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Heterogeneous catalytic ozonation of benzothiazole aqueous solution promoted by volcanic sand

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Abstract

This paper presents experimental results on the catalytic effect of volcanic sands on benzothiazole ozonation. Experiments were assessed at laboratory scale, in a differential circular flow reactor composed of a volcanic sand fixed bed column of $19\,cm^3$ and a $1\,dm^3$ storage tank, operated in batch mode at $20\,°C$ and pH 2–7. Experimental results show that ozone self-decomposition is enhanced by the presence of volcanic sand at all pH. At $pH > pH_{PZC}$, the increase in aqueous ozone decay could be related to ozone interaction with strong Lewis acid on metal oxide surface sites of the volcanic sand. Ozone self-decomposition reactions occurring on the volcanic sand are less affected by the presence of radical scavengers. Benzothiazole removal by ozonation is also enhanced by the presence of volcanic sand. Moreover, the inhibitory effect of free radical scavengers is also impaired by volcanic sand, suggesting that strong Lewis acid surface sites play a key role on the reaction mechanism.
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1. Introduction

Benzothiazoles are organic compounds posing environmental concern, when released into watercourses. These contaminants are frequently present in wastewater from rubber related applications, and could be found in surface and underground water bodies, in soils, and estuarine sediments, causing significant environmental impact [1,2]. Benzothiazoles inhibit micro-organisms activity in conventional biological wastewater treatment systems and most of them are not readily biodegradable [3,4]. Moreover, these compounds can be adsorbed into cell membranes, leading to bioaccumulation and biomagnification [3,5].

Advanced oxidation processes, such as, H_2O_2/UV, photoassisted Fenton, and ozone have been used to oxidise benzothiazole compounds [6–8]. However, the presence of radical scavengers such as carbonates, bicarbonates, and natural organic matter, normally present in water reduce BT removal efficiency in such homogeneous processes, due to the inhibition of radical chain reactions [8].

Recently, ozone combined with activated carbon has been used to oxidise benzothiazole compounds [9–11]. Such heterogeneous treatment has been shown to reduce the inhibition effect produced by radical scavengers. Both homogeneous and heterogeneous reactions are present in combined ozonation/activated carbon, where chemical surface properties play an important role in the reaction mechanism. The generation of secondary radicals from ozone decomposition is promoted by the high electron density of carbon basal planes in activated carbon with basic characteristic, the presence of oxygenated surface groups, and mineral matter, specially iron hydr(oxides) on activated carbon surface, thus increasing benzothiazole removal rate [10,11]. However, the high cost of activated carbon impairs its application at industrial scale, and alternative catalysts should be found.

In this respect, low cost natural solid minerals, such as sand, soils, zeolites, alumina oxide, and goethite, have been recently used in the heterogeneous ozonation of toxic organic pollutants [12–19].

Within this context, this article presents experimental results on benzothiazole (BT) degradation by catalytic heterogeneous ozonation using volcanic sand. Results on ozone self-decomposition in the presence of volcanic sand are also presented here. In particular, the effect of radical scavengers, volcanic sand dosage, and pH were assessed. A full understand-

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ing of this aspect is required in order to design a cost-effective treatment technology, based on catalytic ozonation promoted by volcanic sand.

2. Experimental methods

2.1. Experimental system

Experiments were carried out at 20 °C, in a differential circular flow reactor composed of a volcanic sand fixed bed column (19 cm^3) and a 1 dm^3 storage tank, operated in batch mode. Liquid recirculation using a pump at 1 dm^3 min^{-1} and mechanical stirring at 240 rpm provided mixing. Ozone was produced from dry pure oxygen using an AZCOZON ozone generator rated at 5 g O$_3$ h^{-1}, and pH was adjusted to 2 and 7 using phosphoric acid or potassium phosphate buffer. Typically, O$_2$/O$_3$ gas mixture (120 dm^3 h^{-1}) was fed into the reactor containing 1 dm^3 benzothiazole-free aqueous solution, for about 30 min until dissolved ozone saturation was reached. Then, a set amount of 7 mM benzothiazole stock solution was injected into the reactor and liquid recirculation over the fixed bed column charged with the volcanic sand was started. Samples were quickly drawn into cylinders containing Na$_2$SO$_3$ solution in order to stop ozonation reactions for BT detection, or into syringes containing 2 cm^3 Indigo solution for aqueous ozone determination. In the case of adsorption experiments, ozone was not supplied into the system. When only O$_3$ treatment was applied, volcanic sand was not used.

