Effects of anions on the photocatalytic and photoelectrocatalytic degradation of reactive dye in a packed-bed reactor

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Abstract: The effects of various anions, Cl^-, ClO_4^-, SO_4^{2-}, NO_3^-, HCO_3^-, $H_2PO_4^-$ and $C_2O_4^{2-}$, on the photocatalytic and photoelectrocatalytic degradation of reactive Brilliant Orange K-R have been investigated in a packed-bed photoelectrocatalytic reactor. It was found that the nature and concentrations of these inorganic anions significantly affected the photocatalytic and photoelectrocatalytic degradation performance of the reactive dye. The results indicated that the external electric field was successfully applied to improve the photocatalytic efficiency of reactive Brilliant Orange K-R in the presence of Cl^-, especially at higher concentrations, while other inorganic anions displayed more or less negative effects on the degradation of the dye. The strongest inhibition effect on photocatalytic and photoelectrocatalytic degradation of the dye was observed in the presence of HCO_3^- ions.
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Keywords: photocatalysis; photoelectrocatalysis; electrooxidation; reactive Brilliant Orange K-R; anions

1 INTRODUCTION

Many anions such as NO_3^-, Cl^-, HCO_3^- and SO_4^{2-}, widely present in natural waters, agriculture and industrial wastewaters, have substantial influences on the photocatalytic oxidation of organic pollutants.[1] Although the results reported in the literature are different and even contradictory, a general consensus seems to be obtained that these anions affect the adsorption of the degrading species and act as hydroxyl free radical scavengers. The external anodic bias has been proved to be able to improve the efficiency of charge separation by driving the photogenerated electrons and holes in different directions in the photoelectrocatalytic oxidation process since Fujishima and Honda first introduced the concept of achieving charge separation in a semiconductor system with an anodic bias.[2–9] However, many anions may be poisonous to the photocatalyst, but at the same time they are also supporting electrolytes for the electrochemical process. Therefore, it is of interest to learn how these anions affect the photoelectrocatalyitc process. Candal *et al* found that when potentials were applied across titania coatings the photoelectrocatalytic activities

were not inhibited significantly in the presence of sodium chloride.[3] Zanoni *et al* pointed out that the selection of a supporting electrolyte for the complete degradation of pollutants was critical to the photoelectrocatalytic process.[10] However, their experiments were carried out only at one concentration of inorganic ions. In our previous study, we found that the external electric field depressed the deactivation of TiO_2 photocatalyst in the presence of high concentrations of Cl^- ions in the slurry photoelectrocatalytic reactor.[11] However, many anions, especially high valence ions, have apparent flocculation effects on nanometre Degussa P25, leading to a rapid decrease in the efficiency in addition to OH hydroxyl radical and hole scavenging effect. So, the photoelectrocatalytic degradation efficiencies of organic pollutants were dependent to a considerable extent on not only the nature but also the concentration of these inorganic anions.[11,12]

More recently, our groups have successfully developed a novel continuous flow three-dimensional electrode-packed bed photoelectrocatalytic reactor to investigate the feasibility of the photoelectrochemical

degradation of some pollutants in saline water.[12,13] It was interesting to note that chloride ions had an obvious enhancement effect rather than a scavenging effect on the photoelectrocatalytic degradation of reactive dye and quinoline in saline water in the packed bed photoelectrocatalytic reactor. However, the effects of other inorganic or organic anions on the photoelectrocatalytic degradation of the pollutants are not clear. Thus, in the present paper, the effects of many other anions on the photoelectrocatalytic degradation of reactive Brilliant Orange K-R are discussed in detail.

2 EXPERIMENTAL

2.1 Materials

Reactive Brilliant Orange K-R (RBOKR) was commercial grade reagent with a purity of 95%, the formula is shown in Fig 1. The solutions were prepared with deionized water to the concentration of 0.5 mM. NaCl, NaNO$_3$, NaHCO$_3$, NaH$_2$PO$_4$, Na$_2$SO$_4$, NaClO$_4$ and Na$_2$C$_2$O$_4$ were all analytical grade. Titanium dioxide Degussa P25 is composed mainly of anatase (*c* 70%), having the shape of non-porous polyhedral particles with a mean size of *c* 30 nm and a surface area of 50 m^2 g^{-1}. Analytical grade quartz sand with particulate diameter of 2–4 mm was used as the support of the photocatalyst. The micropore titanium plate was used as electrodes after dealt with diluted sulfuric acid and then washed with deionized water twice, respectively.

