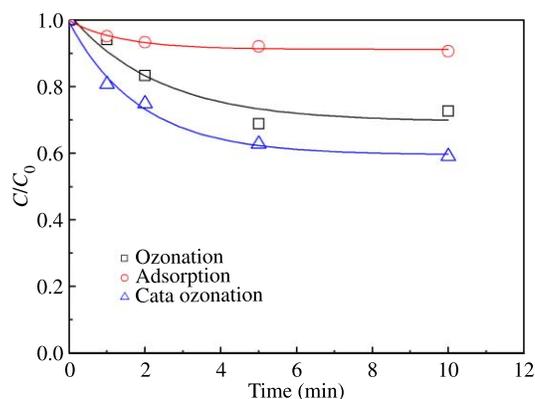
Figure 2 | Comparison of MIB removal of raw bauxite adsorption and ozonation with and without raw bauxite as a catalyst. [MIB] = 100ng·L^{-1}, [O$_3$]$_0$ = 0.5mg·L^{-1}, [Bauxite]$_0$ = 200 mg·L^{-1}, solution pH = 5.7 adjusted with phosphate buffer solution.

Characterization of bauxite and calcined samples

The raw bauxite sample used in this work is hoar with a little yellow. The main diffraction peaks of the XRD pattern in Figure 3 can be readily indexed to an impure bauxite mineral, which contained Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), Boehmite (AlOOH) and Quartz (SiO$_2$).

As seen in Figure 3, thermal treatment of raw bauxite above a certain temperature could change its structure and crystalline form. For improving the catalytic activity of
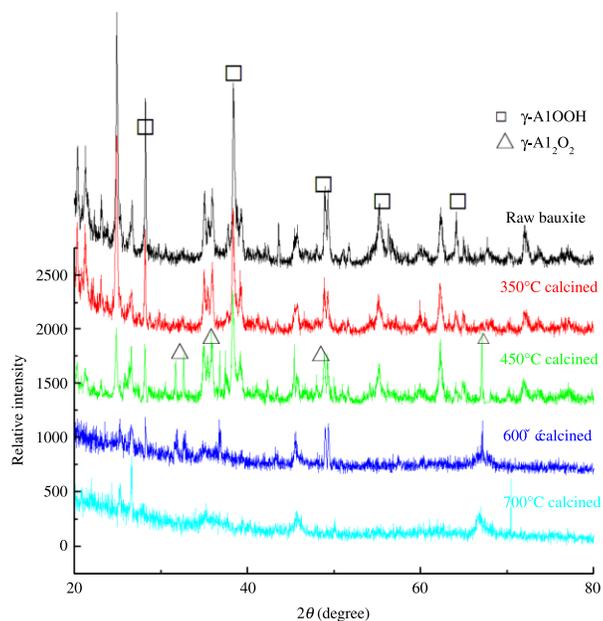

Figure 3 | XRD Characterization of raw Bauxite and samples calcined at different temperatures.

the raw bauxite mineral, thermal treatment of raw bauxite was conducted. As shown in Figure 4, the TG-DTA curves for the calcined process of raw bauxite in air were analyzed, and an extreme mass loss was observed between 400–600°C in the TG curve. At the same temperature zone, there was a remarkable change in the DTA curve. The changes both of the TG curve and the DTA curve exhibited that the structure and crystallographic form of the raw bauxite mineral were transformed between 400–600°C. The raw bauxite mineral samples were calcined under different temperatures, such as 350°C, 450°C, 600°C and 700°C. These calcined bauxite samples were also characterized by XRD equipment, shown in Figure 3. After being calcined under different temperatures, the transformation of crystallographic form took place. As calcining temperature increased, the crystallographic form of AlOOH transformed gradually and disappeared at 600°C. During the calcination process, the crystallographic form of γ-Al$_2$O$_3$ appeared at 350°C. When the temperature increased to 450°C, the crystallographic form of γ-Al$_2$O$_3$ was the main composition. As temperature increased to 700°C, crystallographic form of γ-Al$_2$O$_3$ disappeared. After thermal treatment, the structure and crystallographic form of bauxite changed. So as a mineral material, could the bauxite with easy thermal treatment enhance the degradation of MIB during the ozonation process?
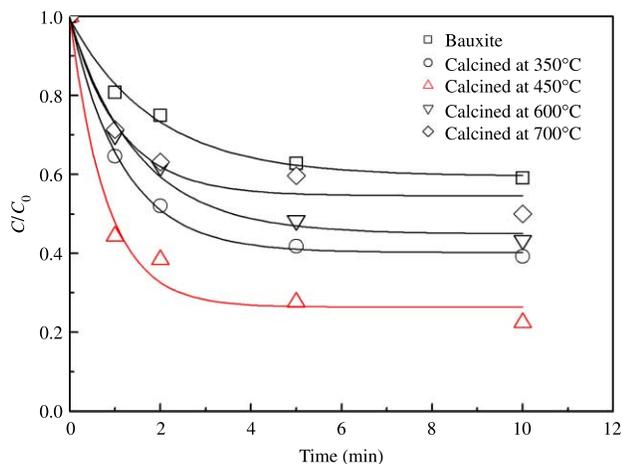
Catalytic activity of thermal treated bauxite

