Catalytic ozonation of dimethyl phthalate and chlorination disinfection by-product precursors over Ru/AC

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ABSTRACT

Catalytic ozonation of dimethyl phthalate (DMP) in aqueous solution (5 mg/L) under various reactions was performed to examine the effect of catalyst dosage, catalyst particle size, ozone dosage, and gas flow rate on the mineralization of DMP. The mineralization of DMP can be achieved via ozonation and the presence of Ru/AC could greatly accelerate the mineralization rate of DMP in ozonation process. In the continuous experiment of the Ru/AC catalyzed ozonation of DMP, total organic carbon (TOC) removals were kept stable around 75% during 42 h reaction. No leaching of ruthenium was observed in the treated water samples. The treatment of natural water using $Ru/AC + O_3$, $Ru/AC + O_2$ and ozonation alone was studied. In the $Ru/AC + O_3$ process, TOC removals, the reductions of the haloacetic acid formation potentials (HAAFPs), and the reductions of the trihalomethane formation potentials (THMFPs) of 11 water samples were 22–44%, 39–61% and 50–65%, respectively. $Ru/AC + O_3$ process was much more effective than ozonation alone for TOC removal and the reduction of disinfection by-product formation potential (DBPFP) in the treatment of natural water. It is a promising water treatment technology.

1. Introduction

In recent years, many organic compounds possessing toxicity, carcinogenicity, mutagenicity and endocrine disrupting effect have resulted in very severe contamination of water. They must be effectively removed from water due to the safety of drinking water. However, most of them are recalcitrant to biodegradation. In this scenario, advanced oxidation processes are drawn many interests with regard to the investigation and evaluation of their efficiencies in the oxidation of the recalcitrant organic compounds [1].

Heterogeneous catalytic ozonation is one of the most promising advanced oxidation technologies. It combines ozone with supported catalysts to achieve the mineralization of dissolved organics at room temperature [2]. The main advantage of the supported catalysts is to avoid the separation of the solid and liquid phase. And also the supported catalysts can increase the ability of ozone for the abatement of refractory organic pollutants [3,4]. In the literatures on this subject, various metal oxides (CeO_2, TiO_2, MnO_2 and Co_3O_4) loaded on some porous materials (alumina, titanium dioxide, and active carbon (AC)) were studied [5–9]. These catalysts enhanced the degradation of organics in water and waste water.

However, their activities and stabilities should be improved further. The investigation of highly active and stable catalyst has never been stopped. Ruthenium catalysts were reported to be very active in wet air oxidation (WAO, also a kind of advanced oxidation technology) [10–12]. In our previous work it was also found Ru/Al_2O_3 was very active in the catalytic ozonation of DMP [13]. Unfortunately, like other metal catalysts, aluminium leaching was observed during the reaction. It is necessary to find stable support for ruthenium catalysts. Active carbon was stable when used as the support of ruthenium catalysts in WAO [14–16]. As the reaction conditions of WAO are more severe than those of ozonation, Ru/AC may be stable in catalytic ozonation.

In most experiments, the performances of catalysts were assessed in deionized water [7–9,17]. However, in practical process catalysts are often used to dispose of natural water. The effect of natural water on the performances of catalysts is very different from that of deionized water. In nature water, the present scavenger substances of hydroxyl radicals (carbonates) would restrain ozonation reaction [18,19]. So assessing the performances of catalysts in natural water is more meaningful than in deionized water.

In the research field of nature water treatment, it has been reported that ozonation could influence the chlorination disinfection by-product formation potential (DBPFP) of water [20,21]. However, the effect of catalytic ozonation on it has rarely been reported.

The main objective of this study was to investigate the catalytic ozonation of dimethyl phthalate (DMP) in aqueous solution

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and DBP precursors in natural water with Ru/AC. These two kinds of organics are both recalcitrant to biodegradation and will cause severe hazard to human health.