2.2 Preparation of packed materials and photoelectrochemical reactor

The packed material, TiO$_2$-loaded quartz sand, which was used for both the photocatalyst of the packed-bed photocatalytic reactor and for the particle electrode of the three-dimensional electrode electrochemical reactor, was prepared by following the method described elsewhere.[12,13]

The set-up used is a continuous flow three-dimensional electrode-packed *bed photoelectrocatalytic* reactor, as described previously.[12,13] The reactor was based on the three-dimensional electrode-slurry photocatalytic reactor[14,15] and the slurry photoelectrocatalytic reactor[16] reported previously.

2.3 Analysis

The degradation of RBOKR in the reaction solution was monitored at the maximum absorption wavelength of 480 nm with a Helios Alpha UV/visible spectrophotometer (Thermo Spectronic) and the conductivity of

the solution was determined by a conductivity meter, DDB-6200 (Shanghai Rex Instrument Factory).

2.4 Procedures

A 500.0 cm^3 solution of RBOKR containing known concentrations of inorganic or organic anions was used to conduct the experiment. The solution of 0.5 mmol dm^{-3} RBOKR without any salts has a conductivity of 0.5 mS cm^{-1} and the conductivities of all the solutions for all the electrolytes studied were carefully adjusted to 3.1, 12.3, 24.1 and 47.2 mS cm^{-1} by adding different contents of salts. The solution was pumped through the photoelectrochemical reactor with a peristaltic pump at the flow of 190 cm^3 min^{-1}, and the residual solution was well stirred by a magnetic stirrer. The reaction was started when the dc power, illumination and compressed air supply were switched on. Except as indicated, general treatment conditions were 30.0 V direct current cell voltage, 0.05 MPa airflow, 0.5 mmol dm^{-3} RBOKR and without adjusting pH value. Once the experiment started, samples were withdrawn from the reservoir at desired intervals for the analyses of the concentration of the dye.

3 RESULTS AND DISCUSSION

3.1 Effect of Cl$^-$ on the degradation of RBOKR

Chloride ions, very common inorganic ions frequently present in natural water or anthropogenic wastewater, have been found to be scavengers for the heterogeneous photocatalytic process by competing for surface active sites and forming the weaker Cl radicals.[17,18] In our previous study, we found that the external electric field depressed the deactivation of TiO$_2$ photocatalyst in the presence of high concentrations of Cl$^-$ ions.[11] The photoelectrocatalytic efficiency of HCOOH decreased initially then increased rapidly with increasing Cl$^-$ ion concentrations in the slurry photoelectrocatalytic reactor.

In this paper the effects of Cl$^-$ ions on the degradation of RBOKR involving electrooxidation, photooxidation and photoelectrocatalytic oxidation are shown in Fig 2. It is clear that with the increase of Cl$^-$ ions, the removal efficiency of RBOKR increased slowly in the direct electrooxidation, while it decreased sharply in the photocatalytic process. Since NaCl is a strong electrolyte, the electrooxidation efficiency of RBOKR in the three-dimensional electrode electrochemical reactor would be enhanced noticeably for increasing
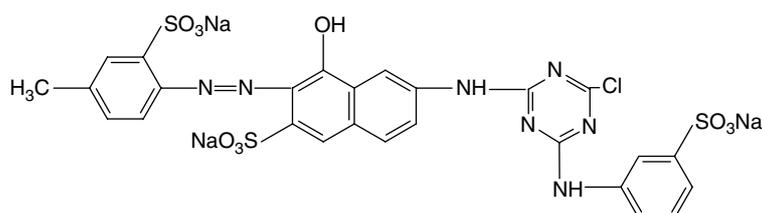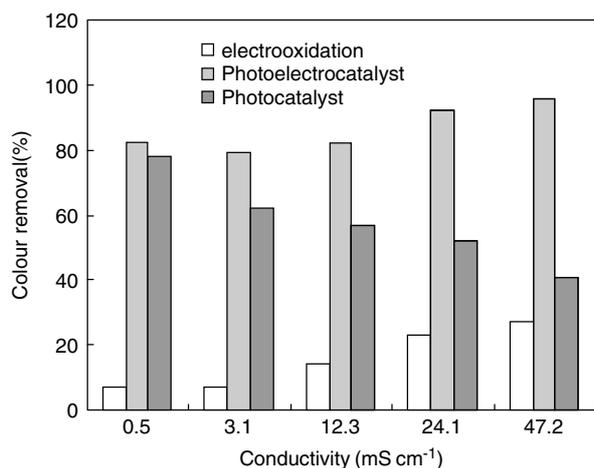

Figure 1. Structure of RBOKR.