The adsorption of all the bauxites used in this experiment was confirmed to be less than 10 percent (detail data is not shown
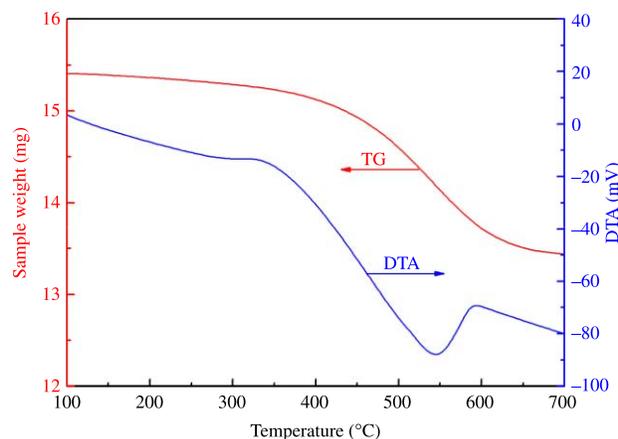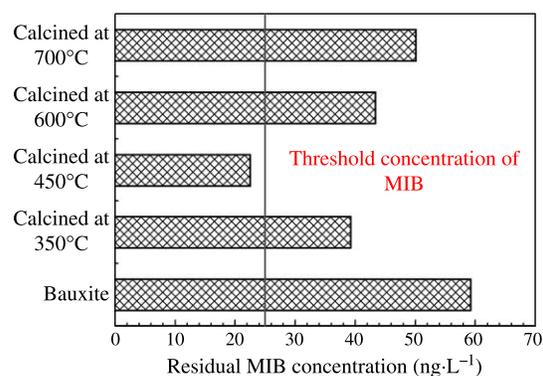

Figure 4 | TG–DTA curves of Bauxite at a heating rate of 10°C min^{-1}.

here). Figure 5 shows the catalytic activities of raw bauxite and calcined bauxites under different temperatures such as 350°C, 450°C, 600°C and 700°C. As a result, all calcined bauxites could enhance the ozonation degradation of MIB. Proper thermal treatment could increase the catalytic activity of raw bauxite. From the results shown in Figure 5, thermal treated bauxite calcined at 450°C exhibited the most extreme catalytic activity during catalyzed ozonation of MIB process. There was a breakpoint (calcined at 450°C) of the catalytic activities of calcined bauxites under different temperature. According to XRD analysis, at this breakpoint, the main composition of thermal treated bauxite was γ-Al_2O_3. The catalytic activity of calcined bauxite increased with the increase of calcination temperature when the temperature was below 450°C. The catalytic activity of calcined bauxite decreased with the increase of calcination temperature when the temperature was above 450°C. As the calcination temperature increased, the content of γ-Al_2O_3 composition exhibited a tendency to increase and then to decrease. When calcination temperature was 450°C, the content of γ-Al_2O_3 reached a maximum during the calcination process. As reported by Chen *et al.* (2006), γ-Al_2O_3 powder could increase the degradation efficiency of MIB during the ozonation process. According to the extreme catalytic activity of bauxite calcined at 450°C, it was concluded that bauxite calcined at 450°C enhanced the degradation efficiency of MIB during ozonation by the formation of γ-Al_2O_3 crystallographic form.