2. Experimental

2.1. Experimental procedures

The experimental apparatus is shown in Fig. 1, which was specifically described in our previous work [13]. Catalyst stability was assessed using continuous experiments, in which DMP solution was pumped into the reactor from the bottom. The reaction conditions were: catalyst dosage, 40 g; catalyst particle size, 1.0–1.5 mm; ozone dosage, 118 mg/h; gas flow rate, 300 mL/min; liquid flow rate, 20 mL/min. Catalyst activity in the treatment of DMP solution and natural water were assessed using semi-batch experiments. 1000 mL of solution was loaded into the reactor before ozone introduction. If not designated, the reaction conditions of the semi-batch experiments were: ozone dosage, 118 mg/h; gas flow rate, 300 mL/min; catalyst or support dosage (if necessary), 2 g/L; particle size, 1.0–1.5 mm; reaction temperature, 25 °C.

2.2. Materials

DMP (A.R.) was obtained from Tianjin Chemical Reagent No. 1 Plant (China). It was dissolved into deionized water to afford a solution of 5 mg/L. Coal-based active carbon (Coal-AC) was purchased from Jiangyan Chemical Auxiliary Agent Factory (Jiangyan, China). Ru/AC catalysts were prepared by the impregnation of Coal-AC into aqueous solution of ruthenium chloride for 2 h in a shaking incubator at a speed of 160 rpm and the temperature of 303 K. After impregnation the suspension was evaporated at 105 °C and then irradiated in a microwave oven (Sanyo, EM-202MS1, China) at 300 W (2.45 GHz) for 3 h. The theoretical load of ruthenium calculated from the amount of solution added by incipient wetness impregnation was 0.5 wt%. The ruthenium load was also determined by a thermogravimetric method, burning away the carbon support and measuring the weight of metal. Three reproducible determinations were within an error of 5%. Fresh catalyst value was comparable to the theoretical load. The characteristics of the Coal-AC and catalysts are shown in Table 1. The chemical composition of the active carbon ashes is shown in Table 2.

Natural water was sampled from Jingmi Cannel (China), where water is supplied to the Beijing Water Plant and then used as drinking water after purification. From upstream to downstream,
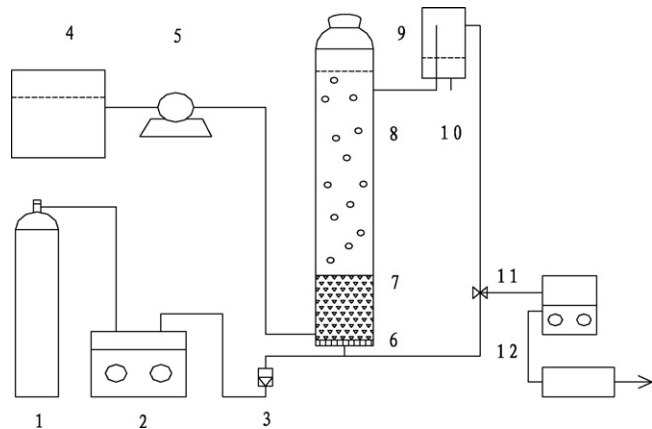

Fig. 1. The schematic diagram of experiment. (1) Oxygen cylinder, (2) ozone generator, (3) gas flow-meter, (4) solution tank, (5) diaphragm pump, (6) gas diffuser, (7) catalyst, (8) glass reactor, (9) gas and liquid separation device, (10) sample tap, (11) ozone gas monitor apparatus, and (12) vent ozone destructor.

Table 1
Characterization of the active carbon and catalyst.

Samples	Particle size (mesh)	BET specific surface area (m²/g)	Ash of AC (%)
AC	6–10	968.9	7.8
Ru/AC	6–10	945.2	–

there were 11 sampling sites (Qiaoxin Town, Beishicao Town, Xingshou Town, Nanshao Town, Machi Kou, Yangfan Town, Hotspring Town, Blue-dragon Bridge, Huoqiying Bridge, Changchun Bridge, and Yuyuan Pond, respectively). The characteristics of 11 raw water samples are summarized in Table 3. Before experiments, raw water was filtered (0.45 μm) to remove suspended particles, bacteria, and algae.

