Ozonation catalyzed by the raw bauxite for the degradation of 2,4,6-trichloroanisole in drinking water

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ABSTRACT

A kind of inexpensive and environmental friendly mineral, the raw bauxite has been used successfully as a catalyst combined with ozonation in the degradation of 2,4,6-trichloroanisole (TCA). The catalyst was characterized by using various analytical techniques. X-ray powder diffraction (XRD) characterization showed that the raw bauxite containing boehmite (γ-AlOOH), kaolinite ($Al_2Si_2O_5(OH)_4$) and quartz (SiO_2), and γ-AlOOH was the major composition. The catalytic ozonation removal effectiveness of TCA was investigated under various physicochemical conditions. Both the adsorption and the single ozonation were not effective for the degradation of TCA, and the presence of the raw bauxite in ozonation enhanced the TCA removal effectiveness. Both the hydroxyl radicals ($^\bullet$OH) scavenging experiment and R_{ct} characterization confirmed that the generation of $^\bullet$OH was accounted for the enhancement of the degradation of TCA. The generation of $^\bullet$OH was inhibited faintly by the presence of both natural organic matters (NOMs) and alkalinity in the natural water during catalyzed ozonation with the raw bauxite. The increasing of both the bauxite dosage and the ozone dosage enhanced the removal effectiveness of TCA. The raw bauxite was an efficient green catalyst for TCA degradation in drinking water.

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1. Introduction

Taste and odor in drinking water are persistent problems for many water supply entities [1]. The taste and odor, which are caused by compounds produced by microorganisms or chemicals, is released to the environmental system intermittently [2]. These compounds are produced at nanogram per liter levels in the source water [3]. Main compounds causing taste and odor are 2-methylisoborneol (MIB), geosmin and 2,4,6-trichloroanisole (TCA) [4]. These compounds can result in musty-earthy in the drinking water. It has been found that these compounds are hardly removed by the conventional treatment process (coagulation, chlorination and sand filtration), due to their low molecular weights

[5]. Oxidants such as chlorine dioxide (ClO_2) and potassium permanganate ($KMnO_4$) are not efficient [6]. A popular method is the use of activated carbon adsorption. However, the powdered activated carbon (PAC) causes problems of the sludge removal and the disposal [7]. The granular activated carbon (GAC) adsorption is also effective in removing these compounds. Nevertheless, hygienic and aesthetic problems arise from enhanced microbial growth on the filters and the presence of invertebrates, mostly nematodes, in the filters, impairing the quality of the drinking water. Recent years, membrane processes have been applied to remove taste and odor compounds. Both reverse osmosis and nanofiltration reduce TCA effectively [8]. Ultrafiltration membrane process alone controls taste and odor problem ineffectively, but ultrafiltration membrane process combined with PAC removes TCA effectively [9]. Various drinking water treatment strategies such as oxidation, active carbon, membrane filtration cannot remove taste and odor compounds drastically. Therefore, it is necessary to explore the new water treatment technology to resolve taste and odor problems in drinking water.

The autodecomposition of ozone results in the formation of hydroxyl radicals ($^\bullet$OH) [10]. Taste and odor compounds are considered to be susceptible for the removal by $^\bullet$OH [11]. Although ozonation is an effective treatment option for the removal of taste and odor compounds, the formation of the hazardous by-product bromate must be controlled [12]. To overcome this drawback,

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ozonation processes are being modified in order to increase their oxidizing capability. Advanced oxidation processes (AOPs) are based on the generation of •OH in water. These highly reactive and nonselective oxidants can oxidize organic compounds. Consequently, various AOPs (such as O_3/H_2O_2, UV/H_2O_2, photocatalytic oxidation with TiO_2, and ultrasonic oxidation) have been investigated as potential methods for removing taste and odor compounds [13–16]. Unfortunately, there were some disadvantages of these AOPs in water treatment application, such as unsedimentation of TiO_2 powder, the short life of UV lamps and ultrasonic irradiation equipment. Combinations of O_3/H_2O_2 or UV/H_2O_2, appeared very simple and easy to carry out, but the residual of H_2O_2 should be taken into account.

As a member of AOPs, heterogeneous catalytic ozonation has received increasing attention due to its potentially higher effectiveness in the degradation of refractory organic pollutants and lower negative effect on water quality, over the last several years [17]. Different supported and unsupported catalysts have been tested in the ozonation of several organic compounds. The heterogeneous catalysts used are usually MnO_2 [18], TiO_2 [19], Al_2O_3 [20,21], α-FeOOH [22,23], activated carbon [24–27], ZnO [28,29], noble metals [30,31] and mixed metal oxides [32]. These catalysts were investigated on degradation different refractory organic pollutants in drinking water or wastewater. However, only few investigations have been reported on the degradation of taste and odor compounds in drinking water by heterogeneous catalytic ozonation. Chen research group has investigated MIB degradation by catalyzed ozonation in the presence of γ-Al_2O_3 or calcined bauxite [33].