Thermal treatment could improve the catalytic activity of bauxite and increase the removal efficiency of MIB. Being different from other contaminants, residual T&O compounds may emit an unpleasant smell depending on their characteristics. Only if the residual concentration of T&O compound was below the threshold concentration, could customers not smell anything (Fabrellas *et al.* 2004). So it is necessary to investigate the residual concentration of MIB after ozonation enhanced by bauxites calcined at different temperatures. Generally, the concentration of MIB in water body was about 100–$200 \, ng \, L^{-1}$ when blue–green algae broke out in summer (Yen *et al.* 2007). So the catalyzed ozonation experiments with raw bauxite and calcined bauxite samples for removing MIB at initial concentration of $100 \, ng \, L^{-1}$ were carried out in the present work. The residual concentrations of MIB after catalyzed ozonation by bauxites calcined at various temperatures were shown in Figure 6. Compared to raw bauxite, all thermal treated bauxites could remove MIB better and achieve lower residual concentrations of MIB. The MIB residual concentration was the lowest by Bauxite450 catalyzed ozonation. Bauxite450 exhibited stronger catalytic activity than any of the other thermal treated bauxite at the same reaction conditions. As seen from Figure 6, the residual concentration of MIB was already below the taste and odour threshold concentration ($25 \, ng \, L^{-1}$) by catalyzed ozonation in the presence of Bauxite450. Although by increasing the dosage of ozone and/or catalyst, the residual MIB concentration of ozonation catalyzed by other bauxites might also be below the taste and odour
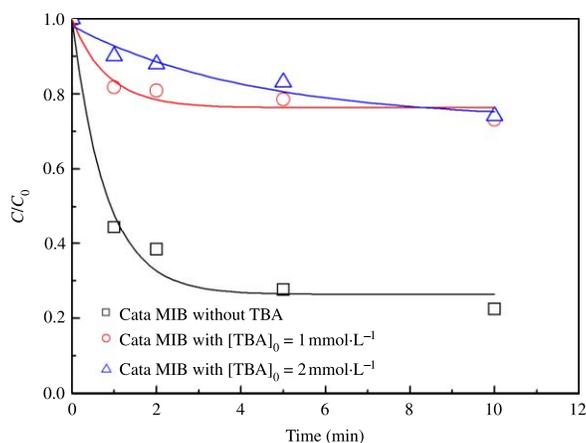

Figure 5 │ Influence of thermal treatment of Bauxite on its catalytic activity in MIB degradation [MIB] = $100 \, ng \cdot L^{-1}$, $[O_3]_0 = 0.5 \, mg \cdot L^{-1}$, [calcined Bauxite]$_0$ = $200 \, mg \, L^{-1}$, solution pH = 5.7 adjusted with phosphate buffer solution.

Figure 6 │ The residual concentration of MIB after catalyzed ozonation by raw bauxite and calcined Bauxite [MIB] = $100 \, ng \, L^{-1}$, $[O_3]_0 = 0.5 \, mg \, L^{-1}$, [calcined Bauxite]$_0$ = $200 \, mg \, L^{-1}$, solution pH = 5.7 adjusted with phosphate buffer solution, the reaction time was 10 min.

threshold concentration, the treatment cost should be taken into account.

