Enhanced inhibition of bromate formation in catalytic ozonation of organic pollutants over Fe–Al LDH/Al₂O₃

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ABSTRACT

Fe–Al layered double hydroxides (Fe–Al LDH, the molar ratio of Fe(II) to Fe(III) was about 1:10) was successfully supported and highly dispersed on mesoporous Al₂O₃ based on the X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis. Fe–Al LDH/Al₂O₃ was more efficient in inhibiting BrO₃[−] formation and removing organic pollutant taking ozonation alone as control. Further investigation indicated that BrO₃[−] reduction by surface Fe(II) was responsible to the complete inhibition of BrO₃[−] formation. Fe(II) was reduced from the Fe(III)-intermediates complex via an electron transfer process and the reaction of Fe(III) and HO₂[−]/O₂[−] in catalytic ozonation. The amount of surface Fe(II) in catalytic ozonation of amitrole (AMT), phenazone (PZ) and 2,4-dichlorophenoxyacetic acid (2,4-D) was 0.34, 2.47 and 3.30 μmol/g, which proved that most of Fe(II) was generated from the reaction of ozone and Fe–Al LDH/Al₂O₃ since 0.33 μmol/g of Fe(II) existed within the catalyst. The increase of ozone amount and the formation of Fe(III)-intermediates complex could enhance the Fe(II) generation, leading to more efficient inhibition of BrO₃[−] formation. Finally, Fe–Al LDH/Al₂O₃ still showed effectiveness in the inhibition of BrO₃[−] and TOC removal for a raw drinking water under the realistic conditions, which could be applied to the BrO₃[−] mineralization in catalytic ozonation of Br[−]-containing drinking water.

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1. Introduction

The application of ozonation in drinking water treatment is widespread throughout the world to address water quality problems caused by taste, odor, micropollutants, etc. [1]. However, there exists an important scientific challenge: controlling BrO₃[−] formation as a result of the ozonation of Br[−]-containing water [1]. Hence, it is very important to minimize or eliminate BrO₃[−] in water treatment due to its carcinogenicity and nephrotoxicity [2].

Three approaches could be used to control BrO₃[−] contamination in the water supply: removal of Br[−] before BrO₃[−] formation via membrane filtration and ion exchange [3,4]; control of BrO₃[−] formation during ozonation by lowering solution pH or adding H₂O₂ or NH₃ [5,6]; and removal of BrO₃[−] after ozonation via adsorption or chemical reduction [7,8]. Among these methods, the minimization of BrO₃[−] formation during ozonation appears as the most promising one since the combination with other treatment process is not necessary. Although the NH₃ addition and pH depression could result in bromate reduction of roughly 50% and may be applicable in treatment plants [9], if source waters have relatively

high NH₃ concentration and alkalinity, the efficiencies of those processes may well be found insufficient [10]. Hence, novel methods are still urgently needed to minimize bromate formation during ozonation.

Recently, there are increasing interests on catalytic ozonation with various catalysts to improve the oxidation efficiency of ozonation [11–13]. Our and other studies have verified that more reactive oxygen species were generated from the interaction of ozone and surface Lewis acid sites of catalysts [14–16]. The organic compounds could be removed more efficiently, while few studies have been conducted to investigate the control of BrO₃[−] formation during the heterogeneous catalytic ozonation [17,18].

In ozonation process, the removal of organic compounds and the oxidation of Br[−] to BrO₃[−] are competitive reactions in consuming the reactive oxygen species [9,19]. BrO₃[−] is also a strong oxidant that can be reduced to Br[−] in water by reduced iron species (Fe²⁺ or Fe⁰) [8]. Moreover, our and other studies have verified that more Fe(II) could be generated from the reaction of Fe(III) and HO₂[−]/O₂[−] due to the complexation of Fe(III) with the oxygen functional groups (–OH and –COOH) of intermediates [20,21]. For example, the reaction rate constant of Fe(III) with HO₂[−]/O₂[−] was only 1.4 × 10⁵ M^{−1} s^{−1}, while it could be greatly enhanced to 2.0 × 10⁶ M^{−1} s^{−1} due to the complexation of Fe(III) with ligand

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[22,23]. Thus, it is necessary to investigate the degradation process of organic compounds with different structure and its influence on the minimization of BrO_3^- formation in catalytic ozonation.