Though taste and odor problem was studied widely, investigations were mainly focused on 2-methylisoborneol and geosmin. Only few published papers were concerned on the degradation of TCA. The natural bauxite is a kind of inexpensive and environmental friendly mineral with a moderate solubility in water. In this paper, the raw bauxite was used as the catalyst in a catalytic ozonation process to remove TCA in drinking water.

2. Experimental

2.1. Chemicals

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

2,4,6-Trichloroanisole was obtained from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan). The stock solution of TCA was prepared at $25 \mu g L^{-1}$ by dissolving $25.0 \mu g$ TCA into 1000 mL ultra-pure water ($18 M\Omega cm$). The stock solution was diluted to the aqueous solutions containing $25 ng L^{-1}$ of TCA for experiments. The purity of the p-chlorobenzoic acid (pCBA) that was purchased from Sigma USA was 98%. A stock solution of pCBA ($3.19 mmol L^{-1}$) was prepared by dissolving it into Milli-Q water. n-Pentane of HPLC grade was purchased from Sigma–Aldrich (USA). 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 ($\geq 18.0 M\Omega cm$) used in this work was produced with a Millipore Milli-Q system.

All the glassware equipments used in the experiments were soaked in the solution of H_2SO_4–$K_2Cr_2O_7$ over night, and then washed by tap water and distilled water for three times, respectively.

2.2. Experimental procedures

The catalyzed ozonation experiments were performed at room temperature ($20 \pm 2 °C$) in a cylinder reactor (3-L) shown in Fig. 1. Ozone was produced by a laboratory ozonizer (DHX-SS-1G, Harbin
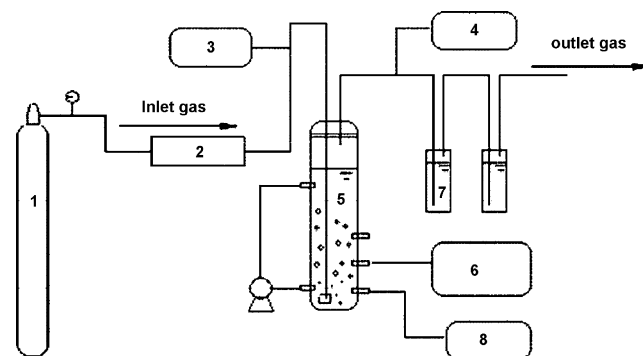

Fig. 1. Scheme of catalyzed ozonation system.
(1) Pressure oxygen container, (2) ozonizer, (3) inlet gas ozone analysis, (4) outlet gas ozone analysis, (5) catalyzed ozonation reactor, (6) GC–MS analysis, (7) KI solution, (8) dissolved ozone analysis.

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, catalysts were dropped into the reactor. 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 can be controlled. The solution pH was adjusted with the phosphate buffer solution at the time the experiments took place.

Experiments to determine R_{ct}, the ratio of hydroxyl radicals concentration to ozone concentration, were carried out in the reactor described above. Ozone was introduced into the reactor as shown above. The stock solution of pCBA and catalysts were quickly introduced into the reactor. The reactor was instantly sealed and the magnetic stirrer was then turned on to initiate the catalytic ozonation experiments. Samples were collected at pre-selected reaction time and the residual ozone was quenched instantly using a sodium sulfite solution (pre-acidified with sulfuric acid to pH 5). Samples were filtered with cellulose acetate filters ($0.45 \mu m$) and were transferred to 25 mL volumetric flasks. The concentrations of pCBA and aqueous ozone were determined as below.

2.3. Analytical methods

2.3.1. 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). Surface area, pore volume and average pore size of the raw bauxite mineral were obtained on a Surface Area and Porosity Analyzer (Micromeritics ASAP 2020, USA). Infrared spectra were measured on a Spectrum One Perkin Elmer Fourier transform infrared spectrum instrument.

2.3.2. Aqueous ozone, 2,4,6-trichloroanisole and p-chlorobenzoic acid

The aqueous ozone concentration was measured with the indigo method [34]. The method of TCA analysis was described by Shin with Agilent GC6890-MS5973N instrument [35]. The water sample (200 mL) was placed in a 250-mL separatory funnel and approximately 8 g KH_2PO_4 were 40 g NaCl were added to the solution. The sample was then extracted with n-pentane (1 mL) by mechanical shaking for 5 min. The organic phase was dried with anhydrous sodium sulfate and transferred to a V-shaped auto-sampling vial. At appropriate times, a 1-μL sample of the solution was injected into the GC system. All mass spectra were obtained with an Agilent 6890-5973N instrument. The ion source was operated in the electron-impact mode (EI; electron energy 70 eV, 230 °C). The full-