Figure 2. Effects of Cl$^-$ concentrations on the electrooxidation, photooxidation and photoelectrocatalytic oxidation of RBOKR.

Figure 3. Effects of ClO$_4$$^-$ concentrations on the electrooxidation, photooxidation and photoelectrocatalytic oxidation of RBOKR.

amounts of Cl$^-$ ions. However, in the photocatalytic process the competition between the dye and Cl$^-$ ions for surface active sites of TiO$_2$ would be noticeable for the higher concentration of Cl$^-$ ions, leading to lower efficiency in photocatalytic reactions. However, it is interesting to note that increasing the amount of NaCl can significantly enhance rather than inhibit the photoelectrocatalytic degradation of RBOKR in this photoelectrocatalytic reactor. For example, when the conductivity of the solution was 24.1 mS cm^{-1}, only 23% and 52% of RBOKR were removed by direct electrooxidation and photocatalytic oxidation processes, respectively, while 92% of RBOKR was removed in photoelectrocatalytic process within the same reaction time, ie, the efficiency of the photoelectrocatalytic process was not only greater than that of the photocatalytic or electrochemical process, but also greater than the sum of the two processes. The enhancement can be interpreted as follows. At lower Cl$^-$ ion concentrations, Cl$^-$ ions competed for oxidizing radicals or active sites of the catalyst, resulting in some degree of scavenging effects. However, with the increase in the concentration of Cl$^-$ ions, the adsorption of Cl$^-$ ions reached equilibrium, thus the surplus free Cl$^-$ ions, as electrolytes, would enhance charge-transfer in the photoelectrocatalytic reactor, leading to an increase in capture effects for photogenerated electrons under an external electric field. Moreover, an increase in the electrolyte concentration could also lead to an increase in the efficiency of RBOKR degradation by direct and/or indirect electrochemical oxidation under high cell voltage. Zanoni *et al* also confirmed the presence of active chlorine in the photoelectrocatalytic process when they used NaCl as the supporting electrolyte.[10] So, the active chlorine may be another reason for the increase in the photoelectrocatalytic efficiency.

3.2 Effect of ClO$_4$$^-$ on the degradation of RBOKR

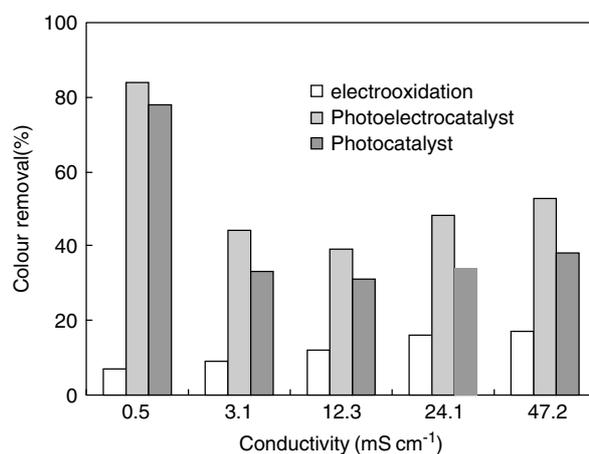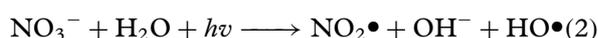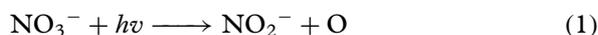In our photoelectrocatalytic experiments, NaClO$_4$ was chosen as a supporting electrolyte so that no

direct electrochemical oxidation interfered with the photoelectrocatalytic process because among the electrolytes studied, NaClO$_4$ had the least electrolytic reaction. Figure 3 shows the effects of NaClO$_4$ on the electrooxidation, photooxidation and photoelectrocatalytic oxidation of RBOKR. It is clear that the photooxidation and photoelectrocatalytic oxidation of RBOKR were decreased significantly in the presence of ClO$_4$$^-$. For example, the photoelectrocatalytic efficiency of RBOKR decreased from 84% at the conductivity of 0.5 mS cm^{-1} to 39% at the conductivity of 12.3 mS cm^{-1}, while the photocatalytic efficiency of RBOKR decreased from 78% to 31%. However, the degradation efficiency of RBOKR by the photoelectrocatalytic process was still higher than that by the photocatalytic process at the same concentration of ClO$_4$$^-$, which indicated that the external electric field depressed the deactivation of catalyst in this photoelectrocatalytic reactor. For example, the photoelectrocatalytic efficiency of RBOKR decreased from 84% at the conductivity of 0.5 mS cm^{-1} to 53% at the conductivity of 47.2 mS cm^{-1}, while the photocatalytic efficiency of RBOKR decreased from 78% to 38%. This indicated that the addition of NaClO$_4$ to the solution would lead to the competition of ClO$_4$$^-$ with RBOKR for the active sites on the surface of TiO$_2$. Another possible reason for this is that ClO$_4$$^-$ in solution may trap OH radicals, thus decreasing the decolorization rate of RBOKR.[19] However, Kim and Anderson observed that though the presence of ClO$_4$$^-$ significantly slowed down the photocatalytic oxidation rate of formic acid, the photoelectrocatalytic efficiency was still much higher than that without addition of ClO$_4$$^-$.[4] Thus this may be due to the difference in the photoelectrocatalytic reactor and that the concentration of ClO$_4$$^-$ used in their experiments was much higher than that in our experiments.