2.2. Materials and analytical methods

Volcanic sand was used in this study, collected from the Chillán volcano, Bío-Bío region (Chile). Volcanic sand was sieved and then washed with de-ionised water, oven-dried at 105 °C for 24 h, and stored in a dessicator until its use. Volcanic sand was characterised using standard techniques, as follows: macroscopic pellets 0.84–1.0 mm mean diameter, ash content 99.7% (on dry weight basis), and bulk density 2.5 g cm^{-3}. Results obtained by nitrogen adsorption isotherms showed that the volcanic sand used in this study is a non-porous material. Data on surface elements as detected by X-ray fluorescence are listed in Table 1. The pH value required by the volcanic sand to give zero net surface charge (pH$_{PZC}$) was 6.8, following procedures described by Stumm and Morgan [20].

Table 1
Metallic composition of volcanic sand, by X-ray fluorescence (in % (w/w) d.b.)

SiO$_2$	63.67
TiO$_2$	0.68
Al$_2$O$_3$	13.92
Fe$_2$O$_3$	4.65
MnO	0.09
MgO	1.19
CaO	2.9
Na$_2$O	3.84
K$_2$0	3.04
P$_2$O$_5$	0.07

BT was provided by Fluka (96% purity). *Tert*-butyl alcohol (*t*-BuOH) and acetic acid (HAc) (Merck, >99% purity) were used here as radical scavengers, since both react very rapidly with hydroxyl radicals (k•$_{OH,t\text{-}BuOH}$ = 5 × 10^8 M^{-1} s^{-1}, k•$_{OH,HAc}$ = 1.7 × 10^7 M^{-1} s^{-1}) but very slowly with ozone ($k_{O_3,t\text{-}BuOH}$ = 0.03 M^{-1} s^{-1}, $k_{O_3,HAc}$ =< 3 × 10^{-5} M^{-1} s^{-1}) [21–23]. All solutions were prepared with ultrapure water obtained from an EASYpure® II RF system.

Ozone concentrations in gas and liquid phases were monitored by UV spectrophotometry (Bausch & Lomb TU-1810 S), using flow cells at 253.7 nm and 258 nm, respectively. Data were registered on-line as a function of time and processed using UV Win 5.0 software. When BT was present, ozone gas was continuously bubbled through the liquid storage tank; dissolved ozone concentration was measured by the Indigo method [24]. BT and oxidation by-products were determined by high-pressure liquid chromatography (HPLC) (Merck-Hitachi, L7100) [8].

3. Results and discussion

3.1. Ozone decomposition in aqueous solution

3.1.1. Effect of radical scavengers on aqueous ozone decomposition in the presence of volcanic sand

The influence of radical scavengers on the ozone decay rate, in the presence and absence of volcanic sand, was assessed using acetic acid at acid (Fig. 1) and basic pH (Fig. 2), respectively. Ozone self-decomposition in the presence of glass wool was also evaluated. Glass wool was used instead of volcanic sand to assess possible ozone self-decomposition in the absence of volcanic sand.

Acetic acid (HAc) features a pK_a = 4.75 and is well known as hydroxyl radical scavenger inhibiting the radical chain mechanism ($k_{HO•,HAc}$ = 1.7 × 10^7 M^{-1} s^{-1}) [21], but reacts slowly with ozone ($k_{O_3,HAc}$ =< 3 × 10^{-5} M^{-1} s^{-1}) [22]. At basic pH, acetic acid is dissociated forming acetate ions (Ac$^-$). Acetate
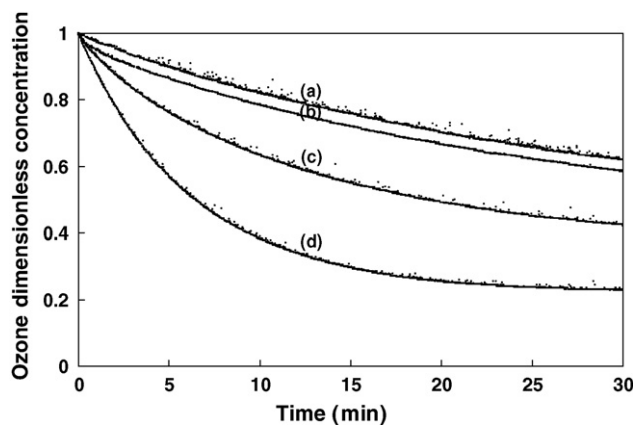

