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Probing the extent of $[O_2]$ depletion and $[Cl^-]$ production simultaneously at an illuminated TiO_2 surface employing simple electrochemical methods

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Abstract

The extent of $[O_2]$ disappearance and Cl^- production simultaneously from the UV-sensitised photodegradation of an aqueous aerated 4-chlorophenol (4-CP) solution at TiO_2 surface have been investigated electrochemically, employing an oxygen sensor probe and a Ag/AgCl potentiometric detector electrode, respectively. The preceding mineralisation of 4-CP was monitored potentiometrically in terms of Cl^- formation with illumination time while O_2 electrode allowed the direct measurement of any change in $[O_2]$ at the illuminated TiO_2 surface. A direct correlation was observed between the rates of O_2 consumption and Cl^- formation in the ongoing photo-process, which provided information that the photomineralisation process is ultimately an *electrochemical process*, in which the anodic (hole consumption) and cathodic (electron consumption) rate must balance.

Keywords: Electrochemical detection; Oxygen sensor; Ag/AgCl potentiometric detector electrode; Chlorophenol; TiO_2 thin film; Photomineralisation

1. Introduction

UV-sensitised photomineralisation of organic pollutants, particularly applying TiO_2 as photocatalyst has received much attention resulting in hundreds of articles and many reviews over the last few years [1–7]. The attractive feature of this methodology is the complete mineralisation of the pollutants in a simple and efficient manner regardless of employing suspended [8–10] or supported TiO_2 catalyst [6,11–13]. However in most of the previous studies, kinetics of the associated photo-process have concentrated on the roles of various parameters, such as semiconductor (nature, surface area, dopants, etc. [4,8]), organic substrate (nature and concentration [12]), and illumination intensity [14] etc. In contrast, for a better understanding of photomineralisation processes, it is also important to consider the role of molecular oxygen [13,15–19]. For photomineralisation to proceed, the photogenerated electrons must be scavenged by electron acceptors (e.g. dissolved O_2), while the holes produced are involved in the oxidation of organic substrates, either directly, or via $^{\bullet}OH$ formation by reaction with water. Hence, the overall rate of the interfacial photochemical process should satisfy the fact that at steady-state the flux of electron consumption across the semiconductor/liquid interface must be balanced by an equivalent flux of hole consumption as investigated by Lewis and coworkers [19]. However, in the majority of previous cases, oxygen is employed as the electron scavenger and thus, it is important to assess oxygen reduction profile (e^- consumption) with the photo-oxidation of organic pollutants (h^+ consumption).

Recently a photocatalytic sensor for monitoring, the chemical oxygen demand (COD), during photolysis was developed by Kim and co-workers [20], where the authors used an oxygen electrode with a TiO_2 coated PTFE membrane attached on the electrode tip. The observed COD value was in close agreement with the COD obtained using conventional methods. Ikeda et al. [21] demonstrated a microelecrode based photoelectrochemical approach to monitor dissolved oxygen during the photo-assisted degradation of ethanol in aqueous solution. Using a partially coated TiO_2–Pd film probed by a carbon fibre micro electrode, they were able to detect dissolved oxygen through the oxidation and reduction processes above the bare TiO_2 and Pd covered surfaces, respectively. Their demonstration provided a considerable insight to the monitoring of any change in dissolved oxygen concentration in close

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vicinity to the illuminated TiO_2 surface. However, following our earlier approaches employing Ag/AgCl micro disc [13] and micro band [15,16] electrodes to monitor Cl^- formation potentiometrically during the photomineralisation of chlorophenols in static and flowing solutions, respectively, and the investigation on O_2 photoreduction kinetics at an illuminated TiO_2 film [17], attempt has been taken in this paper to demonstrate the extent of $[O_2]$ consumption profile and $[Cl^-]$ production simultaneously at an illuminated TiO_2 surface using O_2 sensor probe and Ag/AgCl electrode, positioned together in the photocatalytic system of 4-chlorophenol (4-CP) as a model compound [6].