3.3 Effect of NO$_3$$^-$ on the degradation of RBOKR

The effects of NO$_3$$^-$ on electrooxidation, photooxidation and photoelectrocatalytic oxidation were studied

by adding $NaNO_3$ into solutions of RBOKR, and the results are shown in Fig 4. It is clear that with the increase of NO_3^- ions the photoelectrocatalytic degradation efficiencies exhibit a similar change trend as in the photocatalytic process, ie at lower concentration of NO_3^- ions, the degradation efficiencies decreased, whereas the degradation efficiencies increased slightly at higher concentrations of NO_3^- ions. This indicated that a complicated mechanism was involved in the photocatalytic and photoelectrocatalytic oxidation of RBOKR when NO_3^- ions were present in the solution. It is well known that the hydroxyl radicals formed by interaction of NO_3^- with UV light play an important role in the degradation of micropollutants in natural water.[20] However, another action of nitrate in the photochemistry of organic pollutants is as an inner filter substance to reduce the UV adsorption by TiO_2, resulting in lower photocatalytic activity of TiO_2.[21] So the experimental results can be explained as follows. At lower concentration of NO_3^- ions, most of the NO_3^- ions were adsorbed on the surface of TiO_2, whereas the adsorption of RBOKR onto TiO_2 decreased. Thus it not only lowered the utilization efficiency of TiO_2 for UV irradiation but also hindered the contact of RBOKR with surface active sites on the TiO_2. However, with increasing NO_3^- ion concentrations, as in the case of Cl^-, the surplus free NO_3^- would also enhance charge-transfer in the packed-bed reactor and the capture effect of photogenerated electrons by the external electric field. Also, hydroxyl radicals generated in bulk solution by NO_3^- ion may be available for the degradation of RBOKR:[22]

$$NO_3^- + hv \longrightarrow NO_2^- + O \tag{1}$$

$$NO_3^- + H_2O + hv \longrightarrow NO_2\bullet + OH^- + HO\bullet \tag{2}$$

$$O + H_2O \longrightarrow 2HO\bullet \tag{3}$$

$$2NO_2\bullet + H_2O \longrightarrow NO_2^- + NO_3^- + 2H^+ \tag{4}$$

In addition, an increase in electrolyte concentration of NO_3^- had a lower degradation efficiency than that of Cl^-, which may be due to fewer oxidative species produced in the presence of NO_3^-.

3.4 Effect of SO_4^{2-} on the degradation of RBOKR

Figure 5 shows the effects of Na_2SO_4 on the electrooxidation, photocatalytic oxidation and photoelectrocatalytic oxidation of RBOKR. Obviously, the degradation efficiency of RBOKR by the photocatalytic or photoelectrocatalytic process decreased with the increase in the SO_4^{2-} ion concentrations. However, the degradation of RBOKR by the photoelectrocatalytic process was higher than that by photocatalytic oxidation, especially at lower conductivity of SO_4^{2-}. This indicated that lower concentrations of SO_4^{2-} would inhibit the photocatalytic oxidation of RBOKR significantly, eg the photocatalytic oxidation efficiency of RBOKR reduced from 78% at the conductivity of $0.5\,mS\,cm^{-1}$ to 45% at the conductivity of $3.1\,mS\,cm^{-1}$, whereas no obvious disadvantageous effect was observed in the photoelectrocatalytic oxidation. Furthermore, only 6% and 45% of RBOKR were removed by direct electrooxidation and photocatalytic oxidation processes at the conductivity of $3.1\,mS\,cm^{-1}$, while 83% of RBOKR was removed in the photoelectrocatalytic process. Therefore, electrochemically-assisted photocatalytic oxidation would overcome the detrimental effects of lower concentrations of SO_4^{2-}. However, with the increase of SO_4^{2-}, the reaction of the adsorbed SO_4^{2-} with the positive holes (h^+) and hydroxyl radical (OH), as shown in eqns (5) and (6), would be important:[19]