Mechanism of thermal treated bauxite catalyzed ozonation process

For bauxite calcined at 450°C (abbreviated to Bauxite450) exhibited remarkable catalytic activity and could achieve the concentration of MIB below the threshold concentration, it was presumed that some activity species might be formed in the Bauxite450 catalyzed ozonation system. In general reports about metal oxides catalyzed ozonation, hydroxyl radical (•OH) was the main activity species during the catalyzed ozonation process (Kasprzyk-Hordern *et al.* 2003). To investigate the activity species generated during the Bauxite450 catalyzed ozonation, some experiments were carried out in the presence of *tert*-butyl alcohol (TBA) as an effective scavenger for it did not react with ozone but with •OH (the second reaction rate constant of TBA with •OH radicals is 5.9×10^8 (mol/L)$^{-1}$s^{-1}) (Staehelin & Hoigné 1985). Some inert compounds which could terminate the chain reaction of ozone decomposition might be formed when TBA reacted with •OH. Bauxite450 catalyzed ozonation experiments were conducted in the presence of 1.0 or 2.0 mmol L^{-1} TBA.
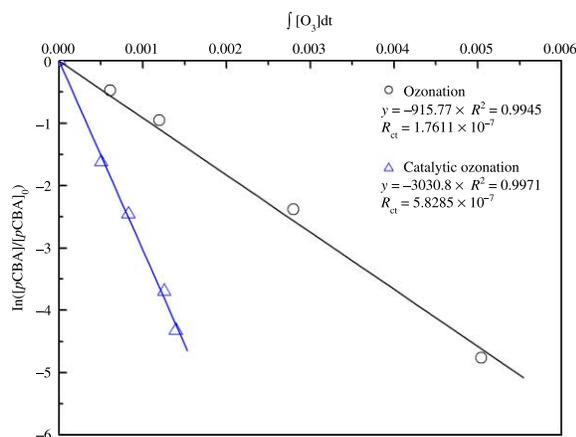
Figure 7 shows the change of MIB concentration during Bauxite450 catalyzed ozonation with or without TBA. The most evident feature of Figure 7 was that the catalytic activity of Bauxite450 was remarkably inhibited by the presence of both 1.0 mmol L^{-1} and 2.0 mmol L^{-1} of TBA. This result indicated that •OH was the main activity species during the Bauxite450 catalyzed ozonation process.

As discussed above, •OH was the main activity species during the Bauxite450 catalyzed ozonaiton process. So determination of the concentration of •OH was very important for investigating the catalyzed ozonation mechanism. R_{ct} value is to express the ratio of •OH exposure and ozone exposure in ozonated water samples (see Equation (1)) (Pi *et al.* 2005). R_{ct} value is constant during the time of ozonation for certain water samples at certain ozone dosage. The R_{ct} value is supposed to be a constant for both ozonation and catalytic ozonation here. *p*-Chlorobenzoic acid (*p*CBA, the reaction rate constants of *p*CBA reacting with ozone and •OH are $k_{O3/pCBA} \leq 0.15$ (mol/L)$^{-1}$s^{-1}, $k_{•OH/pCBA} = 5 \times 10^9$ (mol/L)$^{-1}$s^{-1}, respectively (Pi *et al.* 2005). So in the oxidation process, *p*CBA could react with •OH quickly and was selected as a probe compound to determine the R_{ct} value both in ozonation and catalytic ozonation. From Equations (1) and (2), R_{ct} value shown in Figure 8 could be obtained for both ozonation and catalytic ozonation. The R_{ct} in the sole ozonation process and the Bauxite450 catalyzed ozonation process was 1.76×10^{-7} and 5.83×10^{-7}, respectively. Comparing the R_{ct} values in the two processes, the R_{ct} value of Bauxite450 catalyzed ozonation process was 3.3 times that of sole ozonation. This result showed that the Bauxite450 catalyzed ozonation system could yield more •OH than the sole ozonation system when the initial

Figure 7 │ Inhibition of t-BuOH on Bauxite calcined at 450°C catalyzed ozonation of MIB [MIB] = 100 ng·L^{-1}, [O$_3$]$_0$ = 0.5 mg·L^{-1}, [Bauxite450]$_0$ = 200 mg L^{-1}, solution pH = 5.7 adjusted with phosphate buffer solution.

