Effect of supporting electrolytes in electrochemically-assisted photodegradation of an azo dye

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Abstract

The effect of supporting electrolytes in electrochemically-assisted photodegradation process has been investigated on an azo dye, methyl orange. The electrodes used were prepared by sol–gel dip-coating method. Several common inorganic salts were chosen to act as supporting electrolytes, which was added into the dye solution. The anions consist of SO_4^{2-}, CO_3^{2-}, NO_3^- and Cl^- while cations were Na^+, K^+, Ca^{2+}, NH_4^+ and Mg^{2+}. Linear Sweep Voltammetry was employed to study the photoelectrochemical behaviour of methyl orange solution containing the supporting electrolyte. The presence of certain ions showed pronounced effect towards the rate of photoelectrochemical degradation. The addition of the sodium chloride solution is found to buffer the level of hydrogen ion activity in the solution.
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1. Introduction

Photodegradation process using TiO_2 is a viable technique for the purification of wastewater [1–5]. Numerous studies reported the use of TiO_2 in slurry and immobilised forms to treat various types of organic pollutants [6–8]. Practically, immobilisation method is more preferable over slurry or suspension system because it eliminates the photocatalyst separation steps such as filtration, centrifugation, coagulation or flocculation after photodegradation [9]. These additional processes are costly although slurry system has been proven to be relatively effective.

In immobilisation method, TiO_2 is coated in form of film on a substrate like alumina plate, glass, quartz, ITO glass, titanium plate, zeolites and silica gel [6,9,10]. In the electrochemically-assisted photocatalytic process, the use of conductive supporting material is necessary in order for external applied electrical field to take effect. Meanwhile, the other concern is the addition of suitable supporting electrolyte into the solution, which is also indispensable to maintain the ionic strength in the electrochemical system.

A supporting electrolyte, as well as its concentration should be chosen to minimize the phenomenon of migration of the electroactive species caused by the electrical field and to confine the interfacial potential difference to the distance of closest approach of solvated ions to the electrode [11]. This will minimize uncompensated iR drop, which cause potential-control error and ohmic heating of the solution [12].

The concentration of ionic species in the supporting electrolyte is at least 100 times of the electroactive species and is the principal source of electrically conducting ionic species. It can be inorganic or organic salt, an acid or a base, or a buffer solution such as citrate, phosphate or acetate. The concentration of the supporting electrolyte varies normally between 0.01 and 1.0 M with the concentration of electroactive species being 5 mM or less [11].

In this work the effect of several common inorganic cations and anions as supporting electrolyte towards the photoelectrochemical degradation of methyl orange were studied.

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2. Experimental

2.1. Materials

All chemicals, tetraisoprophyl-orthotitanate (>98% Ti, Merck-Schuchardt), ethanol (Analytical reagent grade, R.G. HmbG Chemical), diethanolamine (Acros Organics), polyethylene glycol (Fluka Chemika), methyl orange (BDH chemicals Ltd.), sodium chloride (Fluka Chemika), sodium sulphate (Fluka Chemika), sodium carbonate (Fluka Chemika), sodium nitrate (Fluka Chemika), calcium chloride dehydrate (Fisher Scientific), potassium chloride (BDH Analar), ammonium chloride (Ajax Chemicals) and magnesium chloride (Prolabs) were used without further purification. All solutions in this experiment were prepared using the deionized water (Milipore Alpha Q system, 18.2 MΩ cm).

2.2. Preparation of precursor solutions

The precursor solution for TiO_2 sol was prepared using the system containing titanium tetraisopropyl-orthotitanate, polyethyleneglycol (molecular weight, $M_w = 2000$), diethanolamine, ethanol and water as reported by Kato [13–15]. Modifications were made on chemical molar ratio and adding sequences. The molarity of alkoxide in the ethanol was 0.94 M with the molar ratio of diethanolamine to the alkoxide of one. The concentration of polyethylene glycol and water to alkoxide was 6 and 0.8 mass%, respectively. The polyethyleneglycol solution was dissolved in the ethanol solution followed by addition of diethanolamine, titanium tetraisoprophyl-orthotianate and water. The mixture was stirred for several hours at room temperature until a clear and transparent sol–gel was obtained.