2. Experimental

2.1. Chemicals

4-CP (99% purity) was obtained from Aldrich (UK) and the solutions of desired concentrations were prepared using double distilled deionised water. Ethanol was used as received from E. Merck, Germany.

2.2. TiO_2 coated thin film preparation

The TiO_2 film was prepared from an ethanolic suspension of Degussa P25 TiO_2, where 5 g of TiO_2 was mixed with 95 cm^3 of ethanol containing 5 cm^3 of 0.5% aqueous glycerin. The mixture was then sonicated for 1 h and stirred for 5 h with a magnetic stirrer. Extra care was given to avoid any evaporation of ethanol, using an air-tight cover. The glass slide (2.0 cm wide and 5.0 cm in length) and oxygen sensor probe were dipped into the suspension, and then dried at room temperature followed by drying with N_2 gas. This process was typically repeated for five times to achieve an even, complete coating. Due to the addition of viscous glycerin, which acts as a binder, a stable coating was resulted.

2.3. Fabrication and calibration of Ag/AgCl detector electrode

A piece of 5 cm long Ag wire (1 mm diameter, 99% purity) was chloridised via the oxidation of 0.1 M KCl solution at 500 mV for 15 min as described earlier [15]. Calibration of the Ag/AgCl electrode was also performed following the previous method [15].

2.4. Photoelectrochemical experimental methodology

The full assembly of the experimental set up consisted of three parts: (i) a photoreactor cell (250 cm^3, made of quartz) with a Teflon lid providing the facility to hold the electrodes and TiO_2 coated glass slide which are dipped in 4-CP solution, (ii) an oxygen sensor connected with the oxygen meter (JENWAY, model 9071 DO_2 meter) and (iii) a Ag/AgCl detector electrode and a saturated calomel electrode (SCE, ORION 7102SC, serving as the reference electrode), were connected with a digital voltmeter via crocodile clips. Both of the sensor probes (i.e. oxygen electrode and Ag/AgCl detector electrode) were positioned ca. 0.50 cm away from the TiO_2 coated interfacial zone. The illumination was, achieved from a mercury-lamp ($\lambda = 420$ nm) and the intensity of the lamp was determined following the method developed by Hatchard and Parker [22]. The degradation of 4-CP was monitored with illumination time via the formation of Cl^- determined by recording the potential difference between the Ag/AgCl detector and SCE reference electrodes using the voltmeter, while the oxygen sensor allowed to monitor the disappearance of dissolved $[O_2]$ as photomineralisation proceeds. A magnetic stirrer was used to facilitate continuous stirring of the substrate solution during photodegradation in order to maintain uniform distribution of the photoproducts in solution. A schematic of the experimental set up adapted in this study is depicted in Fig. 1. In case of the experiments employing oxygen electrode having immobilised TiO_2 on it, no additional TiO_2 coated glass slide was used.

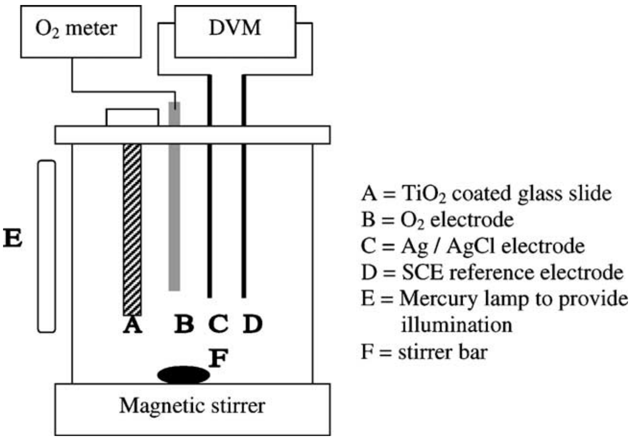

Fig. 1. Schematic of the photoelectrochemical experimental set-up, employed to monitor O_2 disappearance and Cl^- production simultaneously during the photomineralisation of 4-CP.