Figure 8 │ Determination of R_{ct} during ozonation process and catalyzed ozonation process with Bauxite calcined at 450°C [*p*CBA]$_0$ = 3.19 μmol L^{-1}, [O$_3$]$_0$ = 0.5 mg L^{-1}, [Bauxite450]$_0$ = 200 mg L^{-1}, solution pH = 5.7 adjusted with phosphate buffer solution, the reaction time was 10 min.

concentration of ozone was the same.

$$R_{ct} = \frac{\int_t^0 [\cdot OH] dt}{\int_t^0 [O_3] dt} \qquad (1)$$

$$\ln\left\{\frac{[pCBA]_t}{[pCBA]_0}\right\} = -k_{\cdot OH/pCBA} \int_0^t [\cdot OH] dt$$

$$= -k_{\cdot OH/pCBA} R_{ct} \int_0^t [O_3] dt \qquad (2)$$

Catalytic activity of Bauxite450 in enhanced ozonation for degradation MIB

As discussed above, bauxite calcined at 450°C (Bauxite450) exhibited remarkable catalytic activity in the ozonation process and could catalyze ozone decomposition to generate more •OH under subacid conditions. In general, the pH of surface water is in the range of 7–8. So the investigation of the catalytic activity of Bauxite450 for catalyzed ozonation of MIB under a neutral pH range is necessary.

Figure 9 showed the catalytic activity of Bauxite450 at solution pH 7.3. Under this solution pH condition, Bauxite450 also exhibited evident catalytic activity. The removal efficiency of MIB by Bauxite450 catalyzed ozonation was 48.9 percent higher than that of sole ozonation while the removal efficiency of MIB by raw bauxite catalyzed ozonation was only 12.5 percent higher than that of sole ozonation. Calcination treatment improved the catalytic activity of bauxite. The remarkable catalytic activity at solution pH 7.3 made Bauxite450 a potential catalyst of ozonation for surface water treatment.
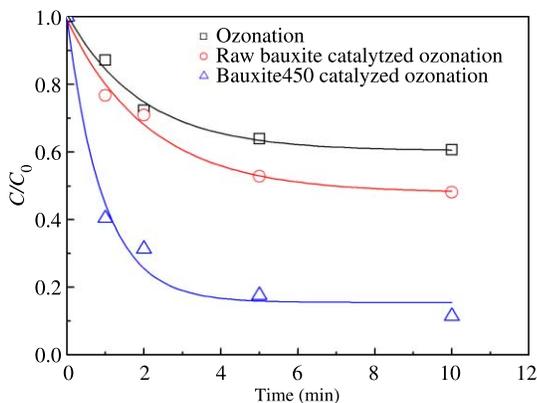
Figure 9 | Catalytic activity of Bauxite450 for catalyzed ozonation of MIB under neutral condition [MIB] = 100 ng L⁻¹, [O₃]₀ = 0.5 mg L⁻¹, [Raw Bauxite]₀ = [Bauxite450]₀ = 200 mg L⁻¹, solution pH = 7.3 adjusted with phosphate buffer solution.

CONCLUSION

Raw bauxite without any treatment was used directly in the catalyzed ozonation of MIB as a typical T&O compound. The introduction of raw bauxite did not enhance the MIB removal efficiency of ozonation. Thermal treatment can change the structure and crystalline form of raw bauxite. According to TG–DTA analysis, the crystalline of bauxite may change during 400–600°C. This result was confirmed by XRD characterization. Bauxite with thermal treatment exhibited some catalytic activity during the catalyzed ozonation process. Bauxite450 (raw bauxite calcined at 450°C) exhibited the most remarkable catalytic activity for the main composition being γ-Al₂O₃. After Bauxite450 catalyzed ozonation, the residual concentration of MIB in water was below the taste and odour threshold concentration. As the main activity species, •OH was generated during the Bauxite450 catalyzed ozonation process according to the TBA inhibiting catalytic activity experiments. By determination of R_{ct} values between the sole ozonation and Bauxite450 catalyzed ozonation, the yield of •OH during the catalyzed Bauxite450 ozonation process was 3.31 times that of the sole ozonation process. The investigation of Bauxite450 catalyzed ozonation of MIB at solution pH 7.3 was carried out. The result that Bauxite450 exhibited remarkable catalytic activity in the normal pH range of surface water made Bauxite450 a potential catalyst for ozonation in surface water treatment. According to the results described above, thermal treated bauxite such as Bauxite450 was an economical and feasible choice for catalyzed ozonation of MIB in drinking water.

ACKNOWLEDGEMENTS

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