2.3. Preparation of TiO_2 thin films

The titanium plates (5 cm × 2 cm) were used as the conductive support for TiO_2. The plate was polished by silicon carbide paper (Bioanalytical system PK-4 polishing kit) and later cleaned with acetone in an ultrasonic bath for 15 min. The treated Ti plate was dried in an oven at 100 °C for 15 min and then dip-coated with sol–gel solution and left to dry at room temperature. The coated electrode was heated at 100 °C for 5 min in oven followed by subsequent dip-coating. An area with size of 1.5 cm × 2.0 cm at the top was left uncoated for the electrical connection. These steps were repeated several times until the amount of TiO_2 loaded was approximately 2.00 mg. Finally, the plate was annealed at 500 °C in a Thermolyne 21100 furnace for 2 h. TiO_2 obtained for this temperature consist of 70% anatase and 30% rutile phases.

2.4. Analytical measurements

The photoelectrochemical measurements were carried out in the two-compartment cell equipped with a quartz window.

The anode and cathode electrodes were separated by polytetrafluoroethylene (PTFE) 0.45 μm membrane. The working electrode was a TiO_2/Ti plate and the counter electrode was a platinum plate (1 cm²). All the potentials were specified against Ag/AgCl reference electrode, which was connected to the assembly via a salt bridge. The electrode potentials and photocurrents were recorded using AMEL general-purpose potentiostat–galvanostat Model 2049. All the potentials were fixed at 1.0 V during photodegradation experiment. Meanwhile, a potensiostat EG&G Princeton Applied Research (PAR) VersaStat driven by model 270 Electrochemical Analysis System software with PC control was used for linear sweep voltammetry (LSV) measurement. The temperature of the solutions was maintained at 313 K throughout the experiments by using a water jacket circulation system around the cell. Tungsten halogen projector lamp (Osram, 300 W and 120 V) was used as the light source, which was placed 8 cm from the sample. Photoreactor cell was filled with 120 cm³ methyl orange solution containing supporting electrolyte. The samples were withdrawn every 30 min thereafter for a period of 120 min. The concentration of the methyl orange in the solution was determined by measuring the absorbance values using UV/vis Perkin-Elmer Lambda 20 Spectrophotometer at 464.5 nm.

3. Results and discussion

3.1. Effect of anions

The effect of anions was investigated by using supporting electrolyte of similar cation, namely Na_2SO_4, $NaNO_3$, Na_2CO_3 and NaCl. The concentration was fixed at 0.1 M and the photoelectrochemical degradation was performed on 10 ppm methyl orange dye with bias potential of 1.0 V. The result presented in Fig. 1 shows a great influence of the anions of supporting electrolyte in the photodegradation process. Significant enhancement in the photodegradation rate occurred in chloride medium while the opposite effect is observed in sulphate and carbonate medium. Meanwhile the performance in nitrate medium is quite similar to the solution without supporting electrolyte.

In the presence of light photoconversion of anions to form highly oxidizing species may occur either by direct photolysis [16] or through a heterogeneous photocatalysis on the electrode surface. However, direct photolysis seems not appropriate in the present case since no degradation of dye was observed when the experiment was conducted under direct illumination without TiO_2. Therefore, the reaction occurred in this system is dominated by heterogeneous process on the electrode surface.

The result in Fig. 2a shows that introduction of NaCl at concentration as low as 0.01 M promotes the degradation rate. The degradation was further enhanced when more chloride ion was introduced. Compared to the virgin dye solution,
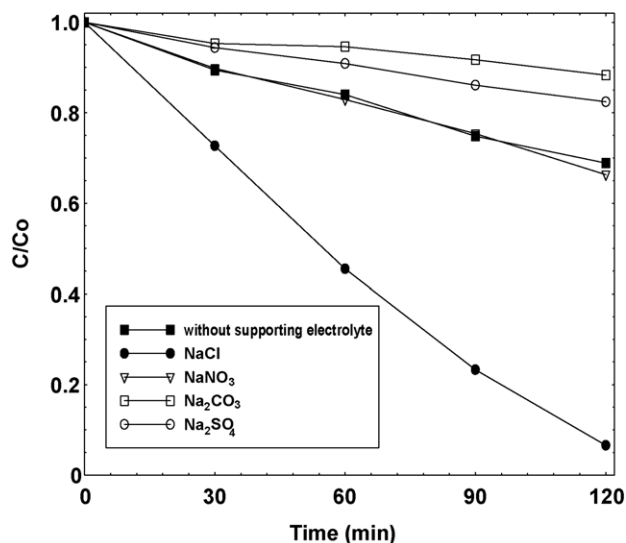
Fig. 1. The photoelectrochemical degradation of methyl orange dependence on supporting electrolyte exhibited with different anions. Methyl orange = 10 ppm, anions = 0.1 M, potential = 1.0 V, illumination = 300 W halogen lamp.