2.3. Analytical methods

The surface area of AC and catalysts was determined from the BET equation applied to the N_2 adsorption isotherms at 77 K, which were obtained using a Micromeritics Gemini 2370 adsorption unit. Elemental analysis of AC was performed with a Fison's Instruments Model 1108 CHS elemental analyzer. Ash content in AC was determined by incineration at 850 °C and ash chemical composition was estimated by X-ray fluorescence. The concentration of ozone in gas and aqueous solution was measured with iodometric and indigo method, respectively [22]. Total organic carbon (TOC) was analyzed with a TOC analyzer (Shimadzu, TOC-Vwp, Japan). Conductivity of water was determined by a conductivity meter (Rex, DDS-307, China). During Ru/AC catalyzed ozonaiton, water samples were withdrawn from the reactor periodically. After filtered with 0.45 μm membrane, the samples were immediately sent to analyze the concentration of the dissolved Ru by ICP-AES (Thermo Electron, IRIS Intrepid, USA).

Trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAFP) were determined according to the methods adopted from 5710B, 5710D, 6232B, 6251B, EPA 551 and EPA 552 [23,24]. Under standard conditions, the samples were buffered at a pH of 7.0, chlorinated with an excess of free chlorine, and stored at 25 °C for 7 d to allow the reaction to approach completion.

THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform, or $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr$, respectively) were analyzed with a liquid–liquid extraction-gas chromatographic method. A HP5890 II GC with an electron capture detector and an HP-5 capillary column (25 m × 012 mm × 0133 μm) was used. Good separations were achieved using 1 μl splitless injection, N_2 carrier gas with a linear velocity of 25 cm/s, and a make-up gas flow rate of 30 mL/min. The oven temperature program was set at 35 °C for 5 min, ramp of 20 °C/min to 180 °C, and final hold time of 3 min. This method achieved detection limits of 0.04–0.1 mg/L, recoveries of 79.48–120.40%, and reproducibilities (R.S.D.) of 2.02–11.15%. The total THM concentration (TTHM), as used by EPA for reporting purposes, was determined by simple summation of individual components.

HAAs (monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid and bromodichloroacetic acid, or MCAA, MBAA, DCAA, TCAA, BCAA, and BDCAA, respectively) were determined using a liquid–liquid extraction-diazomethane methylation gas chromatographic method adopted from EPA 552 and APHA 6251B and optimized for the laboratory conditions. A second and similar GC, detector and column were used. Good separations were achieved using a split 1 μl injection, a linear velocity of carrier gas (N_2) of 16 cm/s, and a make-up gas flow rate of 40 mL/min. The temperature program

Table 2
Chemical composition of the active carbon ashes (wt%).

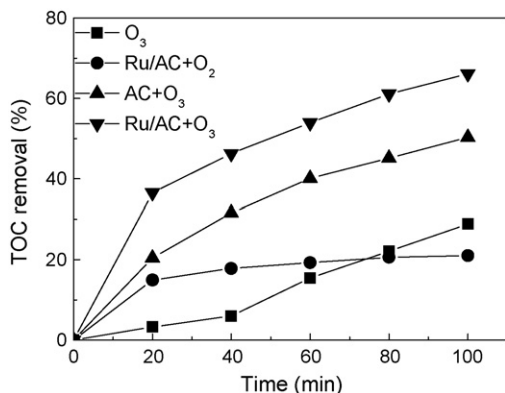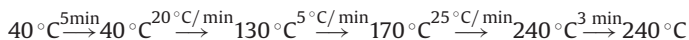| Fe_2O_3	MnO_2	TiO_2	CaO	K_2O	SO_3	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O
3.56	0.02	0.68	0.60	0.32	0.25	0.32	71.70	20.96	0.19	1.40

Fig. 2. TOC removal courses in the treatment of DMP aqueous solution with various processes. Reaction condition: ozone dosage, 118 mg/h; gas flow rate, 300 mL/min; catalyst or support dosage (if necessary), 2 g/L; particle size, 1.0–1.5 mm; reaction temperature, 25 °C.

was:

$$40\,°C \xrightarrow{5\,min} 40\,°C \xrightarrow{20\,°C/\,min} 130\,°C \xrightarrow{5\,°C/\,min} 170\,°C \xrightarrow{25\,°C/\,min} 240\,°C \xrightarrow{3\,min} 240\,°C$$

This method achieved detection limits of 0.04–0.2 mg/L, recoveries of 71.48–125.40%, and reproducibilities (R.S.D.) of 2.07–11.25%. Total HAAs (THAAs) were determined by simple summation of individual components.