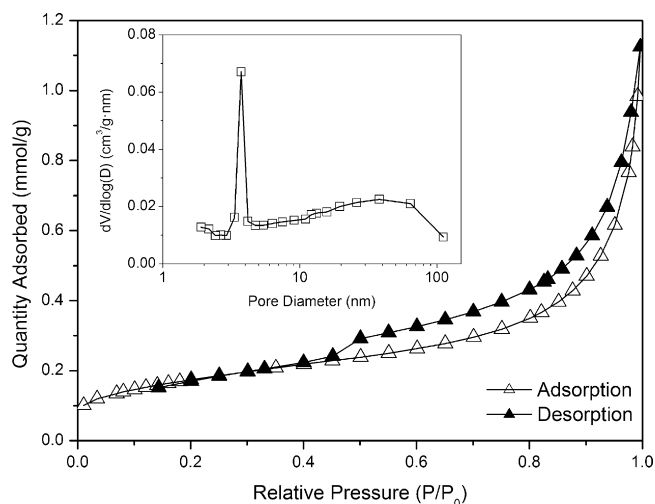**Fig. 2.** Nitrogen adsorption–desorption isotherm of the raw bauxite power and the inset shows its BJH pore size distribution curve.

Fig. 3. XRD pattern of the raw bauxite power.

scan mass spectra were recorded for identification of analytes at high concentration. Confirmation of trace chemicals was by use of two characteristic MS ions and by matching GC retention time. The ions selected in this investigation were m/z 195 and m/z 196 for TCA. The detection limit was $1.0\,ng\,L^{-1}$ and RSD was below 5.6%.

A stock solution of pCBA ($3.19\,mmol\,L^{-1}$) was prepared by dissolving it in distilled water. The concentration of pCBA was analyzed by HPLC (LC-10AVP, Shimadzu, Japan) equipped with UV detection. The chromatograph column used was VP-ODS (Shimadzu, Japan). Samples were analyzed using an eluent (containing 0.5% H_3PO_4 and methanol in the ratio 7:3) at delivered at $1\,mL\,min^{-1}$ and detected at 234 nm. The injection volume was $100\,\mu L$.

3. Results and discussion

3.1. Characterization of the raw bauxite

3.1.1. Surface texture characterization
The surface area and the porosity of the raw bauxite were investigated by using nitrogen adsorption and desorption isotherms (shown in Fig. 2). The isotherm was typical type IV-like with a type H_2 hysteretic loop in the range of 0.5–1.0 P/P_0, which indicates the presence of mesoporous materials. The plot of the pore size distribution (inset in Fig. 2) was determined by using the Barrett–Joyner–Halenda (BJH) method from the desorption branch of the isotherm. The average pore diameter of the raw bauxite was $7.445 \pm 0.02\,nm$. The BET surface area and pore volume of the spherical aggregates were $14.27 \pm 0.02\,m^2\,g^{-1}$ and $0.2657 \pm 0.0003\,cm^3\,g^{-1}$, respectively.

3.1.2. XRD characterization
The raw bauxite sample used in this work was hoar with a little yellow. The XRD pattern of the raw bauxite is shown in Fig. 3. The strong and sharp diffraction peaks indicate that the raw bauxite is well crystalline. However, the main diffraction peaks of the XRD pattern in Fig. 3 can be readily indexed to an impure bauxite mineral. There are three species in the raw bauxite, such as boehmite (γ-AlOOH), kaolinite ($Al_2Si_2O_5(OH)_4$) and quartz (SiO_2), and γ-AlOOH is the major composition.

3.1.3. FT-IR characterization
The FT-IR spectrum (KBr pellets method) of the raw bauxite was measured to investigate the structural information of the raw bauxite and the surface function groups on the mineral surface. The FT-IR
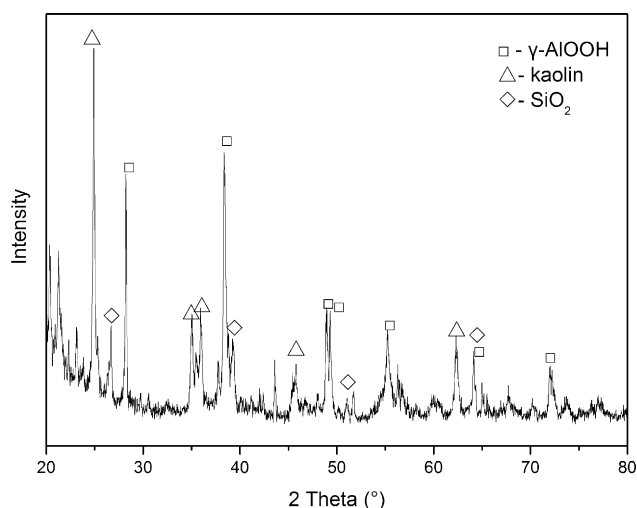
spectrum of the raw bauxite is shown in Fig. 4. The absorbance at $624\,cm^{-1}$ originates from Al–O, and the absorbance at $1100\,cm^{-1}$ originate from Si–O. The presence of water molecule was supported by the appearance of the bending mode at $1640\,cm^{-1}$ and the stretching mode at $3400\,cm^{-1}$. This surface hydroxylation may result in the surface hydroxyl groups formation on the surface of the mineral. The surface hydroxyl groups are very advantageous for the catalytic ozonation or catalytic ozone decomposition. The presence of the surface hydroxyl groups is good for the formation of $^\bullet$OH that can oxidize refractory organic pollutants unselectively.