Fig. 1. Effect of the presence of HAc (0.1 M) on aqueous ozone decomposition in the presence of volcanic sand (15 g dm^{-3}) at 20 °C, pH 2, 125 μM initial ozone concentration: (a) glass wool with radical scavenger; (b) glass wool without radical scavenger; (c) volcanic sand with radical scavenger; (d) volcanic sand without radical scavenger.
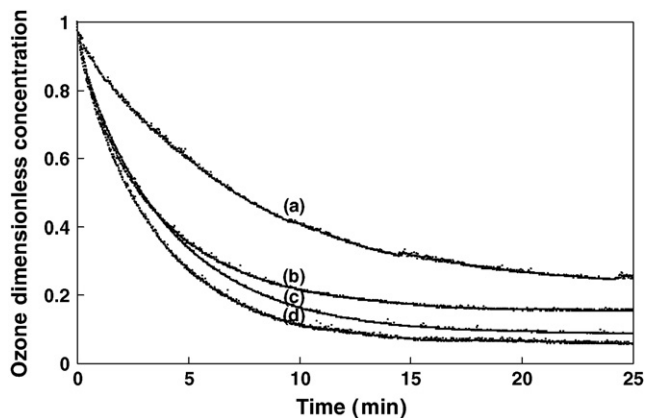
Fig. 2. Effect of the presence of Ac^- (0.1 M) on aqueous ozone decomposition in the presence of volcanic sand ($15\,g\,dm^{-3}$) at 20 °C, pH 8, 104 μM initial ozone concentration: (a) glass wool with radical scavenger; (b) volcanic sand with radical scavenger; (c) glass wool without radical scavenger; (d) volcanic sand without radical scavenger.

ions react very highly with hydroxyl radicals ($k_{HO·,Ac^-} = 8 \times 10^7\,M^{-1}\,s^{-1}$), but very slowly with ozone ($k_{O_3,Ac^-} = < 10^{-4}\,M^{-1}\,s^{-1}$) [23].

Ozone dimensionless concentrations presented in Figs. 1 and 2 were calculated as a fraction of initial concentration of ozone. Fig. 1 shows the effect of radical scavengers at pH 2, using HAc (0.1 M), on ozone decay rate in the presence and absence of volcanic sand ($15\,g\,dm^{-3}$). Experimental data fitted well an apparent first-order kinetic law with respect to ozone dissolved concentration ($r^2 > 0.99$). Table 2 lists the values of corresponding apparent first-order ozone decay rate constants in the presence and absence of volcanic sand, with and without radical scavengers, at pH 2 and 8. Apparent first-order constant increased from $0.5 \times 10^{-3}\,s^{-1}$ in the absence of volcanic sand, to $2.0 \times 10^{-3}\,s^{-1}$, when volcanic sand was present. The presence of radical scavengers led to 20% and 55% decrease in ozone decay rates, in the case of glass wool and volcanic sand, respectively.

Fig. 2 illustrates the influence of radical scavengers at high pH (0.1 M Ac^-, pH 8) on the ozone decay rate in the presence and absence of volcanic sand ($15\,g\,dm^{-3}$). Experimental data shown fitted well an apparent first-order kinetic law with respect to ozone dissolved concentration ($r^2 > 0.99$). In the absence of volcanic sand, ozone decay rate constants showed 54% decrease as compared with rates determined in the presence of acetate ions. However, when volcanic sand was used in the presence of acetate ions, rate constants were not significantly affected. These findings would suggest that ozone decomposition reac-

tions mainly occur on the mineral surface, and is not affected by the presence of radical scavengers.