3. Background of measurement principle

Usually, it is assumed that TiO_2 sensitised complete photomineralisation process proceeds via the simultaneous oxidation (h^+ consumption) and reduction (e^- consumption) reactions at the excited TiO_2 surface. However, photodegradation of 4-CP, mediated by TiO_2 occurs with the following stiochiometry.

$$C_6H_4OH\text{–}Cl + 6.5O_2 \xrightarrow[h\nu \geq E_{bg}]{\text{semiconductor}} 6CO_2 + 2H_2O + HCl \qquad (1)$$

where anodic and cathodic reactions can be summarised as follows:

$$\text{Anodic (oxidation) reaction: } h^{+} + H_2O \rightarrow H^{+} + \bullet OH \;\; \begin{cases} \text{pollutant (4-CP)} \\ \text{minerals } (CO_2 + H_2O + HCl) \end{cases} \tag{2}$$

$$\text{Cathodic (reduction) reaction: } e^{-} + O_2 \rightarrow O_2^{\bullet -} \rightarrow H_2O_2 \rightarrow H_2O \tag{3}$$

It is obvious from the mineralisation stiochiometry that the degradation reaction proceeds via the consumption of 6.5 molecule of O_2 per 4-CP molecule [6], it is very unlikely that [O_2] will remain constant throughout the degradation process. Additionally, since O_2 plays a significant role in controlling the rate by scavenging the photogenerated electrons, it is quite reasonable that there will be a likely depletion effect of [O_2] at the TiO_2 surface. A similar indication on possible depletion effect of [O_2] in the photomineralisation process was also noticed by Vincze and co-workers [13] and Ahmed et al. [15,16], where the authors investigated the role of surface kinetics and mass transport effects in controlling the kinetics of photodegradation of 2,4-dichlorophenol (2,4-DCP) and various substituted monochlorophenols (e.g. 2-, 3- and 4-CP). Whereas, in another paper, Ahmed et al. [17] carried out a quantitative study on the kinetics of O_2 reduction at an illuminated TiO_2 surface, employing channel flow method with electrochemical detection (CFMED). In that paper the authors also noticed a likely correlation between O_2 consumption and Cl^- production rates, measured separately during the photomineralisation process. Surprisingly, apart from this one study, still there is no clear consensus as to the direct correlation between the rates of disappearance of [O_2] with that of photoproduct [Cl^-] formation, despite the possible link between the two processes.

However, it is apparent from the cathodic (reduction) and anodic (oxidation) reaction profile that the photogenerated electrons and holes are simultaneously consumed via the reduction and oxidation reactions as the mineralisation proceeds. Hence, rates of the two half cell reactions must balance. Keeping this vital point in mind, the aim of this paper is to demonstrate a simultaneous measurement to monitoring the depletion and formation kinetics of the two species of interest (O_2 and Cl^-, respectively), employing simple electrochemical methods.

4. Results and discussion

The trends of dissolved [O_2] depletion profile resulting from the TiO_2-sensitised photomineralisation of 2.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} aerated 4-CP solutions were readily explained by referring to the change of [O_2] at the oxygen detector sensor (bare and with TiO_2 coated oxygen electrode), recorded as a function of illumination time at an effective intensity of 1.78×10^{16} q cm^{-3} s^{-1}. The experimental results were analysed in terms of shielding factor,