photoelectrochemical degradation in the presence of NaCl increased by 31–58% depending on its concentrations.

In an aqueous solution it is well known that photodegradation started with the formation of OH$^\bullet$ radical. In an electrochemical system the formation of this highly strong oxidizing agent resulted from oxidation of molecular water or hydroxyl ion on the surface of the electrode, which can be represented by the following equations.

$$TiO_2 + h^+ + OH^- \rightarrow TiO_2 + OH^\bullet \qquad (1)$$

$$TiO_2 + h^+ + H_2O \rightarrow TiO_2 + H^+ + OH^\bullet \qquad (2)$$
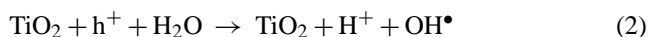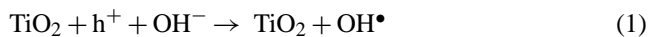
In chloride containing medium another oxidising radical, Cl$^\bullet$ is formed through a competing electrochemical process on the electrode surface.

$$TiO_2 + h^+ + Cl^- \rightarrow TiO_2 + Cl^\bullet \qquad (3)$$
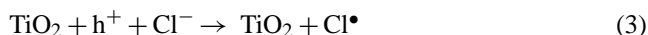
However due to the large quantitative differences between water and chloride ions in the solution, chances for chloride ions to react on the TiO$_2$ surface to produce the radical is relatively low. Therefore, here we suggest two main factors that probably contributed to the enhancement in chloride medium.

Firstly, chloride ion is more favourable in terms of competition to be adsorbed on the electrode surface compared to water or hydroxyl ions. This is due to water being electrically neutral and hydroxyl ion being very low in concentration. Secondly, the chloride medium acts as an electrolyte, which enable electrical conduction in the solution. Although proton and hydroxide ions are produced from water dissociation [12], apart from being low concentration, the existence of methyl orange in the solution reduces their mobility and thereby increases the cell resistance. In the presence of supporting electrolyte this resistance is greatly reduced and thus minimizing uncompensated iR drop and ohmic heating of the
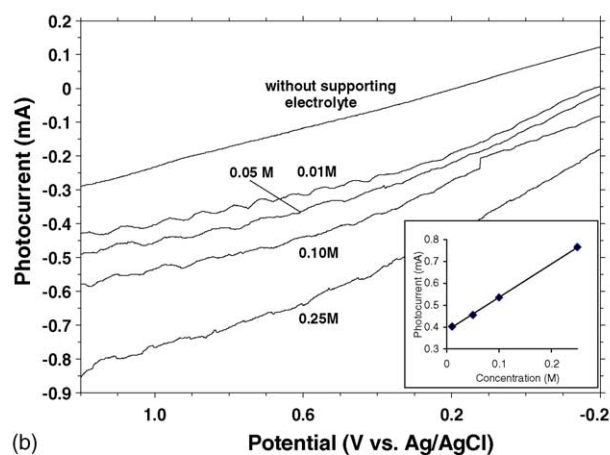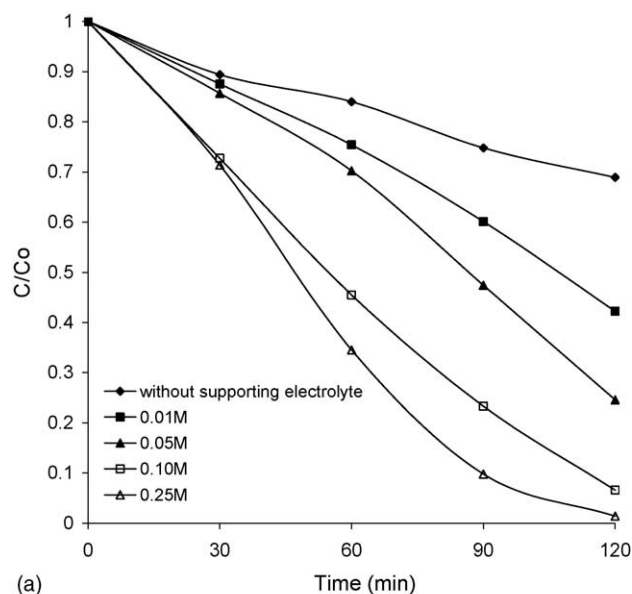