3. Results and discussion

3.1. The catalytic activity of Ru/AC in the mineralization of DMP

Fig. 2 shows TOC removals in the treatment of DMP aqueous solution with various processes. In the Ru/AC+O_2 process TOC removal increased to 21% in 60 min reaction and hereafter kept that level. It indicates that Ru/AC had moderate adsorption capacity of DMP. In the ozonation alone process TOC removal was only 24% in 100 min reaction. In the AC+O_3 process TOC removal was 50% in 100 min reaction, which implies that the active carbon had obvious activity in catalytic ozonation. Rivera-Utrilla and Sanchez-Polo [17] reported that the activity of active carbon in catalytic ozonation was due to its mineral matter and carbon basicity on the surface. Ru/AC+O_3 led to the most effective process for the mineralization of DMP, in which TOC removal was 66% in 100 min reaction. Though DMP could not be completely mineralized in our experiments, the

catalyst of Ru/AC could obviously enhance the mineralization of DMP in ozonation process.

3.2. Effect of catalyst particle size and gas flow rate on TOC removal

Gas–liquid–solid catalytic ozonation is heterogeneous reaction system that involves chemical reactions on the catalyst surface and a series of consecutive-parallel steps of mass transfer. One kind of mass transfer is the external diffusion of reactant molecules (or ozone molecules) between the bulk liquid (or bulk gas) and gas–liquid interface. The other is the internal diffusion of reactant molecules (or by-product molecules) between the catalyst pores and external surface.

In our experiments, catalyst particle size could affect the internal diffusion and hence the mineralization rate of DMP. The effect of catalyst particle size on the mineralization rate is shown in Fig. 3(a). It can be seen that catalyst particle sizes equal to or lower than 1.0–1.5 mm did not affect the process rate. Hence, internal mass transfer resistance was limited to the catalyst particle sizes higher than 1.0–1.5 mm. Consequently, the catalysts with 1.0–1.5 mm particle sizes were used in the rest of experiments.
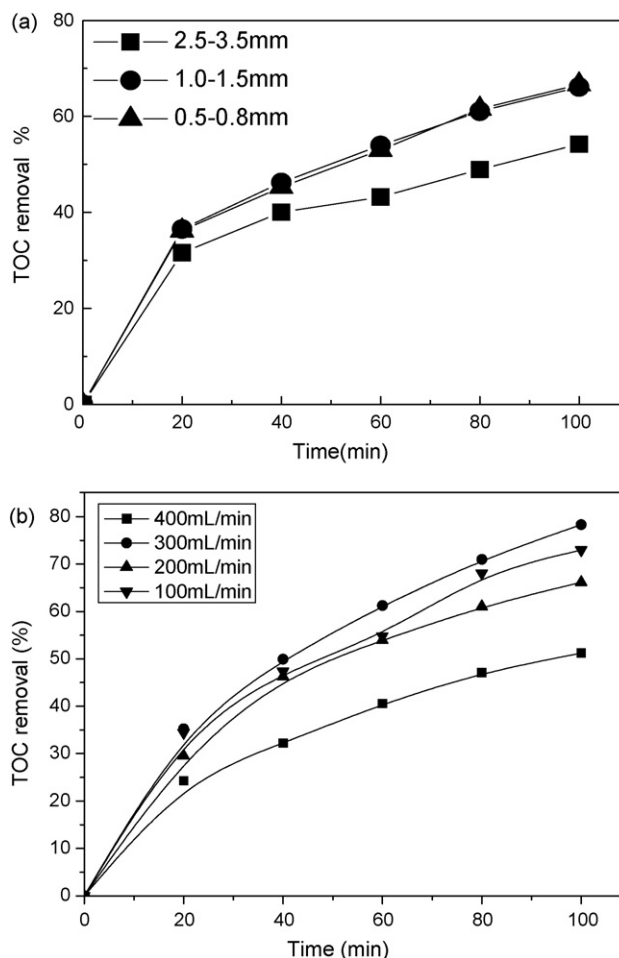
Table 3
Common water quality parameters of 11 water samples.