$$SO_4^{2-} + h^+ \longrightarrow SO_4^{\bullet-} \tag{5}$$

$$SO_4^{2-} + {}^\bullet OH \longrightarrow SO_4^{\bullet-} + OH^- \tag{6}$$

$SO_4^{\bullet-}$ is less reactive than ${}^\bullet OH$ and h^+, therefore, the excess SO_4^{2-} hindered the photocatalytic and photoelectrocatalytic decolorization of RBOKR. Also, the photocatalytic oxidation rate of RBOKR would be
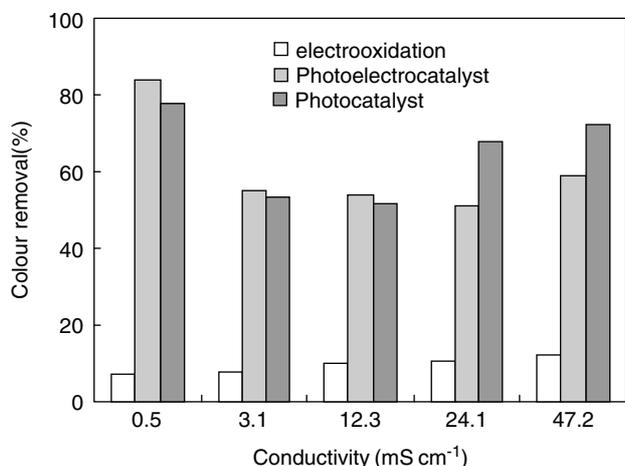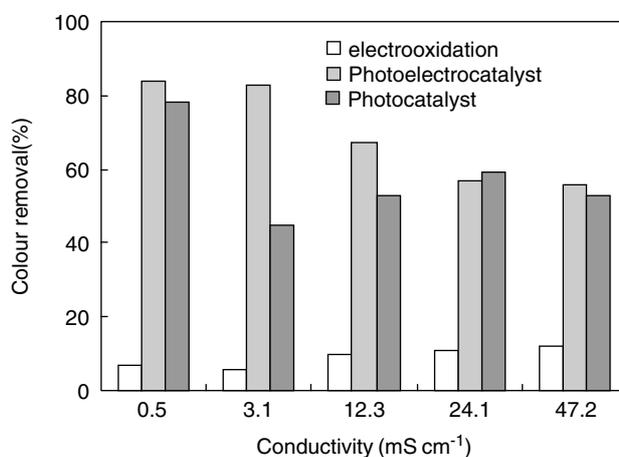

Figure 4. Effects of NO_3^- concentrations on the electrooxidation, photooxidation and photoelectrocatalytic oxidation of RBOKR.

Figure 5. Effects of SO_4^{2-} concentrations on the electrooxidation, photooxidation and photoelectrocatalytic oxidation of RBOKR.

decreased with the increase of SO_4^{2-} as they decrease the adsorption of the dye.

3.5 Effect of HCO_3^- on the degradation of RBOKR

Carbonate and bicarbonate are also very common inorganic salts in natural water and industrial effluents. The presence of carbonate and bicarbonate always exhibited disadvantageous effects on the oxidation of organic pollutants by the photocatalytic process.[1] Furthermore, among the studied anions HCO_3^- had the strongest inhibition on the photocatalytic process. However, the effects of bicarbonate on the photo-electrocatalytic oxidation have not been discussed yet. So, experiments were carried out to investigate the effects of bicarbonate on the photoelectrocatalytic oxidation of RBOKR by adding $NaHCO_3$ in the solution, and the results are shown in Fig 6. It is obvious that although the degradation efficiency of RBOKR by the direct electrooxidation process increased with the increase of HCO_3^-, the photocatalytic and photo-electrocatalytic oxidation of RBOKR were remarkably inhibited in the presence of HCO_3^-. Moreover, the photoelectrocatalytic efficiency of RBOKR decreased from 84% at the conductivity of $0.5\,mS\,cm^{-1}$ to 25% at the conductivity of $3.1\,mS\,cm^{-1}$, while the photocatalytic efficiency of RBOKR was decreased from 78% to 24%. This can be explained by the fact that bicarbonate ions, effective hydroxyl radical scavengers with a higher second-order constant, $3.9 \times 10^8\,M^{-1}\,s^{-1}$,[23] can react with hydroxyl radicals to produce carbonate radicals, which are weak oxidizing agents that hardly react with other organic molecules. On the other hand, the pH of the aqueous solution had significant effect on the photocatalytic oxidation process because the species of the reaction compounds and its adsorption equilibrium on the TiO_2 depend on the pH values of the reaction solution. In our experiments, the pH value of the RBOKR solution containing $NaHCO_3$ was 8–9. Since the iso-electrical point of TiO_2 is at pH 4–6, thus the catalyst's surface will be negatively charged below these pH values.[23] Therefore, the adsorption of RBOKR (a kind of anionic dye in the aqueous solution) onto TiO_2 would be difficult due to the repellent effect of two species with negative charge. Thus the presence of bicarbonate had disadvantageous effects on both photocatalytic and photoelectrocatalytic processes.