3.2. Catalytic activity of the raw bauxite

Both non-catalytic and catalytic ozonation in the presence of the raw bauxite are presented in Fig. 5. The ozonation of TCA in the presence of the raw bauxite showed excellent result, leading to nearly 86.0% conversion of TCA after 10 min of reaction, against approximately 34.6% removal obtained by single ozonation. The adsorption effectiveness of TCA on the raw bauxite has also been determined. Only about 10% conversion TCA can be adsorbed on the surface of the raw bauxite within 10 min. TCA is a non-dissociation compound for its chemical structure. It is confirmed that TCA is not chelated on the surface of the raw bauxite, because of the faint
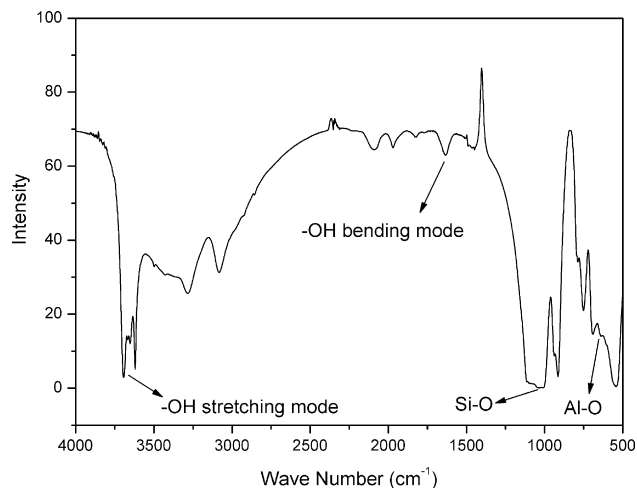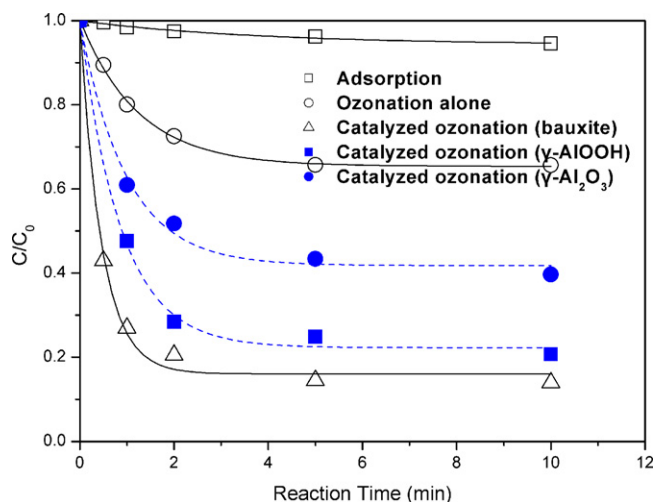

Fig. 4. FT-IR characterization of the raw bauxite.

Fig. 5. Efficiency of catalyzed ozonation in present of the raw bauxite for TCA degradation. Experiment conditions were: $[TCA]_0 = 100\,ng\,L^{-1}$, $[O_3]_0 = 0.5\,mg\,L^{-1}$, $[bauxite]_0 = 200\,mg\,L^{-1}$, solution pH = 6.0 adjusted with phosphate buffer solution, the reaction time was 10 min.

Fig. 6. Effects of the presence and the absence of TBA on catalyzed ozonation TCA in present of the raw bauxite. Experiment conditions were: $[TCA]_0 = 100\,ng\,L^{-1}$, $[O_3]_0 = 0.5\,mg\,L^{-1}$, $[bauxite]_0 = 200\,mg\,L^{-1}$, solution pH = 6.0 adjusted with phosphate buffer solution, the reaction time was 10 min.

adsorption effectiveness. It is obviously that degradation reaction rate is significantly improved by the presence of the raw bauxite. The removal effectiveness of catalytic ozonation in the presence of the raw bauxite was higher than that of ozonation alone and adsorption.

In Fig. 5, the comparison of the catalytic activity between the bauxite and other aluminum oxides is also shown. The activity of the raw bauxite was much higher than that of γ-AlOOH and γ-Al$_2$O$_3$. γ-AlOOH and γ-Al$_2$O$_3$ were used widely in catalyzed ozonation for the degradation of organic pollutants. Additionally, the preparation of γ-AlOOH and γ-Al$_2$O$_3$ was complexed and the content of γ-AlOOH and γ-Al$_2$O$_3$ in mineral was much less than the raw bauxite. Therefore, it is concluded that catalytic ozonation in the presence of the raw bauxite is an effective technology for removing TCA in drinking water.