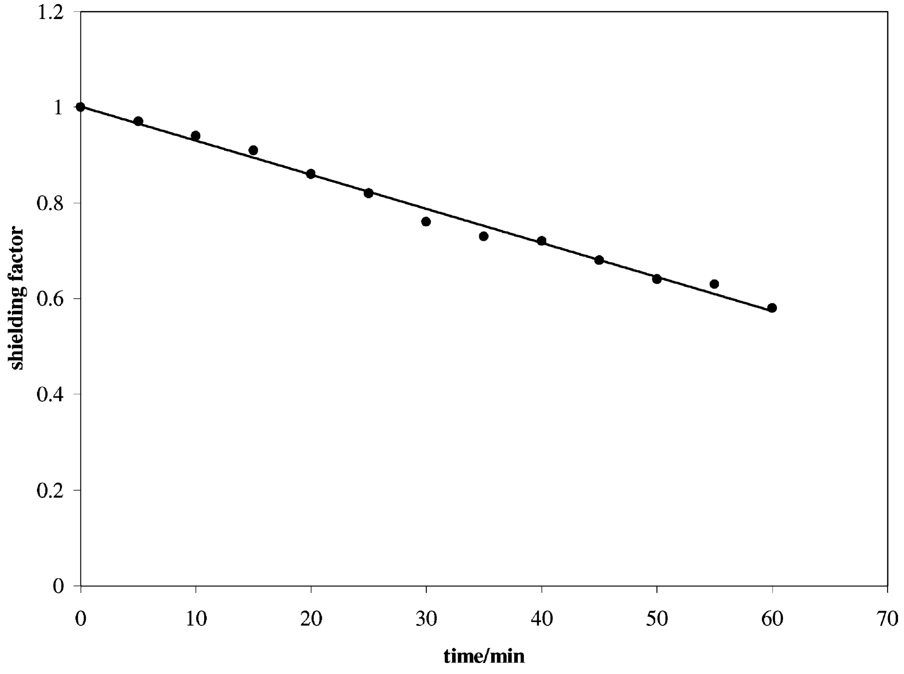

Fig. 2. Plot of shielding factors vs. illumination time obtained due to the disappearance of [O_2] at the illuminated TiO_2 surface during the photomineralisation of 2.0×10^{-4} mol dm^{-3} 4-CP.

which was obtained from:

$$\text{sheilding factor} = \frac{\text{change in } [O_2] \text{ detected with photolysis time}}{\text{bulk } [O_2] \text{ detected without photolysis}} \quad (4)$$

Fig. 2 shows the observed shielding factors recorded as a function of illumination time during the photodegradation of 2.0×10^{-4} mol dm^{-3} 4-CP. Clearly, the shielding factors started with a value of unity when there is no ongoing photoreaction and then subsequently tends to decreasing as the photmineralisation proceeds. This is because with longer illumination time more O_2 molecules become involve in capturing photogenerated electrons, resulting in the formation of $O_2{}^{\bullet -}$, which also participates in the photomineralisation process via the oxidation of organic pollutants. In other words, this observation, no doubt confirms the gradual consumption of O_2 in the preceding mineralisation process. However, apparently a linear relationship between shielding factors and illumination time is evident with a gradient, 7.1×10^{-3} min^{-1}. The initial disappearance rate of $[O_2]$ is, 2.85×10^{-11} mol cm^{-3} s^{-1}, obtained via the following equation:

$$\text{rate} = \text{gradient}\,[O_2]^* \quad (5)$$

where $[O_2]^*$ is the bulk or initial concentration of dissolved oxygen in mol cm^{-3}.

In order to compare the extent of dissolved $[O_2]$ consumption with that of Cl^- production, simultaneous measurements were performed in the same 4-CP solution under identical conditions. After converting the recorded potential difference response to $[Cl^-]$ at the Ag/AgCl indicator electrode, the data shown in Fig. 3 were obtained as a function of irradiation time. It has already been proved in numerous studies [2,3,6] that the initial rate of 4-CP degradation follows the Langmuir–Hinshelwood kinetic scheme. However, the initial photomineralisation rate was directly determined in terms of product $[Cl^-]$ formation with illumination time. A similar rate of Cl^- formation (2.91×10^{-11} mol cm^{-3} s^{-1}) was obtained for the ongoing photo-process, which indicated a direct correlation between simultaneous consumption and formation of the two candidate species of interest under investigation. This observation also implies the analysis of Lewis and co-workers [19] where the authors suggested that water would be the main reactant with photogenerated holes and that organic substrate would have little effect on enhancing the rate of hole capture and consequently the reduction of O_2 (within the flux matching model).