Recently, Fe–Al LDH has been used to reduce BrO_3^- in water via an adsorption process [24,25]. In this study, Fe–Al LDH was supported on mesoporous $\gamma\text{-Al}_2\text{O}_3$ by a hydrothermal hydrolysis process and its performance on catalytic ozonation of refractory organics and BrO_3^- control was also investigated. Three compounds with different structure were selected to evaluate the influence on BrO_3^- control during their degradation process. It has been proven that different amount of intermediates was formed in catalytic ozonation of organic compounds and the complexes of Fe(III) with intermediates ($-\text{OH}$ and $-\text{COOH}$) resulted in different amount of surface Fe(II), leading to different BrO_3^- reduction rate over Fe–Al LDH/ Al_2O_3 . These findings will facilitate the development of catalytic ozonation for purification of Br^- -containing water.

2. Experimental

2.1. Materials and reagents

Aluminum *i*-propoxide, glucose and NaOH were purchased from Beijing Chemical Reagents (Beijing, China). $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, KBrO_3 and KBr were acquired from Yili Company (Beijing, China). 2,4-dichlorophenoxyacetic acid (2,4-D), phenazone (PZ), and amitrole (AMT) were purchased from Acros (Geel, Belgium) and their molecular structures were also provided (Table S1). Raw source water used in this study was obtained from Huanghe River, Zhengzhou, Henan Province, China. All other chemicals were analytical grade and used without further purification. All aqueous solutions were prepared with deionized water.

2.2. Catalyst preparation

Mesoporous Al_2O_3 was prepared as described previously [14]. Based on the reference [24], Fe–Al LDH was supported on Al_2O_3 by co-precipitation method with continuous nitrogen gas bubbling. In a typical procedure, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Fe/Al molar ratio was 1:1) were dissolved in 3 mL of deionized water and 2 g Al_2O_3 was then added to this solution. After the pH was adjusted to 7.0 slowly using NaOH solution (3.0 mol/L), the resulting suspension was transferred immediately into Teflon tubes and kept at 373 K for 24 h. The solid product was isolated by centrifuging, washing with deionized water and finally drying overnight at 40 °C in a vacuum. The obtained Fe–Al LDH/ Al_2O_3 was stored in tightly capped bottles for further use. For a reference, Fe–Al LDH was also prepared by repeating the same procedure described above except the addition of mesoporous Al_2O_3 .

2.3. Characterization

Powder X-ray diffraction (XRD) of the catalyst was recorded on an XDS-2000 Diffractometer (Scintag, Cupertino, CA) with Cu K_α radiation ($\lambda = 1.54059 \text{ \AA}$). The X-ray photoelectron spectroscopy (XPS) data of Fe–Al LDH/ Al_2O_3 was taken on an AXIS-Ultra instrument from Kratos using monochromatic Al K radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charge effects, the binding energies were calibrated using the C_{1s} hydrocarbon peak at 284.80 eV. The zeta potential of catalysts in the KNO_3 ($1 \times 10^{-3} \text{ M}$) solution was measured with a Zetasizer 2000 (Malvern, Worcestershire, UK) with three consistent readings.

2.4. Procedures and analysis

A 300-mL three-neck flask was used as a reactor and the reaction temperature was maintained at 20 °C. In a typical experiment, 220 mL deionized water was placed into the reactor, which was continuously magnetically stirred, and oxygen-ozone gas was bubbled into the reactor to obtain 2.0 mg/L ozone aqueous solution (the oxygen-ozone gas was stopped when the catalytic ozonation reaction started). Then, aqueous suspensions with the desired amount of catalyst and organic compounds, Br^- or BrO_3^- were added into the reactor, which was sealed and magnetically stirred, with a final total volume of 250 mL. In all experiments, the pH of the suspensions was not adjusted during the reaction. In general, the initial suspension pH was about 6, which remained the same within 0.3 units at the end.

Samples were taken at given time intervals (the residual O_3 was liberated by N_2 purging) and filtered through a Millipore filter (pore size 0.45 μm) to remove particles. The filtrates were then divided into several parts for respective measurements of total organic carbon (TOC), BrO_3^- and Br^- by TOC analyzer (TOC-VCPH, SHIMADZU) and ICS-2000 ion chromatography (Dionex Corporations, USA). The ozone was generated by a 3S-A5 laboratory ozonizer (Tonglin Technology, China). All of the experiments were repeated three times.