Sample	Sampling site	TOC (mg/L)	Conductivity (μs/cm)	pH
1	Qiaoxin Town	2.30	334	7.6
2	Beishicao Town	2.25	331	7.7
3	Xingshou Town	2.37	328	8.2
4	Nanshao Town	2.45	331	8.5
5	Machi Kou	2.46	328	8.2
6	Yangfan Town	2.53	326	8.3
7	Hotspring Town	2.45	310	8.4
8	Blue-dragon Bridge	2.49	308	8.3
9	Huoqiying Bridge	2.30	311	7.6
10	Changchun Bridge	2.34	303	7.4
11	Yuyuan Pond	3.29	370	7.2

Fig. 3. Effect of catalyst particle size (a) and gas flow rate (b) on TOC removal.

Gas flow rate could affect the external diffusion and thereby the mineralization rate of DMP. The effect of gas flow rate on the mineralization rate is shown in Fig. 3(b). It can be seen that gas flow rate had positive effect on the TOC removal rate in the investigated range. Once the gas flow rate was beyond 300 mL/min, the increase of the TOC removal rate was not obvious even when the gas flow rate increased further. It implies that in our reaction system, external mass transfer had a great effect on the reaction rate and was a determined rate step.

3.3. Effect of catalyst and ozone dosage on TOC removal

As inferred from Fig. 4(a), the higher the catalyst dosage, the higher the TOC removal rate. The trend was especially obvious for the catalyst dosage <2 g/L. As ruthenium is noble metal, little increase of catalyst dosage would cause great increase of operation expenditure. Thus 2 g/L of catalyst dosage was an appropriate selection in our experiments.

The effect of ozone dosage on the TOC removal rate during the DMP degradation is shown in Fig. 4(b). The TOC removal rate was found to increase as a function of ozone dosage. However, increasing ozone dosage beyond 118 mg/h did not result in significant enhancement of the TOC removal rate. In practical processes, ozone is very expensive. In order to save operation expenditure, ozone dosage of 118 mg/h was recommended. As a consequence, the remaining experimental runs were carried out with ozone dosage of 118 mg/h.
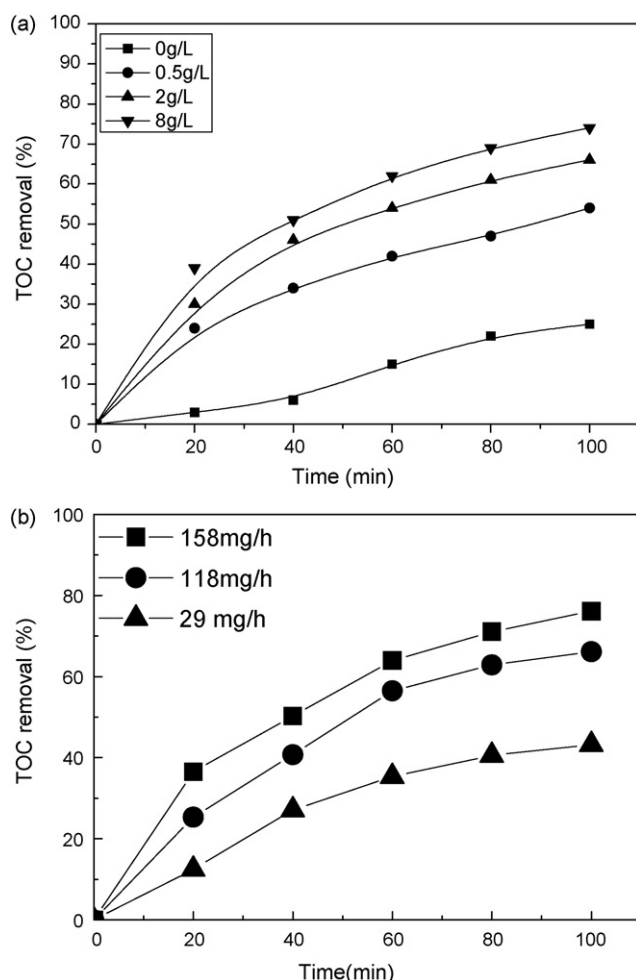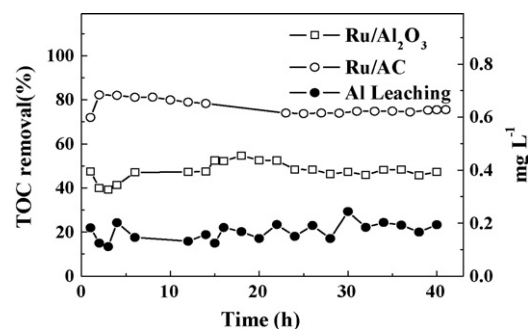