As seen in Table 2, greater ozone decay rates are observed as pH increases. At each pH level, volcanic sand presents a greater effect on ozone decomposition rates. This could be related to different reactivity of ozone toward metal oxide sites of the volcanic sand surface, which exhibit pH-dependent charges ($S–OH_2^+$, $S–OH$, $S–O^-$). The respective densities of these functional groups are influenced by the solution pH [20].

Acidity and basicity are key parameters determining the catalytic properties of metal oxides [14]. The amount and properties of hydroxyl groups depend on the nature of surface metal oxides. Hydroxyl groups formed on metal oxide surfaces behave as Brönsted acid sites. Lewis acids and bases are sites located on the metal cation and coordinatively unsaturated oxygen, respectively [14]. Both Brönsted and Lewis acid sites are thought to be the catalytic active sites on metal oxide surfaces [14].

At pH < pH_{PZC}, surface hydroxyl groups on metal oxide will be in their protonated form:

$$S–OH + H+ \leftrightarrow S–OH_2^+ \qquad (1)$$

On the other hand, when pH > pH_{PZC}, surface hydroxyl groups on metal oxide will be in their deprotonated form:

$$S–OH + OH^- \leftrightarrow S–O^- + H_2O \qquad (2)$$
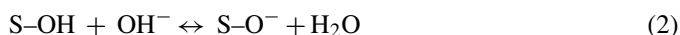
Experimental results suggest that ozone decay rates in the presence of volcanic sand are governed by radical generation, where ozone interactions with volcanic sand surface sites play an important role. At pH > pH_{PZC}, the increase in aqueous ozone decay in the presence of volcanic sand could be related to ozone interaction with strong Lewis acid on metal oxides surface sites. Ozone could react with acid surface groups of metal oxide with subsequent decomposition. However, ozone aqueous decomposition is reduced in the presence of strong Lewis bases commonly present in water such as carbonates, sulphates, chlorides, nitrates, etc. Such components compete for interaction with strong Lewis acid sites where ozone aqueous decomposition takes place. Due to its resonance structure ozone features high electron density on one of its oxygen atom, resulting in strong affinity to Lewis acid sites on the surface of metal oxide [14].

3.1.2. Effect of volcanic sand dosage on aqueous ozone decomposition

In order to determine the contributions of homogenous and heterogeneous reactions on aqueous ozone decomposition promoted by volcanic sand, experiments were performed at various volcanic sand dosages ($1.0–20.0\,g\,dm^{-3}$). The initial dissolved ozone concentration was 125 μM at pH 2.0. Results shown in Fig. 3 indicate that the ozone decay rate increased with increasing volcanic sand dosage. Experimental data of the ozone initial decay rate fitted well an apparent first-order kinetic rate law with respect to dissolved ozone concentration ($r^2 > 0.99$). Fig. 4 illustrates the estimated overall apparent first-order rate constants, $k_{overall}^{O_3}$, as a function of volcanic sand dosages. $k_{overall}^{O_3}$ include both, the ozone aqueous decomposition by heterogeneous

Table 2
Effect of radical scavengers on the apparent first-order ozone decay rate constants (s^{-1}) in the presence and absence of volcanic sand

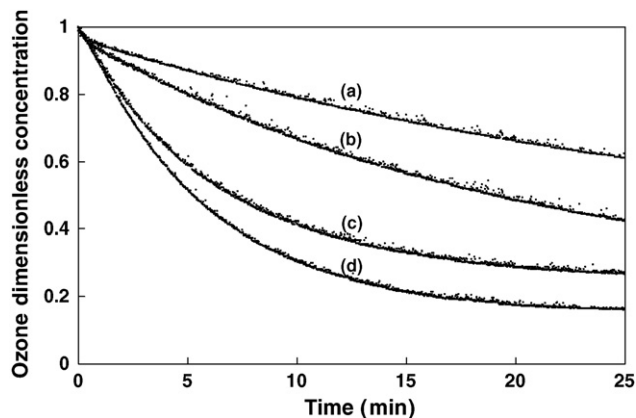| Materials	pH 2		pH 8	
	HAc (0 M)	HAc (1 M)	Ac^- (0 M)	Ac^- (1 M)
Glass wool	0.5×10^{-3}	0.4×10^{-3}	3.7×10^{-3}	1.7×10^{-3}
Volcanic sand	2.0×10^{-3}	0.9×10^{-3}	4.3×10^{-3}	3.7×10^{-3}