Fe(II) on the surface of Fe–Al LDH/ Al_2O_3 was determined using a phenanthroline spectrophotometric method [26]. 1,10-phenanthroline was used as a probe agent for the detection of Fe(II), and could take up Fe(II) from the surface of the solid-phase Fe–Al LDH/ Al_2O_3 via a specific chelating reaction. The samples were prepared as follows: the catalyst dispersions under different conditions were filtered and the resulting solid was resuspended in 10 mL of deionized water. After the addition of 1.0 mL of 1,10-phenanthroline solution and reaction for 10 min, the new dispersion was filtered and the filtrates were analyzed by recording the absorbance at 510 nm. As a reference, no Fe(II) was detected in the filtrates from Fe–Al LDH/ Al_2O_3 dispersions from different reaction conditions. The concentration of ozone dissolved in the aqueous phase was determined with the indigo method [27].

The samples for GC–MS analysis were prepared by the following procedure. The suspensions of Fe–Al LDH/ Al_2O_3 with different pollutants after reaction with ozone for 15 min were filtered. The resulting solution and Fe–Al LDH/ Al_2O_3 particles were evaporated by the freeze-drying method separately. The residues were dissolved with 2.0 mL dichloromethane and the main products on the surface of Fe–Al LDH/ Al_2O_3 could be extracted by dichloromethane. Then, the suspension was trimethylsilylated with 0.1 mL of hexamethyldisilazane and 0.05 mL of chlorotrimethylsilane at room temperature. The mixture was shaken vigorously for about 60 s and then allowed to stand for 5 min at room temperature. Precipitate was separated by filtration prior to chromatographic analysis. GC–MS analysis was carried out on Agilent 6890GC/5973MSD with a DB-5 MS capillary column. The chromatographic conditions were as follows: the initial column temperature was held for 20 min at 353 K, ramped at 3.5 K/min to 553 K.

3. Results and discussion

3.1. Characterization of Fe–Al LDH/ Al_2O_3

As shown in Fig. 1, the as-prepared Fe–Al LDH exhibited symmetric reflections of the basal (003) and (006) planes, which were the characterization of typical layered structure of LDH. However, no XRD diffraction peaks of LDH structure were observed in the supported sample, which was presumably due to its low loading

Fig. 1. XRD patterns of as-prepared Fe-Al LDH. The inset showed the XRD patterns of (a) Al_2O_3 , (b) Fe-Al LDH/ Al_2O_3 .

content (10wt%) and high dispersion on Al_2O_3 . Therefore, the supported sample was designated Fe-Al LDH/ Al_2O_3 .

The oxidation state of iron on the surface of Fe-Al LDH/ Al_2O_3 was confirmed by XPS analysis and the results were shown in Fig. 2. The peaks at 709.0 and 711.5 eV for the binding energies of $\text{Fe}2p_{3/2}$ were assigned to Fe(II) and Fe(III) species, in which the molar ratio of Fe(II) to Fe(III) on the surface of Fe-Al LDH/ Al_2O_3 was about 1:10. Fig. 3 presented the zeta potential changes of different samples with the pH of the solution. The upward shift of PZC (point of zero charge) from 6.3 for Al_2O_3 used as support to 9.3 was observed after the loading of Fe-Al LDH. Hence, the positively charged surface should favor the BrO_3^- adsorption on the surface of Fe-Al LDH/ Al_2O_3 at neutral pH values. Besides, the stronger Lewis acid sites within the catalyst should cause the more chemisorbed water enhancing the interaction with ozone, resulting in higher catalytic reactivity [14].

3.2. Catalytic ozonation of organic pollutant and BrO_3^- formation inhibition over Fe-Al LDH/ Al_2O_3

Fig. 4 compared the TOC removal of 2,4-D in ozonation and catalytic ozonation over Fe-Al LDH/ Al_2O_3 . Obviously, the TOC removal efficiency in catalytic ozonation was much higher than that in ozonation alone. About 82% of TOC was removed under the latter condition at a reaction time of 60 min, while only 28% of TOC was removed under the former condition. Fig. S1 depicted the effect of *tert*-butanol (a strong $\cdot\text{OH}$ radical scavenger) on 2,4-D

Fig. 2. XPS spectrum of $\text{Fe}2p$ in Fe-Al LDH/ Al_2O_3 .