Fig. 5. The stability of Ru/Al$_2$O$_3$ and Ru/AC along with the time.

3.4. The stability of the Ru/AC catalyst

From above discussion, it can be concluded that Ru/AC was active in the catalytic ozonation of DMP. In order to investigate the stability of Ru/AC, continuous experiments were performed. The reaction conditions were mainly inferred from the results of the semi-batch experiments. The experimental results are shown in Fig. 5. The results of the Ru/Al$_2$O$_3$ catalyzed ozonation of DMP in continuous experiments were also given in Fig. 5, which was specifically described in our previous work [13]. In the Ru/AC catalyzed ozonation of DMP, the TOC removals were kept stable around 75%, higher than those with Ru/Al$_2$O$_3$. No Ru leaching was detected in the solution within the detection limit of ICP-AES (0.5 ppm). However, the leaching concentration of aluminium was about 0.15 mg/L in the Ru/Al$_2$O$_3$ catalyzed ozonation of DMP. So the catalyst of Ru/AC possessed higher activity and stability than Ru/Al$_2$O$_3$ in the catalytic ozonation of DMP.

3.5. The removal of HAAs and TOC in natural water with Ru/AC

As mentioned above, good catalyst should be active not only in deionized water but also in natural water. So the catalytic performances of Ru/AC were further investigated in natural water.

The results of the natural water treatment using ozonation alone, Ru/AC + O$_2$ and Ru/AC + O$_3$ processes are shown in Fig. 6. In the treatment of 11 water samples using the Ru/AC + O$_2$ process, the TOC removals were 4–10% after 100 min reaction. Thus the adsorption capacity of active carbon for organic compounds in natural water was weak. In the ozonation alone process, the TOC removals were 14–29% after 100 min reaction. In the Ru/AC + O$_3$ process, the TOC removals were 22–44% after 100 min reaction (Fig. 6(a)). It is obvious that the Ru/AC catalyst could effectively enhance the mineralization of organic compounds in the catalytic ozonation of natural water.

MCAA, MBAA, DCAA, TCAA, BCAA, and BDCAA were observed in the 11 water samples after they were chlorinated. Their concentrations were given in Table 4. The concentrations of TCAA, which possesses the highest carcinogenic risk among haloacetic acids, were higher than half of the HAAFPs of 11 water samples. The HAAFPs of the 11 water samples were about 100 μg/L, higher than the guideline value (60 μg/L) in EPA [23,25]. This indicates that the chlorinated water would cause high carcinogenic risk. Considering water safety, the source water of Beijing city should be pretreated to remove DBP precursors before chlorination.

From Fig. 6 it can be seen that after the 11 water samples were pretreated by the Ru/AC + O$_2$ process, the reductions of the HAAFPs and THMFPs were little. Thus the active carbon possessed weak adsorption capacity of DBP precursors. In the ozonation alone process, the reductions of the HAAFPs were 5–36%. In the Ru/AC + O$_3$

Fig. 4. Effect of catalyst (a) and ozone (b) dosage on TOC removal.

Table 4
Concentration of various haloacetic acids, HAAFPs and THMFPs of 11 water samples.

