Production and contribution of hydroxyl radicals between the DSA anode and water interface

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Abstract

Hydroxyl radicals play the key role during electrochemical oxidation and photoelectrochemical oxidation. The production and effect of hydroxyl radicals on the interface between DSA anode and water was investigated by examining the quenching effect of iso-propanol on Orange II decolorization. We observed that with an increase in electrode potential from 4 to 12 V across electrodes at pH 7.0, the contribution percentage of hydroxyl radicals increased dramatically. More OH radicals were produced in acidic and alkaline conditions than at neutral conditions. At electrode potential of 4 V, the contribution percentage of hydroxyl radicals was obviously higher at near neutral pH conditions, while removal efficiency of Orange II achieved was the lowest concurrently. Finally, for photocatalytic oxidation, electrochemical oxidation, and photoelectrochemical oxidation using the same DSA electrode, the effect of hydroxyl radicals proved to be dominant in photocatalytic oxidation but the contribution of hydroxyl radicals was not dominant in electrochemical oxidation, which implies the necessity of UV irradiation for electrochemical oxidation during water treatment.

Key words: hydroxyl radicals; DSA electrode; photoelectrocatalysis; Orange II

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Introduction

Although conventional technologies such as biological and chemical treatments are efficient for the treatment of most wastewater, new technologies are still required to assist these conventional water treatment technologies to comply with increasingly severe legislations in the future. Advanced oxidation processes (AOPs) are characterized by the production and use of OH radicals (2.72 V/NHE), which are the most reactive radicals in aqueous solution (Andreozzi et al., 1999). Organics can be degraded and mineralized to carbon dioxide, water and inorganics or, at least, harmless products by OH radicals. Since AOPs, such as electrolysis, photocatalysis, and ozonation, exhibit excellent ability to degrade a large variety of the organic pollutants, especially toxic and refractory pollutants (Pelegrini et al., 2001; Huber et al., 2003; Rosenfeldt and Linden, 2004), AOPs have been drawing increasing attention around the world.

Electrocatalysis and photocatalysis have been widely studied for the removal of toxic pollutants. Organic pollutants can be effectively removed by the two AOPs, which are highly economical in the removal of organics of low concentrations and the pretreatment of concentrated organics. The energy consumption of the two AOPs still remains high (Hoffman et al., 1995; Trasatti, 1995; Chen, 2004), however, and more effective reactive systems are needed to utilize energy more efficiently. One way to increase AOPs efficiencies is to produce more OH radicals during organics degradation. If the production and contribution of OH radicals to the degradation of pollutants can be determined under different reaction conditions, then an optimal reactive system can be selected to improve the energy utilization and degradation efficiency.

Alcohols are commonly used to estimate the OH radicals' oxidation mechanism (Sun and Pignatello, 1995; Ilisz and Dombi, 1999; Daneshvar et al., 2004; Li et al., 2009). Iso-propanol (ISO) can scavenge hydroxyl radicals and it is often used as the quencher of OH radicals to evaluate their production. The inhibitive effect of ISO on the oxidation processes involved is indicated by the decline in reaction rate constants. In this study, the roles of OH radicals were investigated in the oxidation of an azodye Orange II by examining the decolorization rates of Orange II with and without ISO under different electrode potentials and initial pH conditions. The effect of ultraviolet irradiation on the production of OH radicals during electrochemical

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oxidation was also investigated.

1 Materials and methods

1.1 Materials

Orange II was purchased from the Beijing Chemical Reagents Company and used without further purification. The DSA anode (Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$) electrode (4×6 cm) was provided by the Beijing Titanium Industrial and Trade Company. Other chemicals used including ISO were of analytical-reagent grade. Deionized and doubly distilled water was used throughout this study.

1.2 Production and determination of OH radicals

Electrochemical oxidation of Orange II was carried out in a semi-cylindrical reactor. Titanium wire was used as the cathode and a 20-cm^2 effective working area of anode was employed. The reactor was as used in our previous study (Li et al., 2006). The available volume of the reactor was 150 mL, with 125 mL of Orange II solution (20 mg/L) added. The dosage of ISO was 0.01 mol/L (Sun and Pignatello, 1995; Ilisz and Dombi, 1999; Daneshvar et al., 2004; Li et al., 2009). An 8-W low pressure UV lamp emitting a wavelength of 254 nm was situated parallel to the DSA electrode at a distance of 120 mm. All experiments were conducted at neutral pH for 60 min unless otherwise stated. A UVmini1240 UV-Vis spectrophotometer (Shimadzu, Japan) was employed to measure the concentration of Orange II in samples at 484 nm, which corresponded to the maximum absorption of the dye.