3.3. Scavenging effect of tert-butyl alcohol (TBA) on catalyzed ozonation

The low reaction rate constants reported in the literature for the ozonation of TCA explained why such compound could not be removed by ozone [4]. TCA of low reactivity towards ozone may be oxidized by secondary oxidants produced during the decomposition of ozone in aqueous solution. It is speculated that some active species are produced during the catalyzed ozonation process in the presence of the raw bauxite. In general reports about metal oxides catalyzed ozonation, •OH was the main activity species during the catalyzed ozonation process [17,18]. To investigate the activity species generated during the raw bauxite catalyzed ozonation, some experiments were carried out in the presence of TBA as an effective scavenger [36]. At the same time, TBA cannot be adsorbed on the surface of metal oxides, for physical–chemical property of TBA. The raw bauxite catalytic ozonation experiments were conducted in the presence of $1.0\,mmol\,L^{-1}$ or $2.0\,mmol\,L^{-1}$ TBA.

The results in Fig. 6 show that the ozonation of TCA catalyzed by the raw bauxite is strongly inhibited in the presence of TBA. The most evident feature of Fig. 7 is that the inhibiting effects with $1.0\,mmol\,L^{-1}$ and $2.0\,mmol\,L^{-1}$ of TBA are the same. This experimental observation indicates that •OH is the main activity species during the raw bauxite catalytic ozonation process.
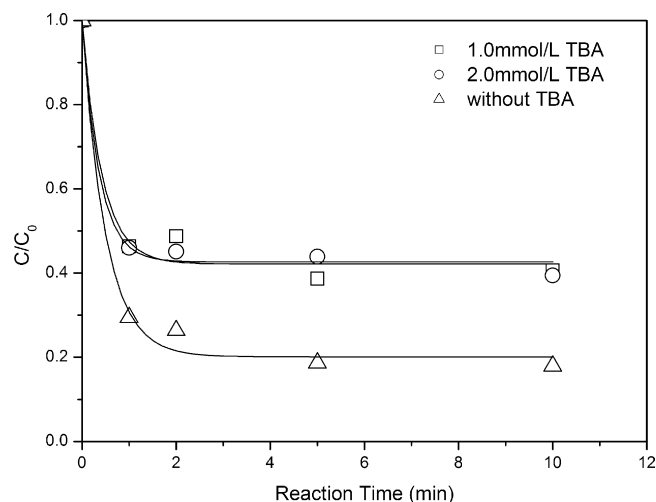
3.4. Oxidation of TCA in natural waters

To simulate the catalytic ozonation of TCA under the real treatment condition, experiments were performed in the natural waters (SH Water and LH Water). In addition to TCA, a small amount of pCBA ($3.19\,\mu mol\,L^{-1}$) as a •OH probe compound was added in the solution of the natural water to estimate the concentration of •OH during both ozonation and catalyzed ozonation in the presence of the raw bauxite. Fig. 7 shows the removal effectiveness of TCA by the single ozonation and catalytic ozonation in two kinds of the real water. Compared with the results in Fig. 5, the removal efficiencies of the single ozonation and catalytic ozonation in two kinds of real water were less than that in the buffered Milli-Q water. The removal effectiveness of TCA in single ozonation in SH Water was closed to that in the buffered Milli-Q water. Especially, the removal effectiveness of TCA in the single ozonation in LH Water was deceased to 21.4%. Both in SH Water and in LH Water, the catalytic activity of the raw bauxite in catalytic ozonation process was inhibited. The inhibiting effect of SH Water was weaker than that of LH Water. The water quality of SH Water and LH Water was accounted for
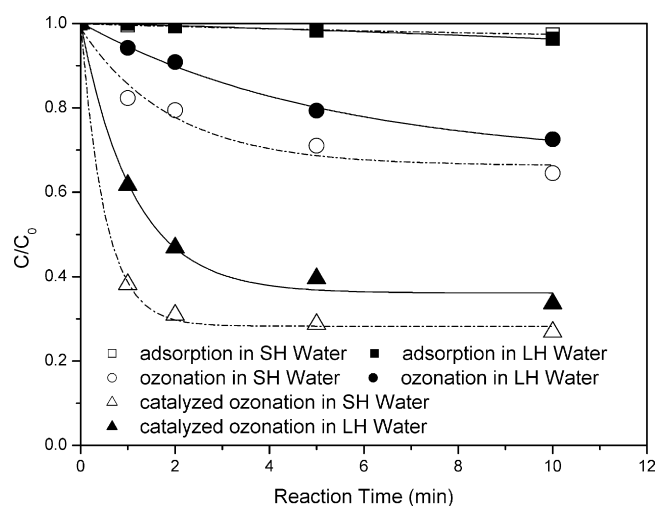
Fig. 7. Efficiency of ozonation TCA in natural water within the raw bauxite and without the raw bauxite. Experiment conditions were: $[TCA]_0 = 100\,ng\,L^{-1}$, $[O_3]_0 = 0.5\,mg\,L^{-1}$, $[bauxite]_0 = 200\,mg\,L^{-1}$, the reaction time was 10 min.

Table 1
Water quality parameters of the natural water used in experiments.