Water samples	MCAA (μg/L)	MBAA (μg/L)	DCAA (μg/L)	TCAA (μg/L)	BCAA (μg/L)	BDCAA (μg/L)	HAAFP (μg/L)	THMFP (μg/L)
1	6.5	26.1	0.2	51.6	1.3	6.8	92.5	151.1
2	7.3	28.4	0.2	53.9	1.4	6.4	97.7	147.9
3	7.5	27.3	0.0	51.5	0.9	6.2	93.3	161.7
4	7.6	26.4	0.0	52.0	0.8	6.1	92.7	157.9
5	7.8	26.4	0.1	52.7	0.8	6.2	94.3	164.9
6	8.7	28.2	0.1	55.1	0.9	6.0	99.0	164.1
7	7.0	27.2	0.6	60.7	1.6	6.3	103.4	161.4
8	6.8	26.4	0.3	56.5	1.5	6.1	97.9	167.6
9	6.0	25.1	0.1	55.9	1.6	6.2	94.8	152.9
10	6.9	25.9	0.4	57.5	1.8	6.3	99.0	150.9
11	27.5	31.1	0.0	76.2	2.1	7.0	144.0	222.8

process, the reductions of the HAAFPs were 39–61%. Only when the 11 water samples were pretreated by the Ru/AC + O$_3$ process, the HAAFPs could decrease to the values (33.5–59.8 μg/L) below the guideline value of EPA. So Ru/AC catalyzed ozonation was much more effective than ozonation alone for the reduction of HAAFP. It was also much more efficient than ozonaiton alone for the reduction of TCCA formation potential (Fig. 6(c)). Though in the Ru/AC + O$_3$ process the reductions of the HAAFPs of the 11 water samples were 50–65%, Ru/AC catalyzed ozonation was only a little more efficient than ozonation alone for the reduction of THMFP (Fig. 6(d)). This is perhaps because that the reductions of the HAAFPs of the 11 water samples in the ozonation alone process were already high.

From above discussions it can be concluded that Ru/AC catalyzed ozonation would be a promising water treatment process for the mineralization of hazardous organic compounds which are recalcitrant to biodegradation.

4. Conclusions

Ru/AC was an active catalyst in the catalytic ozonation of DMP and could improve greatly the mineralization of DMP in semi-batch experiments. In the continuous experiments of Ru/AC catalyzed ozonation of DMP, TOC removals were kept stable around 75% for 42 h and no ruthenium was observed in the samples withdrawn from the reactor. Ru/AC catalyzed ozonation was more effective than ozonation alone for TOC removals and the reductions of DBPFP in the treatment of natural water.

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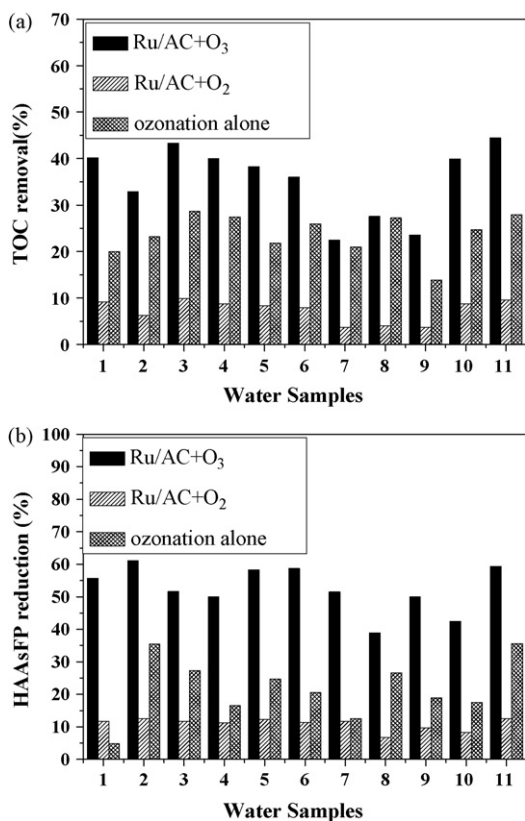

Fig. 6. TOC removal (a), HAAFP reduction (b), TCCA formation potential reduction (c), and THMFP reduction (d) in the treatment of natural water using the Ru/AC + O$_3$, Ru/AC + O$_2$ and ozonation alone processes.

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