3.6 Effect of $H_2PO_4^-$ on the degradation of RBOKR

The effects of $H_2PO_4^-$ on the electrooxidation, photooxidation and photoelectrocatalytic oxidation of RBOKR were studied by adding NaH_2PO_4 to a solution of RBOKR. As shown in Fig 7, the removal efficiencies of RBOKR by photocatalytic oxidation and photoelectrocatalytic oxidation processes were all depressed significantly in the presence of $H_2PO_4^-$ ions. For instance, the photoelectrocatalytic efficiency of RBOKR decreased from 84% at the conductivity
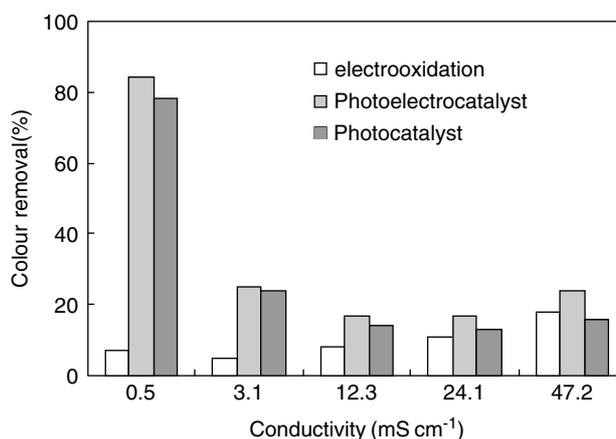

Figure 6. Effects of HCO_3^- concentrations on the electrooxidation, photooxidation and photoelectrocatalytic oxidation of RBOKR.
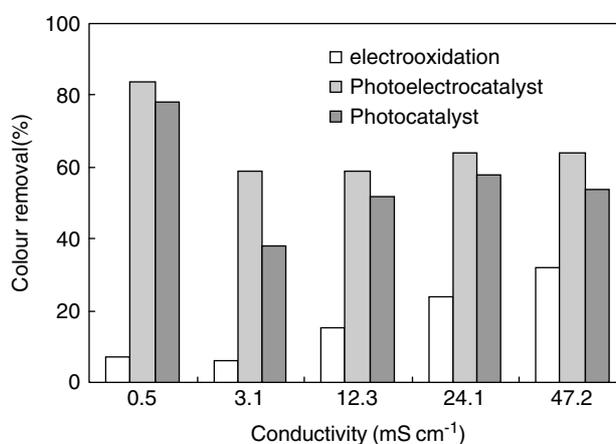

Figure 7. Effects of $H_2PO_4^-$ concentrations on the electrooxidation, photooxidation and photoelectrocatalytic oxidation of RBOKR.

of $0.5\,mS\,cm^{-1}$ to 64% at the conductivity of $47.2\,mS\,cm^{-1}$, while the photocatalytic efficiency of RBOKR decreased from 78% to 54%. In our previous study, the deleterious effects of $H_2PO_4^-$ on the photooxidation and photoelectrocatalytic oxidation were also observed in a slurry photoelectrocatalytic reactor. The strong inhibition was mainly attributed to the coagulation role of NaH_2PO_4, which was also reported by Bekbölet et al.[24] However, in the present study, the coagulation effect should not be a problem in our packed-bed photoelectrocatalytic reactor because TiO_2 was immobilized on quartz sand. The inhibition effect of $H_2PO_4^-$ may be explained by the competitive adsorption of $H_2PO_4^-$ with substrate onto the surface of TiO_2 and that $H_2PO_4^-$ can react with h^+ and •OH to form a less reactive species, $H_2PO_4•$.[19]