Water sample	DOC (mg C L^{-1})	UV$_{254}$[a]	SUVA[b]	Turbidity (NTU)
SH Water	4.708	0.048	1.02	0.55
LH Water	5.905	0.103	1.74	1.2

Water sample	Hardness[c] (mg L^{-1})	Alkalinity[d] (mg L^{-1})	Solution pH	Temperature (°C)
SH Water	59.43	90.25	7.34	20
LH Water	106.55	115.25	7.25	20

[a] UV$_{254}$ is an absorbance measurement using a cell of 10 mm length. UV$_{254}$ can characterize the organic pollutant with aromatic compounds.

[b] SUVA: specific ultraviolet absorbance at 254 nm, SUVA = (UV$_{254}$/DOC) × 100, the value of SUVA is strongly correlated with percent aromaticity of natural organic matter in water. SUVA is used to characterize the aromaticity of natural organic matter.

[c] Hardness is to denote the concentration of Ca^{2+} and Mg^{2+}. The value of hardness is calculated as CaCO$_3$ (mg L^{-1}).

[d] Alkalinity is to denote the concentration of HCO$_3^-$ and CO$_3^{2-}$. The value of alkalinity is calculated as CaCO$_3$ (mg L^{-1}).

the inhibiting effect on the removal effectiveness both in single ozonation and catalytic ozonation. In natural water, there are many matrix, such as natural organic matters (NOMs), rigidity and alkalinity. The water quality parameters of SH Water and LH Water are shown in Table 1. In LH Water, DOC, hardness, and alkalinity were all much higher than that in SH Water. Both in the single ozonation and catalytic ozonation, NOM and alkalinity are the main inhibiting factors, as the inhibitor of •OH. Therefore, both in the single ozonation and catalytic ozonation, the removal effectiveness of TCA in LH Water were lower than that in SH Water. This result is due to the high •OH scavenging capacity by the water matrix in SH Water, such as NOM and alkalinity.

To define and calibrate ozonation and catalyzed ozonation with respect to its oxidation capacity, it is necessary to estimate the oxidant concentrations whereas ozone can be readily measured, there are no fast and easy methods to determine the •OH concentration during ozonation and catalyzed ozonation. The R_{ct} concept was used to quantify oxidation during single ozonation and catalytic ozonation in the presence of the raw bauxite in this study. The selected probe compound was pCBA, which reacts with •OH with a second order rate constant $k = 5.2 \times 10^9$ (mol L^{-1})$^{-1}$ s^{-1} [37]. The R_{ct} value, which is defined as the ratio of the •OH exposure to the ozone exposure (see Eq. (1)), can be determined by measuring decreases of the concentrations of pCBA and ozone during ozonation [37]. For high scavenging capability for •OH of pCBA, natural organic matter and HCO$_3^-$ do not react with •OH both in ozonation and catalyzed ozonation in the presence of pCBA. Therefore, the reaction of •OH in natural water is shown in Eq. (2). Rearranging and integrating Eq. (2) obtains Eq. (3) that is shown below. Eq. (3) shows that the relative decrease in concentration of a probe compound at any time t is an indirect measurement of the •OH exposure, for the reaction period from time $t = 0$ until that reaction time. According to Eqs. (1) and (3), Eq. (4) can be obtained. Based on Eq. (4), R_{ct} can be determined.

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

$$\frac{d[pCBA]}{dt} = k_{\cdot OH/pCBA}[\cdot OH][pCBA] \tag{2}$$

$$\ln\left\{\frac{[pCBA]_t}{[pCBA]_0}\right\} = -k_{\cdot OH/pCBA}\int_0^t [\cdot OH]\,dt = -k_{\cdot OH/pCBA}R_{ct}\int_0^t [O_3]\,dt \tag{3}$$

Table 2
R_{ct} of ozonation and catalyzed ozonation in natural water.

	R_{ct} in ozonation alone	R_{ct} in catalyzed ozonation
SH Water	3.98×10^{-7}	4.92×10^{-6}
LH Water	7.58×10^{-8}	2.02×10^{-6}

$$\ln\left\{\frac{[pCBA]_t}{[pCBA]_0}\right\} = -k_{\cdot OH/pCBA}R_{ct}\int_0^t [O_3]\,dt \tag{4}$$

The R_{ct} value can express •OH yields both in the single ozonation and in catalytic ozonation. Table 2 summarizes R_{ct} values of the single ozonation and catalytic ozonation both in SH Water and in LH Water. In the natural water, there are many •OH inhibitors. The presence of •OH inhibitor can affect the formation of •OH. In the single ozonation, ozone can decompose to form •OH. The variation of water matrix in SH Water and LH Water, resulted in the difference of R_{ct}. The presence of NOM and alkalinity inhibited the generation of •OH, which resulted in lower R_{ct} in LH Water. The presence of the raw bauxite improved the •OH yields in the natural water. The raw bauxite catalyzed ozone decomposition to form •OH. Therefore, catalytic ozonation can enhance the removal effectiveness of TCA in the natural water. However, the R_{ct} value in SH Water was higher than that in LH Water. The presence of NOM and alkalinity inhibits the •OH formation during catalyzed ozonation with raw bauxite faintly.