2 Results and discussion

2.1 Effect of potentials across the electrodes on the production of OH radicals

The efficiencies of electrochemical oxidation can be manipulated by changing the potentials across the electrodes, on which the production of hydroxyl radicals is expected to be highly dependent. The effect of potentials across the electrodes on the decolorization rate of Orange II (K_{app}, apparent rate constants of pseudo first-order) within 60 min was investigated from 4 to 12 V in the presence and absence of ISO. The results are illustrated in Fig. 1. The K_{app} increased gradually with an increase in electrode potentials in the absence of ISO. It is well accepted that a series of oxidizing species such as hydroxyl radical, ozone and hydrogen peroxide can be generated during the electrochemical process (Zhou et al., 2005). The increase in K_{app} indicates that more and more oxidizing species were generated on DSA with the increase of the potentials. On the other hand, the K_{app} values at 4, 8, and 12 V were 0.0087, 0.0128, and 0.0145 min^{-1}, respectively. The K_{app} values at 8 and 12 V were much higher than that at 4 V. By contrast, in the presence of ISO, the K_{app} (quenching) values at 4, 8, and 12 V reached 0.0086, 0.0104 and 0.0110 min^{-1}, respectively. Obviously, the quenching effect was more significant at 8 and 12 V than at 4 V. This indicates
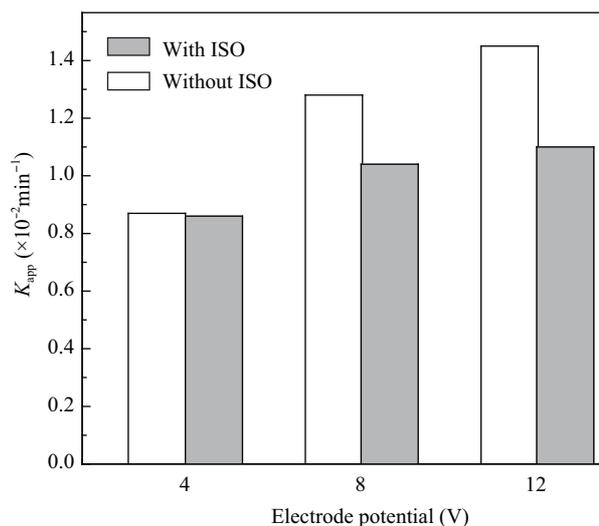

Fig. 1 Effect of potential across the electrodes on K_{app} (apparent rate constant of pseudo first-order) in the presence and absence of ISO (iso-propanol) at pH 7.0.

that hydroxyl radicals played a more important role under higher electrode potentials.

During electrochemical oxidation, the hydroxyl radicals generated were quenched by ISO. The decrease in the apparent rate constant (pseudo first-order) K_{app} resulting from ISO quenching can be used to indicate the contribution percentage (P) achieved by hydroxyl radicals, which is calculated by the following equation (Li et al., 2009):

$$P = (1 - K_{app(quenching)}/K_{app}) \times 100\%$$

As illustrated in Fig. 2, the contribution percentages of hydroxyl radicals for electrochemical oxidation were 1.1%, 18.8%, 24.4% at 4, 8, and 12 V, respectively. This indicates that the higher the electrode potentials, the more hydroxyl radicals were involved in the process. On the other hand, although series of oxidizing species are produced during electrochemical oxidation, their oxidizing abilities are different. The redox potentials of hydroxyl radical, ozone and hydrogen peroxide, for example, are 2.72, 2.076 and 1.776 V, respectively (Jiang and Lloy, 2002). Hydroxyl radicals are especially more reactive than other species, and most of organics are attacked with rate
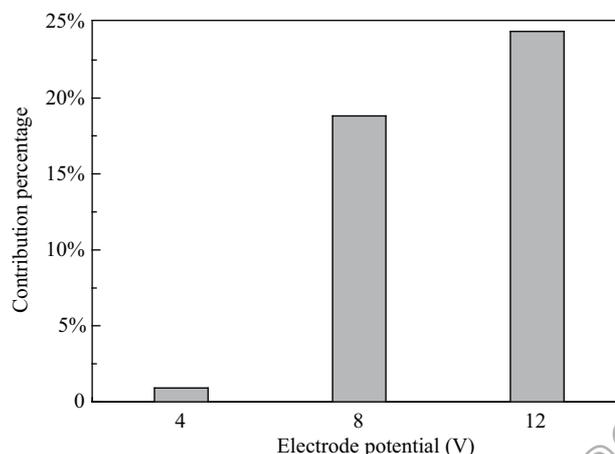

Fig. 2 Contribution percentage of hydroxyl radicals under electrode potentials at 4, 8, and 12 V at pH 7.0.

constants usually in the order of 10^6–10^9 $(mol/L)^{-1}$ sec^{-1} (Andreozzi et al., 1999). As a result, the more oxidizing species generated with increasing electrode potentials, the more important the role hydroxyl radicals played.