Fig. 3. Effect of volcanic sand dosage on ozone decay rate using O_3/VS at 20 °C, pH 2, 125 μM initial ozone concentration: (a) 1 g dm^{-3}, (b) 5 g dm^{-3}, (c) 15 g dm^{-3}, and (d) 20 g dm^{-3}.

reactions taking place on volcanic sand surface and homogeneous reactions present in the liquid bulk. Reactions on the volcanic sand might involve several steps such as ozone adsorption, ozone surface decomposition reactions, ozone decomposition reactions at the solid–liquid interface, and propagation reactions in the solution bulk. In this case, the process rate is assumed to be controlled by chemical reactions. Ozone aqueous decomposition reactions in the presence of volcanic sand could be expressed by a simplified kinetic equation involving the two phases as follows:

$$-\frac{dC_{O_3}}{dt} = (k_{homo}^{O_3} + k_{hetero}^{O_3} C_{S-OH})C_{O_3} \qquad (3)$$

Integrating, with initial conditions $C_{O_3} = C_{O_30}$ and assuming C_{S-OH} constant, leads to

$$\ln \frac{C_{O_3}}{C_{O_30}} = -(k_{homo}^{O_3} + k_{hetero}^{O_3} C_{S-OH})t = -k_{overall}^{O_3} t \qquad (4)$$

with

$$k_{overall}^{O_3} = k_{homo}^{O_3} + k_{hetero}^{O_3} C_{S-OH} \qquad (5)$$

where C_{O_3} and C_{O_30} are the dissolved ozone concentrations at any time t and time zero, respectively. C_{S-OH} is a pseudo-
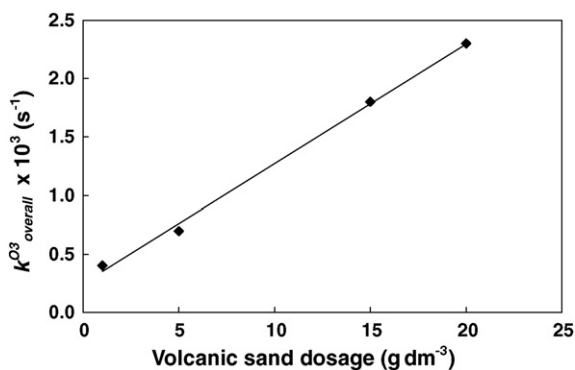

Fig. 4. Variation of apparent first-order constant of the global ozone decomposition reactions ($k_{overall}^{O_3}$) as a function of volcanic sand dosage.

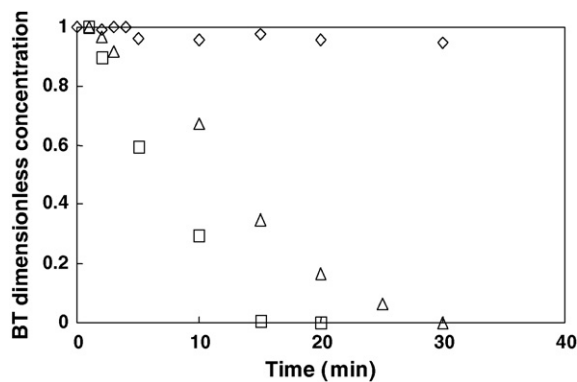Fig. 5. Comparison of advanced treatment processes in BT aqueous removal: (◇) VS, (△) O_3, (□) O_3/VS. Twenty degree celcius, pH 2, 222 μM initial concentration BT, 10 g dm^{-3} VS.