3.5. Effect of catalyst dosage on catalytic activity

The catalyst dosage is an important parameter in the catalytic ozonation, and •OH would be expected at the higher catalyst dosage. In addition, in order to avoid the use of the excess catalyst, it is necessary to find out the optimum catalyst dosage for the efficient application. Many authors have investigated the reaction rate as a function of the catalyst dosage in the catalytic ozonation process using various catalysts. The influence of catalyst dosage from 100 mg L^{-1} to 500 mg L^{-1} on the degradation of TCA has been analyzed. Fig. 8 shows the effect of various catalyst dosages on the removal effectiveness of TCA by catalytic ozonation. It seems that the catalyst dosages exertes a positive influence on the both removal rate appreciably. These results demonstrate the effectiveness of
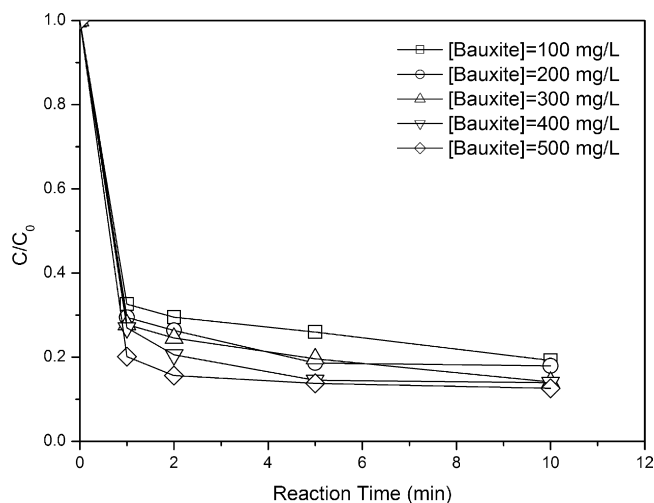
Fig. 8. Effects of bauxite dosage on the efficiency of catalyzed ozonation. Experiment conditions were: [TCA]$_0$ = 100 ng L^{-1}, [O$_3$]$_0$ = 0.5 mg L^{-1}, solution pH = 6.0 adjusted with phosphate buffer solution, the reaction time was 10 min.
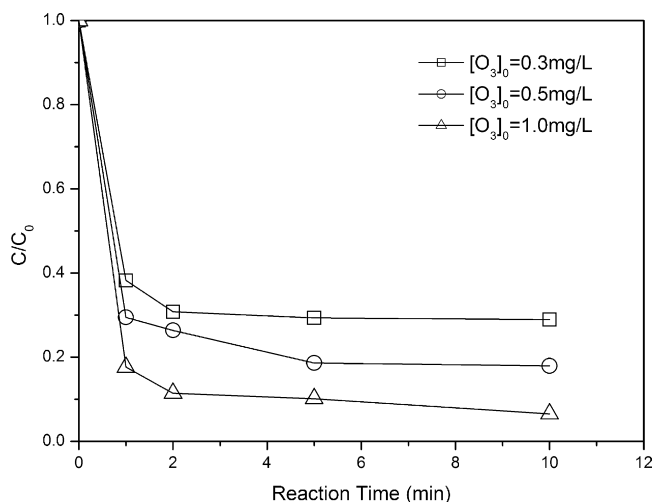
Fig. 9. Effects of ozone dosage on the efficiency of catalyzed ozonation. Experiment conditions were: $[TCA]_0 = 100 \, ng \, L^{-1}$, $[bauxite]_0 = 200 \, mg \, L^{-1}$, solution pH = 6.0 adjusted with phosphate buffer solution, the reaction time was 10 min.

Table 3
Recycling of the raw bauxite in catalyzed ozonation.[a]

Recycling times	The removal effectiveness of TCA (%)
1 time	95.2
2 times	94.3
3 times	92.4
4 times	95.4
5 times	98.5

[a] Experiment conditions were: $[TCA]_0 = 100 \, ng \, L^{-1}$, $[O_3]_0 = 0.5 \, mg \, L^{-1}$, $[bauxite]_0 = 200 \, mg \, L^{-1}$, the reaction time was 10 min.

Fig. 10. Variation of the residual aluminum concentration in water after catalyzed ozonation. Experiment conditions were: $[TCA]_0 = 100 \, ng \, L^{-1}$, $[O_3]_0 = 0.5 \, mg \, L^{-1}$, $[bauxite]_0 = 200 \, mg \, L^{-1}$, solution pH = 6.0 adjusted with phosphate buffer solution, the reaction time was 10 min.

the raw bauxite as a catalyst in catalyzed ozonation process. The removal effectiveness of TCA was enhanced by increasing the raw bauxite dosage. In catalyzed ozonation process, many literatures reported that the dosage of catalyst was positive for the removal of organic pollutants [27–29]. More dosage of catalyst can give more active site for the catalytic reaction. The increasing of the active site is accounted for the removal of the organic pollutant. In general, many literatures reported that the surface hydroxyl groups of the metal oxide were the active site of catalyzed ozonation [17,20,23]. More dosage of catalyst can give more surface hydroxyl groups for the catalyzed ozonation reaction. The raw bauxite is a mixture of γ-AlOOH, γ-Al$_2$O$_3$, SiO$_2$, and so on. The surface hydroxyl groups covered the surface of the raw bauxite. Fig. 4 confirms this result. More dosage of the raw bauxite can give more surface hydroxyl groups as active site of catalyzed ozonation reaction. Therefore, there is a positive effect of the dosage of the raw bauxite.