2.2 pH-dependence on the production of OH radicals

2.2.1 K_{app} under different pH conditions in the presence and absence of ISO

As presented in Fig. 3a and b, regardless of whether ISO was present or absent, both acidic and alkaline conditions favored the decolorization of Orange II and the highest decolorization rate of Orange II was observed at pH 2.0. The pH conditions can influence the adsorption of dye molecules onto the catalyst surface (Fox and Dulay, 1993). On DSA anode (Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$) surface, 70% of the surface oxide is TiO$_2$. The point of zero charge (PZC) of the TiO$_2$ (Degussa P-25) is at pH 6.8. The anatase content is 80% for Degussa P-25. TiO$_2$ used for the preparation of the electrode is pure anatase and it can be deduced that the PZC for pure anatase TiO$_2$ is about 6.8 (Poulios and Tsachpinis, 1999). TiO$_2$ surface is positively charged in acidic media (pH < 6.8) and negatively charged under alkaline conditions (pH > 6.8). For Orange II, the pK_{a1} value for the deprotonation of the naphthalene OH is 11.4 and pK_{a2} value for the deprotonation of SO$_3$H group is approximately 1 (Bandara et al., 1999). Orange II molecules are negatively charged in almost the entire pH range studied. Therefore, the lower the solution pH, the stronger the adsorption of the dye on TiO$_2$ surface from electrostatic attraction, which is also well documented by Konstantinou and Albanis (2004). It is widely accepted that photocatalytic oxidation mainly occurs on the catalyst surface (Hu et al., 2003). From this point of view, the decolorization rate was expected to achieve a peak value at pH 2.0 due to stronger adsorption.

Conversely, however, OH radicals have different performances in alkaline solutions compared with that in acidic conditions. Specifically, OH radicals are more easily generated in alkaline solution via the oxidization of more hydroxide ions available on TiO$_2$ surface and are also the dominant species at neutral and high pH conditions

(Sharma et al., 1995). At pH > 6.4, OH and O$_2^{\bullet-}$ radicals are easier to diffuse from the negative surface of TiO$_2$ into the bulk solution, which avoids the recombination of OH radicals (Zhang et al., 1998). Even though, as illustrated in Fig. 3, the decolorization rate at pH 12.0 was much lower than that at pH 2.0, this implied the total effect mentioned above is not comparable to the effect of electrostatic forces between dyes and TiO$_2$.

2.2.2 Contribution percentage of OH radicals under different pH conditions

Acidic and alkaline conditions were favorable for the decolorization of Orange II during electrochemical oxidation. Different from the decolorization rate achieved under different pH conditions (Fig. 4). The contribution percentage of hydroxyl radicals under 12 V at pH 2.0, 5.0, 7.0, 9.0, and 12.0 were 2.4%, 14.5%, 24.1%, 6.7% and 10.9%, respectively. This indicated that the contribution percentage of hydroxyl radicals reached its peak value near neutral pH conditions. A similar phenomenon was also observed at 8 V. By contrast, the positive holes were regarded as the major oxidation species at low pH, while OH radicals were the dominant species at neutral or alkaline conditions during photocatalytic oxidation using
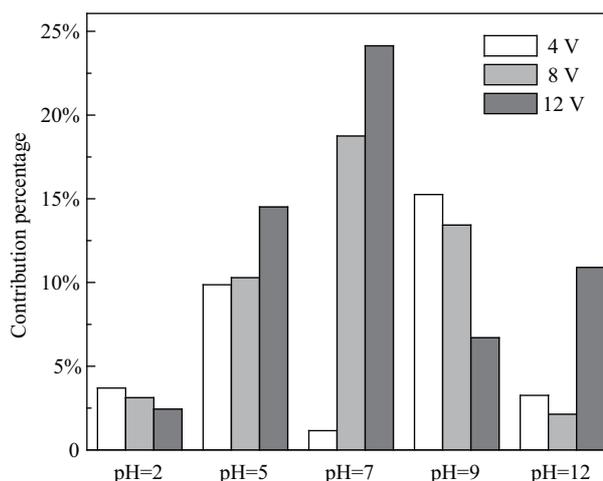