Fig. 2. (a) The photoelectrochemical degradation of methyl orange, (b) current–potential curves of methyl orange (inset shows photocurrent versus concentration of NaCl, potential at 1.0 V): dependence on the concentration of NaCl. Methyl orange = 10 ppm, potential vs. Ag/AgCl, illumination = 300 W halogen lamp.

solution. This explains the increase in the photodegradation efficiency even though with introduction of a low concentration of NaCl (0.01 M). Luo and Hepel [17] observed that photoelectrocatalytic degradation of naphthol blue black using WO$_3$ electrode in chloride medium required less electrical power compared to other media (NaClO$_4$, KNO$_3$ and Na$_2$SO$_4$).

Fig. 2b shows the photocurrent value increasing as more concentrated NaCl was used. The increase in photocurrent was linearly dependent to the concentration of chloride in the solution (Inset in Fig. 2b.). Increasing of chloride ions provides better conducting medium for the transfer of electroactive species in the bulk solution to electrode surface.

As shown in Fig. 2a, the rate of degradation and the amount degraded increase as the concentration of NaCl increases from 0.01 to 0.10 M. However, further increase in NaCl molarity to 0.25 M resulted in only a slight increase
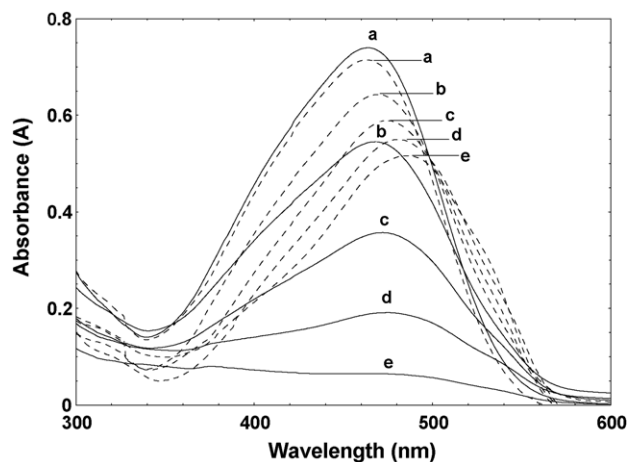
Fig. 3. UV–vis absorption spectra recorded at different time intervals for methyl orange containing 0.1 M NaCl (solid line), blank solution (broken line) at (a) 0 min, (b) 30 min, (c) 60 min, (d) 90 min and (e) 120 min.

in degradation. This observation suggests that 0.1 M NaCl is sufficient to provide the necessary conducting medium for photodegradation.

Fig. 3 shows the changes in UV absorption spectra for methyl orange solution after photoelectrochemical degradation for every 30 min intervals for a total irradiation time of 120 min in the presence and in the absence of 0.1 M NaCl as supporting electrolyte. Besides the drop in absorbance with time, the shift of the wavelength at maximum absorbance (λ_{max}) could be observed clearly for the solution without supporting electrolyte. This indicates that the solution acidity has increased which is a normal phenomenon during photodegradation process. The changes in acidity may be resulted from photodegradation products or in the case of photoelectrochemical reaction may be due to counter electrode process or competing oxidation reactions. Therefore, if the aqueous solution is not well buffered, the solution acidity will increase. The fact that the shift in λ_{max} is less obvious in solution with NaCl shows that the supporting electrolyte helped to buffer the solution.