3.6. Effect of ozone dosage on catalytic activity

Another important parameter that influences the catalytic ozonation process is the ozone dosages. The experiments have been carried out with varying the ozone dosage from $0.3 \, mg \, L^{-1}$ to $1.0 \, mg \, L^{-1}$. Fig. 9 shows the influence of ozone dosage on the removal effectiveness of TCA as a function of the reaction time. Obviously, the ozone dosage influenced the removal effectiveness positively. When the ozone dosage increased from 0.3 $mg \, L^{-1}$ to $1.0 \, mg \, L^{-1}$, the removal effectiveness of TCA in catalytic ozonation increased from 71.0% to 93.5% in 10 min. This enhancement of the removal effectiveness is believed to be due to the generation of more •OH.
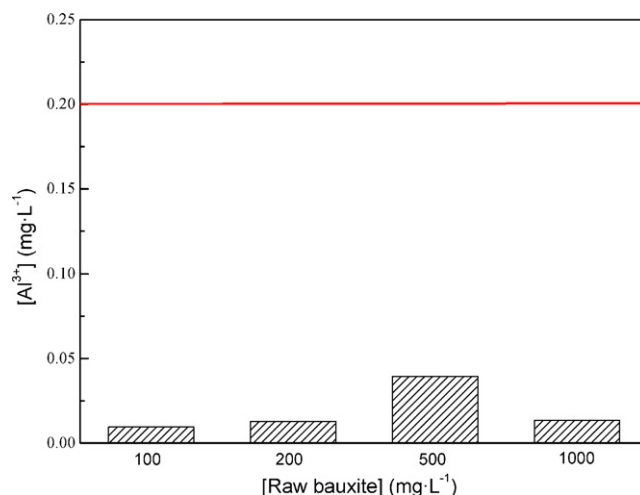
3.7. Recycling of the raw bauxite in catalyzed ozonation

The raw bauxite was further used repeatedly in the catalyzed ozonation in order to find out whether the activity of the raw bauxite would deplete. The raw bauxite particles used in the batch experiment were reclaimed by filtration through a cellulose acetate filter, then dried at 70 °C, and reused in the catalyzed ozonation. The variation of the removal effectiveness of TCA in catalyzed ozonation was very faint, shown in Table 3. When the raw bauxite was reused for five times, the removal effectiveness of TCA was 98.5%. The results indicate that the activity of the raw bauxite is relative stable.

3.8. Concentration of the residual aluminum in water after catalyzed ozonation

On the basis of XRD analysis, boehmite (γ-AlOOH), kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) and quartz (SiO$_2$) are the main composition of raw bauxite. The presence of silicates in the composition helps to keep aluminum complexed but not as free. Additionally, the concentration of the residual aluminum in drinking water has relationship with health risk of human. Therefore, the residual aluminum was concerned. So, the concentration of the residual aluminum after catalyzed ozonation was analyzed, as shown in Fig. 10.

Based on Fig. 10, it is conclude that there is the dissolution of aluminum after catalyzed ozonation. As the dosage of the raw catalyst increased, the concentration of the residual aluminum increased. However, the concentration of the residual aluminum was faint. This concentration lever of the residual aluminum was not dangerous to human health. In China, the criterion of the residual aluminum is $0.2 \, mg \, L^{-1}$, shown in Fig. 10 as the red line. The concentration of the residual aluminum is lower than criterion of drinking water in China. Therefore, the application of catalyzed ozonation with the raw bauxite in drinking water treatment is feasible.

4. Conclusions

Based on experimental data the following conclusion can be drawn:

(1) 2,4,6-Trichloroanisole was effectively removed by catalytic ozonation in the presence of the raw bauxite. Increasing in both the catalyst and the ozone dosage were able to improve the removal effectiveness of TCA. The presence of NOM and alkalinity inhibited the •OH formation faintly during the catalytic

ozonation with the raw bauxite. Catalytic ozonation was an effective technology for removing TCA in drinking water.

(2) According to TBA inhibiting experiments, $^{\bullet}$OH was generated in the catalytic ozonation process in the presence of the raw bauxite. By determination of R_{ct} values, the generation of more $^{\bullet}$OH was accounted for the enhancement of TCA degradation.

(3) Catalytic ozonation in the presence of the raw bauxite was an effective technology for removing TCA in natural water. The presence of NOM and alkalinity inhibited the $^{\bullet}$OH formation faintly during the catalytic ozonation with the raw bauxite.

Acknowledgements

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