concentration and represents the concentration of volcanic sand active surface sites. $k_{homo}^{O_3}$ and $k_{hetero}^{O_3}$ represent the rate constants of ozone decay due to global homogeneous and heterogeneous reactions, respectively. The $k_{overall}^{O_3}$ values were obtained from the line slopes shown in Fig. 3, at different volcanic sand dosages. Then, those values were plotted as a function of volcanic sand dosage as shown in Fig. 4. The line slope in Fig. 4 is the value of apparent second-order rate constant of ozone decay due to heterogeneous reactions ($k_{hetero}^{O_3} = 0.10 \times 10^{-3}$ g^{-1} dm^3 s^{-1}), and the intercept of the line with "Y" axis is the value of apparent first-order rate constant of homogenous reactions ($k_{homo}^{O_3} = 0.25 \times 10^{-3}$ s^{-1}) ($r^2 > 0.99$). These results show that aqueous ozone decay rate by ozone interaction with strong Lewis acids on metal oxide sites of the volcanic sand surface is higher than by those reactions taking place in the liquid bulk.

3.2. BT degradation

3.2.1. BT aqueous removal by single ozonation and catalytic ozonation processes

Fig. 5 compares the BT dimensionless concentration as a function of ozonation time (20 °C, pH 2, 222 μM initial BT concentration) during homogenous ozonation, O_3 (ozone dissolved concentration 83 μM); adsorption on volcanic sand, VS (10 g dm^{-3}); and heterogeneous catalytic ozonation promoted by volcanic sand, O_3/VS (10 g dm^{-3}, ozone dissolved concentration 42 μM) treatments, in the absence of radical scavengers. Dimensionless concentrations were calculated as a fraction of initial BT concentration.

As shown in Fig. 5, simultaneous O_3/VS process increased BT removal rate, as compared with single O_3 treatment. On the other hand, BT removal rate by adsorption process on VS was not significant under conditions used here.

The overall BT ozonation rate in the presence of volcanic sand could be expressed as follows:

$$-\frac{dC_{BT_{overall}}}{dt} = (k_{homo}^{BT} + k_{hetero}^{BT} C_{S-OH})C_{BT} \qquad (6)$$

Table 3
Contribution of ozone reaction and radical reaction mechanism to BT oxidation using O_3 and O_3/VS treatment processes

pH	O_3			O_3/VS		
	$k_{overall}^{BT}$ (s^{-1})	δ^{O_3} (%)	$\delta^{\cdot OH}$ (%)	$k_{overall}^{BT}$ (s^{-1})	δ^{O_3} (%)	$\delta^{\cdot OH}$ (%)
2	1.5×10^{-3}	23	77	2.2×10^{-3}	15	85
7	2.2×10^{-3}	15	85	4.1×10^{-3}	8	92

with

$$k_{homo}^{BT} = k_1^{BT}C_{O_3} + k_2^{BT}C_{\cdot OH} \tag{7}$$

and

$$k_{hetero}^{BT} = k_3^{BT}C_{O_3} + k_4^{BT}C_{\cdot OH} \tag{8}$$

Integrating, with initial conditions $C_{BT} = C_{BT0}$ leads to

$$\ln\frac{C_{BT}}{C_{BT0}} = -(k_{homo}^{BT} + k_{hetero}^{BT}C_{S-OH})t = -k_{overall}^{BT}t \tag{9}$$

with

$$k_{overall}^{BT} = k_{homo}^{BT} + k_{hetero}^{BT}C_{S-OH} \tag{10}$$

where C_{O_3} is the dissolved concentration of ozone. C_{BT}, and C_{BT0} are the concentrations of BT at any time t and time zero, respectively. $C_{\cdot OH}$ and C_{S-OH} represent the hydroxyl radical concentration and volcanic sand active surface site concentrations, respectively. k_1^{BT}, k_2^{BT}, k_3^{BT}, k_4^{BT}, k_{homo}^{BT}, and k_{hetero}^{BT} represent the BT oxidation rate constants corresponding to: homogeneous reaction with ozone, homogeneous reaction with hydroxyl radicals, heterogeneous reaction with ozone, heterogeneous reaction with hydroxyl radicals, global homogeneous and heterogeneous reactions, respectively.