3.7 Effect of $C_2O_4^{2-}$ on the degradation of RBOKR

Oxalic acid, an organic pollutant resulting from some industrial treatment processes (textile industry, metallurgy, etc), has always been used as a sacrificial agent to decrease the photogenerated electron–hole
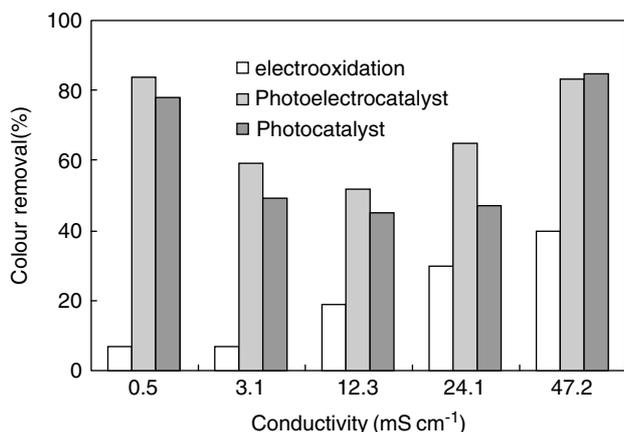
Figure 8. Effects of $C_2O_4^{2-}$ concentrations on the electrooxidation, photooxidation and photoelectrocatalytic oxidation of RBOKR.

recombination and increase the efficiency of some photoreduction process at the semiconductor–electrolyte interphase.[25] So, oxalate would affect the photocatalytic oxidation both by acting as an anion and a co-existing organic pollutant when present in the wastewater. Figure 8 shows the effects of $Na_2C_2O_4$ on the electrooxidation, photocatalytic oxidation and photoelectrocatalytic oxidation of RBOKR. In contrast with other inorganic ions, the electrooxidation played a more important role in RBOKR degradation in the presence of $Na_2C_2O_4$ under the same conductivity conditions. However, in the photocatalytic oxidation and photoelectrocatalytic oxidation of RBOKR, the removal efficiencies of RBOKR decreased at first and then increased with the increase of $C_2O_4^{2-}$ concentration. The inhibition effect of oxalate on the degradation of the dye was also observed with TiO_2 but not found with modified titania, $Ag-TiO_2$ catalyst, by Sörensen and Frimmel.[22] Calvo *et al* also found that although the presence of oxalate inhibited the photoelectrocatalytic oxidation of salicylate, complete mineralization of salicylate was still achieved in the mixtures.[26] The addition of $Na_2C_2O_4$ played two roles in the photodegradation of RBOKR. The first one was that $C_2O_4^{2-}$ would change the surface charge of TiO_2 and result in a change of distribution of dye molecules between solution and TiO_2 surface in which $C_2O_4^{2-}$ has faster adsorption kinetics than RBOKR. The other was that the adsorbed $C_2O_4^{2-}$ would react with the positive holes (h^+) and hydroxyl radicals.[18] In the presence of lower concentrations of $C_2O_4^{2-}$ only a small part of the active sites was occupied by $C_2O_4^{2-}$, leading to little decrease in the photodegradation efficiency of RBOKR.