Fig. 3. Plot of the zeta potential as a function of pH for different suspensions in the presence of KNO_3 (1×10^{-3} mol/L): (a) Al_2O_3 , (b) Fe-Al LDH/ Al_2O_3 .

Fig. 4. TOC removal efficiency of 2,4-D (a) in ozonation and (b) catalytic ozonation over Fe-Al LDH/ Al_2O_3 (initial pH 6.0, catalyst concentration 0.25 g/L, initial concentration of ozone in solution 2.0 mg/L, 2,4-D concentration 45.2 $\mu\text{mol/L}$).

degradation in ozonation and catalytic ozonation over Fe-Al LDH/ Al_2O_3 . Obviously, 2,4-D removal efficiency was greatly inhibited from 98% to 70% and from 78% to 65% via the addition of *tert*-butanol in ozonation and catalytic ozonation, respectively. *Tert*-butanol exhibited a more negative effect on the 2,4-D degradation in catalytic ozonation over Fe-Al LDH/ Al_2O_3 than that in ozonation process. It indicated that $\cdot\text{OH}$ was present and involved in efficiently catalytic ozonation of 2,4-D and Fe-Al LDH/ Al_2O_3 accelerated more ozone transformation into $\cdot\text{OH}$ radicals.

The dissolved Fe^{3+} and Al^{3+} in solution after reaction were measured using ICP-AES to confirm the degree of dissolution of Fe and Al from catalyst. As shown in Table S2, there was no Fe^{3+} and 0.18 mg/L Al^{3+} in solution for Fe-Al LDH/ Al_2O_3 , while the concentration of leached Fe^{3+} and Al^{3+} from Fe-Al LDH was 5.58 and 6.38 mg/L. Especially, Fe-Al LDH/ Al_2O_3 could be reused for at least six cycles and exhibited no significant loss of activity in Fig. S2. It indicated that Fe-Al LDH/ Al_2O_3 was an effective and stable catalyst for catalytic ozonation. Moreover, the ozonation by-product, BrO_3^- was also efficiently controlled in catalytic ozonation process. As shown in Fig. 5, the BrO_3^- concentration increased quickly in ozonation and reached 20 $\mu\text{g/L}$, which is considerably above the allowable limit of 10 $\mu\text{g/L}$. In contrast, almost no BrO_3^- was detected in Fe-Al LDH/ Al_2O_3 - O_3 system, indicating that the BrO_3^- formation was completely inhibited. Moreover, even when the Br^- initial concentration and ozone dose increased, the BrO_3^- concentration after 60 min reaction is still below 10 $\mu\text{g/L}$ in catalytic ozonation (Fig. S3).

Fig. 5. BrO_3^- formation in (a) ozonation and (b) catalytic ozonation over Fe–Al LDH/ Al_2O_3 (initial pH 6.0, catalyst concentration 0.25 g/L, initial concentration of ozone in solution 2.0 mg/L, 2,4-D concentration 45.2 $\mu\text{mol/L}$, initial Br^- concentration 1.25 $\mu\text{mol/L}$).

3.3. Mechanism for BrO_3^- inhibition over Fe–Al LDH/ Al_2O_3

As shown in Fig. 6, about 45% of BrO_3^- (0.33 $\mu\text{mol/L}$) was adsorbed on Fe–Al LDH/ Al_2O_3 and 0.14 $\mu\text{mol/L}$ Br^- was generated only in the presence of PZ and BrO_3^- , which could be attributed to the BrO_3^- reduction by Fe(II) species formed during Fe–Al LDH/ Al_2O_3 preparation based on XPS analysis [28]. However, 82% of BrO_3^- (0.64 $\mu\text{mol/L}$) was converted into Br^- (0.40 $\mu\text{mol/L}$) in the Fe–Al LDH/ Al_2O_3 – O_3 system during the PZ degradation process.