Methyl orange in carbonate medium shows the lowest photoelectrochemical degradation rate (Fig. 2a). This result was expected because carbonate ion act as radical scavenger and causes inhibition [18] as shown in Eqs. (4) and (5). Hydroxyl radical produced are converted to the hydroxide ion thereby decreasing the concentration of these oxidizing agents. As a consequence, photodegradation process occurs at a very slow rate, only depending on the reaction of dye molecules at the electrode surface.

$$HCO_3^- + OH^\bullet \rightarrow CO_3^{-\bullet} + H_2O \tag{4}$$

$$CO_3^{2-} + OH^\bullet \rightarrow CO_3^{-\bullet} + OH^- \tag{5}$$
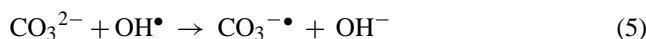
Sulphate ions will also react to retransform hydroxyl radical to hydroxide ion as expressed in Eq. (6). However, its scavenging behaviour seems less effective compared to car-
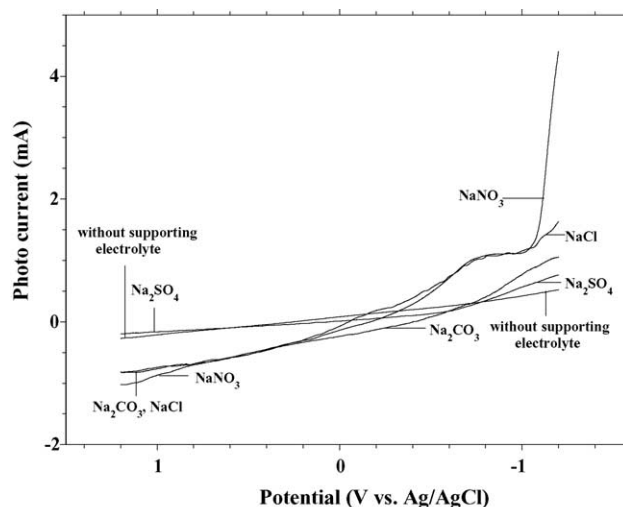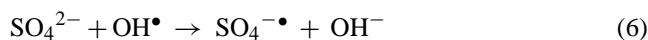

Fig. 4. Linear sweep voltammograms for electrode in methyl orange containing supporting electrolyte exhibited with different anions. Methyl orange = 10 ppm, anions = 0.1 M, illumination = 300 W halogen lamp.

bonate anions.

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

The photocatalytic reaction in the presence of NO_3^- under irradiation of $\lambda < 380$ nm is likely to increase the concentration of hydroxyl radicals as denoted by Eq. (7) [19] and thereby increasing the photodegradation rate.

$$NO_3^- + H_2O + h\nu \rightarrow NO_2^\bullet + OH^\bullet + OH^- \tag{7}$$
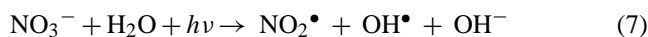
Nevertheless, the results in this experiment showed that the degradation rate is almost the same as without supporting electrolyte. Direct photolysis of nitric ions to produce the hydroxyl radical as well as $NO_2^\bullet$ did not occur. If the reaction in this study follows Eq. (8), the role of $NO_2^\bullet$ towards the photodegradation process is not well understood. Under these circumstances, it is appropriate to infer that the competitive reaction occurred at TiO_2 surface is much more predominant than reaction on nitrate ion. The UV/vis absorbance spectra for methyl orange added with different supporting electrolytes of 0.1 M indicate appearance of another peak for nitrate ions while other anions did not show extra peaks.

The photoelectrochemical characteristic of methyl orange solution in different supporting electrolyte is shown as linear sweep photovoltametry scans in Fig. 4. Blank methyl orange solution without addition of any supporting electrolyte was used as control set. Sulphate containing solution showed the lowest anodic photocurrent (positively biased) while nitrate, carbonate and chloride solutions showed higher values. The differences in photocurrent value indicate different degree of participation of anions in photodegradation reaction and their oxidation behaviour. These behaviours can be explained by the standard half reduction potential for anions listed in Table 1. The higher the positive potential values, the stronger the oxidizing behaviour of the ions. Therefore, solutions containing chloride and nitrate ions show higher photocurrent