REFERENCES
1 Bhatkhande DS, Pangarkar VG and Beenackers AA, Photocatalytic degradation for environmental applications—a review. *J Chem Technol Biotechnol* **77**:102–116 (2002).
2 Butterfield IM, Christensen PA, Hamnett A, Shaw KE, Walker GM, Walker SA and Howarth CR, Applied studies on immobilized titanium dioxide films as catalysts for the photeclectrochemical detoxification of water. *J Appl Electrochem* **27**:385–395 (1997).
3 Candal RJ, Zeltner WA and Anderson MA, Effects of pH and applied potential on photocurrent and oxidation rate of saline solutions of formic acid in a photoelectrocatalytic reactor. *Environ Sci Technol* **34**:3443–3451 (2000).
4 Kim DH and Anderson MA, Photoelctrocatalytic degradation of formic acid using a porous TiO_2 thin-film electrode. *Environ Sci Technol* **28**:479–483 (1994).
5 Liu H, Cheng S, Wu M, Wu H, Zhang J, Li W and Cao C, Photoelectrocatalytic degradation of sulfosalicylic acid and its electrochemical impedance spectroscopy investigation. *J Phys Chem* **104A**:7016–7020 (2000).
6 Pelegrini R, Peralta-Zamora P, Andrade AR, Reyes J and Duran N, Electrochemically assisted photocatalytic degradation of reactive dyes. *App Catal B* **22**:83–90 (1999).
7 Vinodgopal K, Hotchandani S and Kamat PV, Electrochemical assisted photocatalysis. TiO_2 particulate film electrodes for photocatalytic degradation of 4-chlorophenol. *J Phys Chem* **97**:9040–9044 (1993).
8 Vinodgopal K, Stafford U, Gray KA and Kamat PV, Electrochemically assisted photocatalysis. 2. The role of oxygen and reaction intermediates in the degradation of 4-chlorophenol on immobilized TiO_2 particulate films. *J Phys Chem* **98**:6797–6803 (1994).
9 Fujishima A and Honda K, Electrochemical photolysis of water at a semiconductor electrode. *Nature* **238**:37–37 (1972).
10 Zanoni MVB, Sene JJ and Anderson MA, Photoelectrocatalytic degradation of Remazol Brilliant Orange 3R on titanium dioxide thin-film electrode. *J Photochem Photobiol A* **157**:55–63 (2003).
11 Xiong Y, An TC, Zha CH and Zhu XH, Effect of inorganic ions on photoelectrocatalytic degradation of formic acid in the presence of inorganic ions. *J Appl Geochem* (in press).
12 An TC, Zhang WB, Xiao XM, Fu JM, Sheng GY and Zhu XH, Photoelectrocatalytic degradation of quinoline with a novel three-dimensional electrode-packed bed photocatalytic reactor. *J Photochem Photobiol A: Chem* **161**:233–242 (2004).
13 Zhang WB, An TC, Xiao XM, Fu JM, Sheng GY, Cui MC and Li GY, Photoelectrocatalytic degradation of reactive Brilliant Orange K-R in a new continuous flow photoelectrocatalytic reactor, *Appl Catal A:General* **255**:221–229 (2003).
14 An TC, Zhu XH and Xiong Y, Synergic degradation of reactive Brilliant Red X-3b using 3-D-photocatalytic reactors. *J Envion Sci Health* **36A**:1796–1811 (2001).
15 An TC, Zhu XH and Xiong Y, Feasibility study of photoelectrochemical degradation of methylene blue aqueous solutions with three dimensional electrodes-photocatalytic reactor. *Chemosphere* **46**:897–903 (2002).
16 An TC, Xiong Y, Li GY, Zha CH and Zhu XH, Synergetic effect in degradation of formic acid using a new photoelectrochemical reactor. *J Photochem Photobiol A: Chem* **152**:155–165 (2002).
17 Chen HY, Zahraa O and Bouchy M, Inhibition of the adsorption and photocatalytic degradation of an organic contaminant in an aqueous suspension of TiO_2 by inorganic ions. *J Photochem Photobiol A: Chem* **108**:37–44 (1997).
18 Sökmen M and Ozkan A, Decolourising textile wastewater with modified titania: the effects of inorganic anions on the photocatalysis. *J Photochem Photobiol A* **147**:77–81 (2002).
19 Hu C, Yu JC, Hao Z and Wong PK, Effects of acidity and inorganic ions on the photocatalytic degradation of different azo dyes. *Appl Catal B* **46**:35–47 (2003).
20 Zepp RG and Wolfe NI, Abiotic transformation of organic chemicals at the particle–water interface, in *Aquatic Surface*

Chemistry, ed by Stumm W. Wiley, New York, pp 423–456 (1987).

21 Zhu Z, Zhang M, Xia Z and Gary KCL, Titanium dioxide mediated photocatalytic degradation of monocrotophos. *Water Res* **29**:2681–2688 (1995).

22 Sörensen M and Frimmel FH, Photochemical degradation of hydrophilic xenobiotics in the UV/H$_2$O$_2$ process: influence of nitrate on the degradation rate of EDTA, 2-amino-1-naphthalenesulfonate, diphenyl-4-sulfonate and 4,4′-diaminostilbene-2,2′-disulfonate. *Water Res* **31**:2885–2891 (1997).

23 Kim DH and Anderson MA, Solution factors affecting the photocatalytic and photoelectrocatalytic degradation of formic acid using supported TiO$_2$ thin films. *J Photochem Photobiol A* **94**:221–229 (1996).

24 Bekbölet M, Boyacioglu Z and Özkaraova B, The influence of solution matrix on the photocatalytic removal of color from natural waters. *Wat Sci Technol* **38**:155–162 (1998).

25 Franch MI, Ayllon AA, Peral J and Domenech X, Photocatalytic degradation of short-chain organic diacids. *Catal Today* **76**:221–233 (2002).

26 Calvo ME, Candal RJ and Bilmes SA, Photooxidation of organic mixtures on biased TiO$_2$ films. *Environ Sci Technol* **35**:4132–4138 (2001).