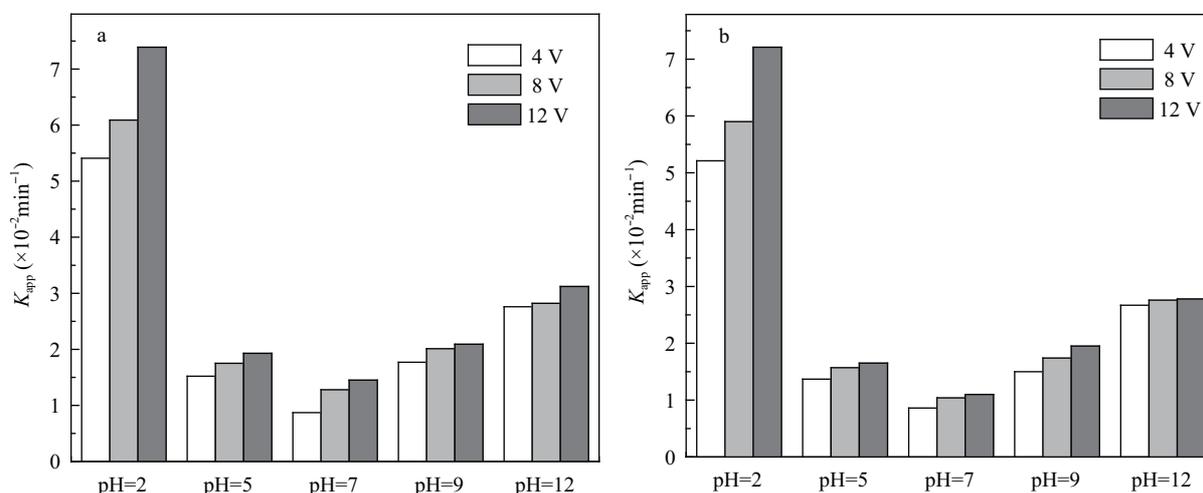**Fig. 4** Contribution percentages of hydroxyl radicals under different pH conditions.

Fig. 3 Effect of solution pH values on K_{app} in the absence (a) and presence (b) of ISO.
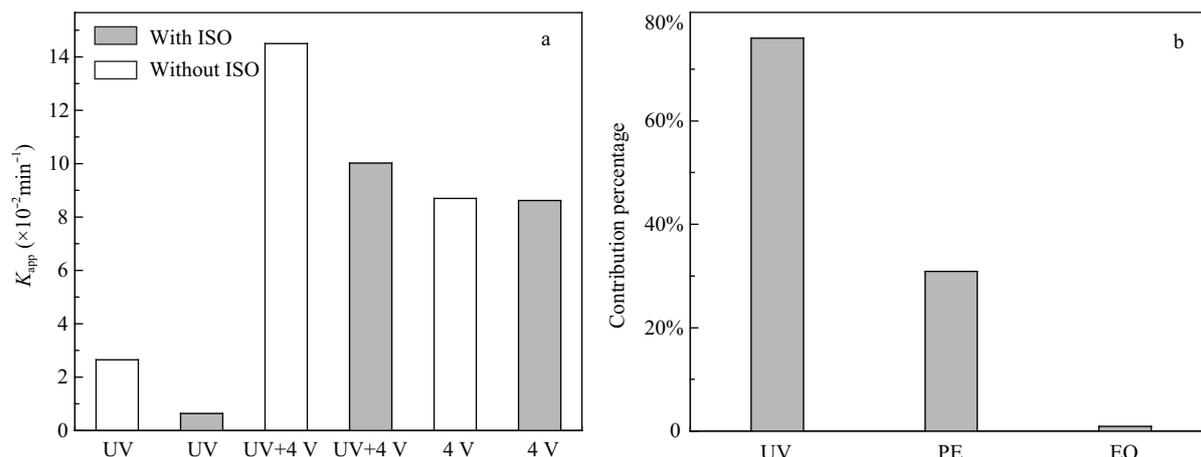
Fig. 5 K_{app} in the presence and absence of ISO at pH 7.0 (a), and contribution percentage of hydroxyl radicals by the different degradation process (b). UV: ultraviolet irradiation; PE: photoelectrochemical oxidation; EO: electrochemical oxidation.

CdS (Tang and Huang, 1995). Accordingly, the roles of OH radicals were highly dependent on reactive systems and conditions. Consequently, the more neutral the reaction solution, the higher the contribution percentage of OH radicals.