Experimental data fitted well an apparent first-order kinetic rate law with respect to BT concentration as described in Eq. (9). As seen in Fig. 5, the largest BT removal rate was attained in the case of heterogeneous catalytic ozonation promoted by volcanic sand. The value of the BT apparent first-order ozonation rate constant increased 32% when volcanic sand was added (see Table 3). The observed increase in the BT removal rate, when volcanic sand was applied, could be related with radical enhancement promoted by catalytic ozone decomposition on the strong Lewis acid on metal oxide sites of the volcanic sand surface.

3.2.2. Effect of pH on BT removal

The effect of pH (2 and 7) on BT removal was evaluated using O_3 (ozone dissolved concentration ranged 10–83 μM), and O_3/VS (10 g dm^{-3}, ozone dissolved concentration ranged 6–42 μM) treatments.

As illustrated in Fig. 6, the BT removal increased as pH raised from 2 to 7. Combined O_3/VS treatment enhanced BT removal at both pH levels. It is seen that over 40% of BT was destroyed after 5 min ozonation in the presence of volcanic sand at pH 2, as compared with more than 10 min in the case of homogeneous ozonation; a similar trend is observed at pH 7. The fast
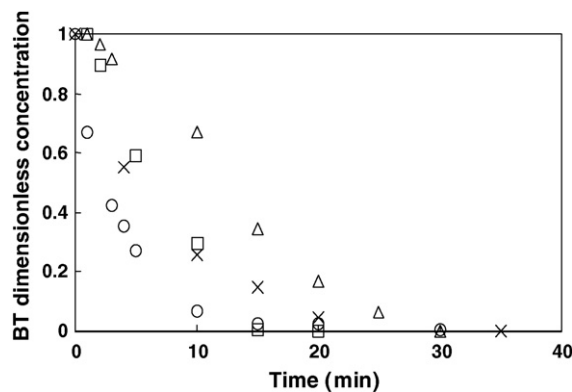

Fig. 6. Effect of pH on BT removal rate: pH 2 ($\triangle$, O_3; $\square$, O_3/VS); pH 7 ($\times$, O_3; $\bigcirc$ O_3/VS). Twenty degree celcius, 222 μM initial BT concentration, 10 g dm^{-3} VS.

BT oxidation reaction in the presence of volcanic sand suggests that active surface sites enhance ozone decomposition into free radicals, either by generation of hydroxyl radicals, or by production of reactive oxygen radicals. This enhancement could be connected with ozone and volcanic sand surface interactions.

3.2.3. Effect of the presence of radical scavengers on BT removal

The influence of *t*-BuOH on BT removal rates was evaluated at 20 °C, pH 2, initial BT concentration of 222 μM, and ozone dissolved concentration 104 μM; using O_3, and O_3/VS processes.

As seen in Fig. 7 the rate of BT oxidation decreases when radical scavengers are present. This effect is reduced in the case of O_3/VS treatment. Indeed, BT reaches about 60% of its initial level in the absence of free radical scavengers after 5 min of simultaneous treatment, while 75% of BT is still observed when radical scavengers are presented. However, when homogeneous ozonation treatment was applied only 10% BT was removed after 5 min in the presence of radical scavengers. The reduction on BT removal rate by the presence of *t*-BuOH could be related
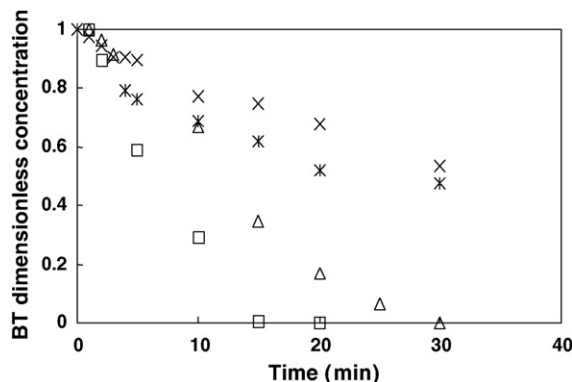

Fig. 7. Effect of the presence of *t*-BuOH on BT removal rate: ($\times$) O_3 (310 mM *t*-BuOH); (✳) O_3 (0 mM *t*-BuOH); ($\triangle$) O_3/VS (310 mM *t*-BuOH); ($\square$) O_3/VS (0 mM *t*-BuOH). Twenty degree celcius, pH 2, 10 g dm^{-3} VS, and 222 μM BT initial concentration.

with the inhibition of radical chain reactions taking place in the solution bulk. *t*-BuOH reduces ozone decomposition, acting as radical scavengers. These findings suggest that in the combined O_3/VS process BT oxidation reactions take place mainly on the volcanic sand surface.