Fig. 6. Br^- formation (B) as a result of BrO_3^- reduction (A) in (a) ozonation, (b) BrO_3^- adsorption and (c) catalytic ozonation over Fe–Al LDH/ Al_2O_3 (initial pH 6.0, catalyst concentration 0.25 g/L, initial concentration of ozone in solution 2.0 mg/L, initial BrO_3^- concentration 0.78 $\mu\text{mol/L}$, PZ concentration 45.2 $\mu\text{mol/L}$).

The reduction efficiency of BrO_3^- increased with the increase of ozone dose and BrO_3^- initial concentration (Figs. S4 and S5). In contrast, neither BrO_3^- reduction nor Br^- formation was observed in PZ– O_3 system. Moreover, BrO_3^- reduction and TOC removal of 2,4-D solution were almost completely inhibited with the addition of phosphate into Fe–Al LDH/ Al_2O_3 – O_3 system (Fig. 7). It was because that the adsorption of BrO_3^- and the interaction of O_3 with Fe–Al LDH/ Al_2O_3 were both greatly inhibited, since phosphate could cause permanent blockage of the catalysts active surface sites and decrease their catalytic activity via replacing the surface hydroxyl group and forming complex with Fe(III) within the catalyst [29–31]. The above results confirmed that BrO_3^- reduction happened on the surface of Fe–Al LDH/ Al_2O_3 .

To confirm the roles of Fe(II) and the complexes of iron with organics for the BrO_3^- reduction to Br^- , the removal of BrO_3^- in the presence of Fe(II), Fe(III) and/or HA without ozone was further investigated. As shown in Fig. S6, only 22.4% of BrO_3^- was reduced to Br^- by Fe(II) alone (curve a) at 14 h due to the rapid oxidation of Fe(II) by oxygen in water, while the reduction rate was significantly enhanced and 81.6% of BrO_3^- was reduced (curve b) in the presence of HA and Fe(II). While no significant BrO_3^- reduction was observed in Fe(III) and HA containing solution (curve c) because the Fe(II) formation via an electron transfer process within the complex of HA–Fe(III) is a very slow process (about several hundred hours) [28]. The results indicated that BrO_3^- was reduced by Fe(II) [24,25] and enhanced by the complexes of iron and HA. Fig. 8 showed the BrO_3^- reduction was significantly promoted in catalytic ozonation of different organic pollutant with the order of $\text{AMT} < \text{PZ} < 2,4\text{-D}$. The amount of surface Fe(II) on Fe–Al LDH/ Al_2O_3 in catalytic ozonation of different organic pollutant was also determined and the results were shown in Table 1. Obviously, 0.33 $\mu\text{mol/g}$ of Fe(II) was detected on the surface of Fe–Al LDH/ Al_2O_3 in aqueous suspension, which was attributed to the formed Fe(II) during the catalyst preparation (XPS analysis in Fig. 2). The amount of surface Fe(II) increased greatly during the catalytic ozonation of different organic pollutants and the amount of surface Fe(II) was 0.34, 2.47 and 3.30 $\mu\text{mol/g}$ for AMT, PZ and 2,4-D respectively, which agreed well with the results of BrO_3^- reduction. Fig. S7 further depicted the bromine mass balance during bromate reduction under different conditions. The results indicated that the structure of organic compound has a positive effect on the catalytic reduction of BrO_3^- and the surface Fe(II) for BrO_3^- reduction mainly came from the generation of Fe(II) in catalytic ozonation over Fe–Al LDH/ Al_2O_3 . Moreover, organic compounds

Fig. 7. Effect of PO_4^{3-} (5 mmol/L) on BrO_3^- reduction and the TOC removal of 2,4-D (inset) in catalytic ozonation over Fe–Al LDH/ Al_2O_3 : (a) without PO_4^{3-} , (b) with PO_4^{3-} (initial pH 6.0, catalyst concentration 0.25 g/L, initial concentration of ozone 2.0 mg/L, initial BrO_3^- concentration 0.78 $\mu\text{mol/L}$, initial 2,4-D concentration 45.2 $\mu\text{mol/L}$).

Fig. 8. Effect of organic pollutant on BrO_3^- reduction in catalytic ozonation over Fe–Al LDH/ Al_2O_3 : (a) AMT, (b) PZ, (c) 2,4-D (initial pH 6.0, catalyst concentration 0.25 g/L, initial concentration of ozone in solution 2.0 mg/L, initial BrO_3^- concentration 0.78 $\mu\text{mol/L}$, initial pollutants concentration 45.2 $\mu\text{mol/L}$).

and their catalytic ozonation byproducts had a positive effect on the enhancement of Fe(II) generation.