2.3 Effect of ultraviolet irradiation on the generation of hydroxyl radicals

At pH 7.0, the contribution percentages of hydroxyl radicals during electrochemical oxidation at 4 and 12 V were only 1.1% and 24.1%, respectively, indicating the insignificant role of OH radicals. To enhance the generation of hydroxyl radicals, ultraviolet irradiation was of good assistance for electrochemical oxidation. A synergy was observed between ultraviolet irradiation and electrochemical oxidation, which has been well documented in the literature (Pelegrini et al., 1999, 2001). The effect of UV 254 nm irradiation is illustrated in Fig. 5a. The K_{app} value of photocatalytic oxidation under ultraviolet irradiation alone (UV), electrochemical oxidation alone (EO), and photoelectrochemical oxidation (PE, electrochemical oxidation under ultraviolet irradiation) was 2.7×10^{-3}, 8.7×10^{-3}, and 1.45×10^{-2} min^{-1}, respectively. The K_{app} value of ultraviolet assisted electrochemical oxidation was 1.21 times the total amount of ultraviolet irradiation and electrochemical oxidation, indicating a synergetic effect. This synergy was ascribed to the generation of an increased number of active sites using a DSA type electrode in the presence of 254 nm ultraviolet irradiation, in which the physicosorbed hydroxyl radicals were created (Pelegrini et al., 2001). Basically, the enhanced generation of hydroxyl radicals resulted from the accelerated separation of photogenerated electrons and holes with the help of an anodic bias to TiO$_2$ film and thus the lifetime of active holes and electrons was largely extended (Ward and Bard, 1982; Vinodgopal et al., 1993).

As presented in Fig. 5b, the contribution percentages of OH radicals by UV, EO, and PE were 76.0%, 0.9%, 30.9%, respectively. This implied that although electrochemical oxidation is well accepted as an AOPs, OH radicals do not play the dominant role for organics oxidation using DSA. Generally, AOPs are all characterized as the production

and use of OH radicals. By contrast, the highest contribution percentage of OH radicals for photocatalytic oxidation under ultraviolet irradiation indicated that photocatalytic oxidation was a qualified AOPs.

Oxidation processes above oxygen evolution potential (OEP) consist of electrochemical combustion (oxidation by OH radicals) on nonactive electrodes such as PbO$_2$ and SnO$_2$, and electrochemical conversion (oxidation by higher oxides MO$_{x+1}$) on active electrodes such as RuO$_2$ and IrO$_2$ (Comninellis, 1994). In addition, direct electron transfer (direct oxidation) is also assumed to occur on the interface between electrodes and water regardless of whether the electrode potential on the anode is higher or lower than OEP. This is why the contribution percentage of OH radicals was not as obvious as expected during electrochemical oxidation. The electrochemical oxidation mechanism on the interface between electrode and water is demonstrated in Fig. 6.
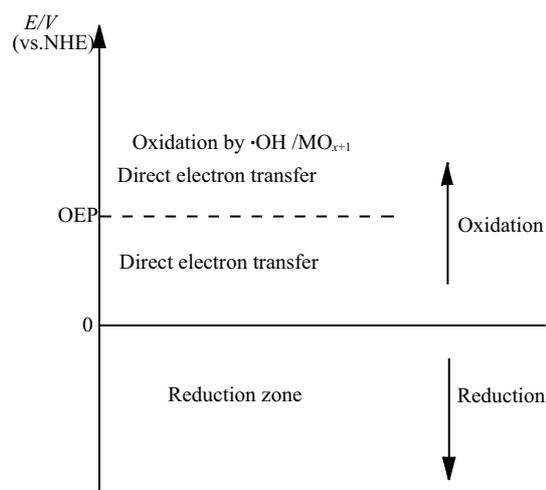

Fig. 6 Oxidation mechanism of organics by electrochemical oxidation processes (Qu and Liu, 2007).

3 Conclusions

The production and contribution of hydroxyl radicals varied during electrochemical oxidation and photoelec-

trochemical oxidation under different reaction conditions. With an increase in electrode potential across the electrodes, the contribution percentage of hydroxyl radicals increased dramatically. The contribution of hydroxyl radicals was particularly high at near neutral pH conditions. Finally, the contribution of hydroxyl radicals was dominant in photocatalytic oxidation but the contribution of hydroxyl radicals was negligible in electrochemical oxidation, which implied the necessity of UV irradiation for electrochemical oxidation during water treatment.

Acknowledgements

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