In order to determine the contributions of ozone and radical reaction mechanism to BT removal in the presence of volcanic sand, estimations from separated experiments were carried out. Results are summarised in Table 3. The contribution of ozone direct oxidation reaction to the overall BT removal (δ^{O_3}) was determined using Eq. (13), as described below

$$-\frac{dC_{BToverall}}{dt} = [k_1^{BT}C_{O_3} + k_2^{BT}C_{\cdot OH}$$
$$+ (k_3^{BT}C_{O_3} + k_4^{BT}C_{\cdot OH})C_{S-OH}]C_{BT} \qquad (11)$$

When *t*-BuOH was presented in the system, hydroxyl radicals were scavenged ($C_{\cdot OH} = 0$), then Eq. (11) can be rewritten as

$$-\frac{dC_{BToverall}}{dt} = [k_1^{BT}C_{O_3} + k_3^{BT}C_{O_3}C_{S-OH}]C_{BT} = k_{obs}^{BT}C_{BT} \qquad (12)$$

The combined contribution of direct ozone reaction to BT removal (δ^{O_3}) is calculated from the experimental BT removal rates obtained when *t*-BuOH was present ($k_{obs}^{BT} = 0.34 \times 10^{-3}\,s^{-1}$) and absent ($k_{overall}^{BT}$), at the same pH condition, as follows:

$$\delta^{O_3}\,(\%) = \frac{k_{obs}^{BT}}{k_{overall}^{BT}} \times 100 \qquad (13)$$

The value of radical oxidation reaction contributions to the overall BT removal due to ozonation in the presence of volcanic sand ($\delta^{\cdot OH}$) was obtained by difference

$$\delta^{\cdot OH}\,(\%) = 100 - \delta^{O_3}(\%) \qquad (14)$$

Table 3 shows the contribution of ozone and radical reactions to the overall BT oxidation rate when O_3 and O_3/VS treatment processes were applied. In both cases, the contribution of the radical indirect reaction increases when pH raised. Moreover, this effect is much greater in the case of O_3/VS process. The reaction mechanism would be characterised by a combination of competing homogeneous and heterogeneous reactions: a direct reaction of molecular ozone, and an indirect reaction involving non-selective free radicals. The contribution of heterogeneous reactions in the simultaneous O_3/VS process seems to be fundamental on BT removal. In this system, the strong Lewis acid on metal oxide sites of the volcanic sand surface could act as initiators and/or promoters of radical chain reaction, accelerating ozone decomposition in the solution bulk. As the result of ozone adsorption and its conversion O-radicals [25] or HO• radicals [26] are generated (the $O_2^{\bullet-}$ transfers an electron to another ozone molecule to form an ozonide anion, $O_3^{\bullet-}$, which is the chain reaction promoter and produces HO• radicals). Free radicals can initiate a radical chain reaction both on the surface of the catalyst and in the bulk of the aqueous phase. Radicals are

then continuously generated by the dissolved ozone interaction with the volcanic sand surface.

4. Conclusions

Experimental results show that ozone self-decomposition is enhanced by the presence of volcanic sand at all pH. Ozone decomposition in the presence of volcanic sand could be related to different reactivity of ozone toward metal oxide active surface sites, which exhibit pH-dependent charges. Ozone self-decomposition reactions occurring on the volcanic sand are less affected by the presence of radical scavengers. Benzothiazole removal by ozonation is also enhanced by the presence of volcanic sand. The rate of benzothiazole removal increases with pH, showing greater effect in the case of heterogeneous ozonation. Moreover, the inhibitory effect of free radical scavengers is also impaired by volcanic sand, suggesting that surface sites play a key role on the reaction mechanism.

Acknowledgements

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