Table 1
The half reduction equations and potentials for various types of anions

Half reduction equation	Potential, E (V)	Eq.
$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	+0.17	(8)
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36	(9)
$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$	+0.80	(10)
$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$	+0.10	(11)
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+0.96	(12)
$NO_3^- + 5H^+ + 4e^- \rightarrow 1/2\,N_2O + 5/2\,H_2O$	+1.11	(13)
$NO_3^- + 6H^+ + 5e^- \rightarrow 1/2\,N_2 + 3H_2O$	+1.24	(14)
$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$	+0.87	(15)

value than sulphate ions. On the other hand, although methyl orange in carbonate medium shows high anodic current but it exhibited the lowest photoelectrochemical degradation performance. This is due to active participation of carbonate ions in transformation of hydroxyl radicals to hydroxide ions, which in turn reduce the photodegradation rate.

3.2. Effect of cations

It is obvious from the previous section that chloride containing medium showed the best efficiency. It is also necessary to determine the roles of cations in this medium. Thus further investigations were done using Na^+, K^+, Ca^{2+}, NH_4^+ and Mg^{2+} ions. The result in Fig. 5 shows that except for Mg^{2+} all cations Na^+, K^+, Ca^{2+} and NH_4^+ act to promote the photodegradation rate.

Introduction of Na^+, K^+, Ca^{2+} and NH_4^+, which are the electron scavengers act to reduce the charge recombination process. On the other hand, Mg^{2+} acts to reduce the photoelectrochemical degradation rate by reacting with dye molecules to create dye complexes or ligands which are more difficult to be degraded. Furthermore dye complexes may be
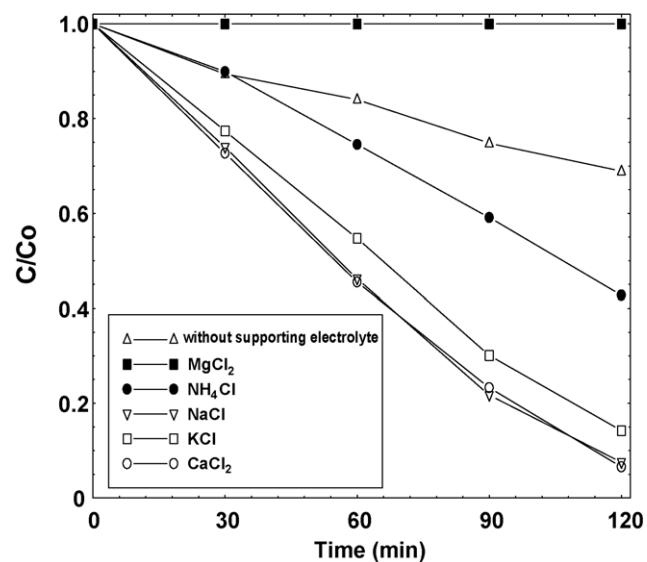

Fig. 5. The photoelectrochemical degradation of methyl orange dependence on supporting electrolyte exhibited with different cations. Methyl orange = 10 ppm, cations = 0.1 M, potential = 1.0 V, illumination = 300 W halogen lamp.

adsorbed on the electrode surface and caused deactivation. The formation of metal–dye complexes was reported in several literatures [20–22].

4. Conclusion

Supporting electrolytes is essential in providing the conducting medium for the reaction involving electroactive species to occur at electrode surface in electrochemically-assisted system. Addition of a small amount of supporting electrolyte greatly influenced the dye degradation performance. Chloride ion promotes the degradation rate while sulphate and carbonate ions show opposite effect. Meanwhile the presence of nitrate ion seems to have no effect on the photodegradation. On the other hand the presence of various counter ions such as sodium, potassium, calcium and ammonium in the chloride medium enhanced the photodegradation efficiency while the presence of magnesium ion inhibits the reaction. The present study indicates that some ions are unsuitable to be used as supporting electrolyte as they are not truly inert in the potential range of the experiment and may react with the electrode or with the products of the electrode reaction. Nevertheless, the desired properties of solution for photoelectrochemical degradation may be achieved by using sodium chloride, although, it may not be completely inert. Thus the use of appropriate supporting electrolyte reduces the cell resistance and buffers the solution, which in turn enhances the degradation performance.

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