Hence, the intermediates generated in catalytic ozonation of 2,4-D, PZ and AMT over Fe–Al LDH/ Al_2O_3 for 15 min were monitored by GC–MS analysis (all the identified compounds were unequivocally identified using the NIST98 library database with fit values higher than 90%). As shown in Tables S3–S6, for PZ and 2,4-D, the detected product in solution was mainly small molecular organic compound, such as glycerol, indicating their structure was completely destroyed. While organic acid that containing carboxylic group was found on the surface of Fe–Al LDH/ Al_2O_3 . In contrast, no product for AMT was detected either in solution or on the surface of catalyst. According to the previous work [16,32], adsorbed $\text{HO}_2^-/\text{O}_2^-$ could be generated from the interaction of O_3 and Fe–Al LDH/ Al_2O_3 . The reaction rate constant of Fe(III) with $\text{HO}_2^-/\text{O}_2^-$ was $1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [22], while the rate constant could be increased ten times to $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ since the complexation of Fe(III) with ligands can decrease the Fe(III)/Fe(II) redox potential [20,23]. Clearly, the enhancement of surface Fe(II) formation could be attributed to the complexation of Fe(III) by oxygen functional

Fig. 9. BrO_3^- formation and TOC removal (inset) in (a) ozonation and (b) catalytic ozonation over Fe–Al LDH/ Al_2O_3 treatment of Br^- -containing raw drinking water (initial pH 8.0, catalyst concentration 0.25 g/L, initial concentration of ozone in solution 2.0 mg/L).

group of the intermediates in ozonation of different pollutants. It resulted in different BrO_3^- reduction rate in catalytic ozonation of different pollutant over Fe–Al LDH/ Al_2O_3 . The results indicated that the reduction of adsorbed BrO_3^- to Br^- was proven to be responsible for the BrO_3^- formation inhibition.

3.4. Performance of Fe–Al LDH/ Al_2O_3 for BrO_3^- inhibition in realistic conditions

The performance of Fe–Al LDH/ Al_2O_3 was further evaluated by the treatment of Br^- -containing raw drinking water via catalytic ozonation. In the raw water (Table S7), the concentration of TOC and Br^- was 3.6 mg/L and 1.07 $\mu\text{mol/L}$, and the alkalinity was 190 mg/L (CaCO_3). As shown in Fig. 9, the BrO_3^- concentration increased greatly with the reaction time (0.6 $\mu\text{mol/L}$ at 60 min) and almost no TOC was removed in ozonation. While the BrO_3^- formation was significantly inhibited in the presence of Fe–Al LDH/ Al_2O_3 and 25% of TOC could be removed in the above catalytic ozonation process. These findings may be applied to the minimization of BrO_3^- formation in catalytic ozonation of Br^- -containing raw drinking water.

4. Conclusions

Fe–Al LDH/ Al_2O_3 was proven to be an effective and stable ozonation catalyst. BrO_3^- formation could also be efficiently inhibited via surface reduction, especially in catalytic ozonation of organic pollutant with this order $\text{AMT} < \text{PZ} < \text{2,4-D}$. Surface Fe(II) was proven to be the reactive species for BrO_3^- reduction and its generation could be greatly enhanced by the Fe(III)-intermediates complex via an electron transfer process and the reaction of Fe(III) and $\text{HO}_2^-/\text{O}_2^-$ in catalytic ozonation. Hence, different amount of oxygen functional group generated in catalytic ozonation of organic pollutant would result in different BrO_3^- reduction rate over Fe–Al LDH/ Al_2O_3 . Fe–Al LDH/ Al_2O_3 still showed effectiveness for the inhibition of BrO_3^- formation and TOC removal for a Br^- -containing raw drinking water under the realistic conditions.

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Table 1

The amount of surface Fe(II) in catalytic ozonation of different organic pollutant over Fe–Al LDH/ Al_2O_3 .

Pollutant	Control	AMT	PZ	2,4-D
Fe(II) ($\mu\text{mol/g}$)	0.33	0.34	2.47	3.30

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2015.07.057>.

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