Following this approach investigations were further explored for both cases (i.e. O_2 consumption and Cl^- production) considering the degradation pattern of 5.0×10^{-4} and 1.0×10^{-3} mol dm^{-3} 4-CP solution at the same intensity as mentioned earlier. The corresponding observed rates are cited in Table 1. These data again clearly implies that under identical conditions the kinetics of O_2 consumption and Cl^- formation, resulting from photocatalytic oxidation of 4-CP, satisfies a valid measurement of the preceding photomineralisation process. The correlation strongly suggests that the flux matching idea of Lewis [19] represents a good description of the photomineralisation process.

Having successfully investigated the extent of O_2 depletion and Cl^- formation at an illuminated TiO_2 thin film immobilised on a glass slide, the methodology was further

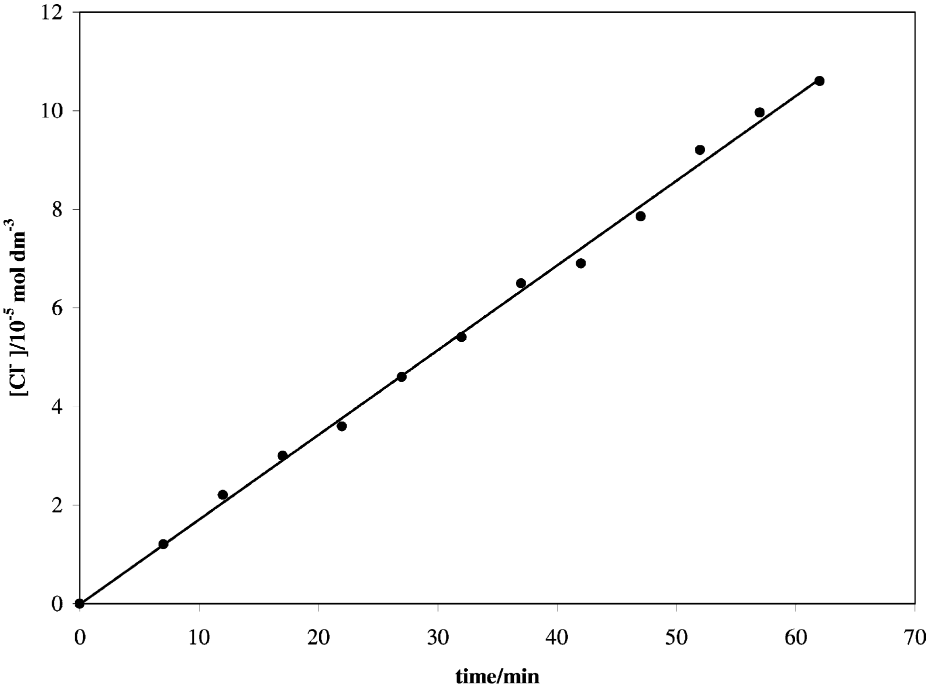

Fig. 3. $[Cl^-]$ production as a function of illumination time during the photomineralisation of 2.0×10^{-4} mol dm^{-3} 4-CP.

Table 1
Rates of $[O_2]$ disappearance and $[Cl^-]$ production, measured employing bare O_2 electrode and Ag/AgCl electrode, respectively

[4-CP] (mol dm^{-3})	O_2 depletion rate (mol cm^{-3} s^{-1}) ($\times10^{-11}$)	$[Cl^-]$ formation rate (mol cm^{-3} s^{-1}) ($\times10^{-11}$)
2.0×10^{-4}	2.85	2.91
5.0×10^{-4}	3.55	3.36
1.0×10^{-3}	3.84	3.95

applied using directly TiO_2 coated oxygen electrode and Ag/AgCl detector electrode. Photomineralisation was carried out taking into account the above mentioned concentrations of aerated 4-CP solutions. Measured rates for both cases are summarised in Table 2. Again the observed rates for both electron and hole consumptions matches, which provided informations, that the photomineralisation process is ultimately an *electrochemical process*, in which the anodic (i.e. hole consumption via the photo-oxidation of 4-CP) and cathodic (i.e. electron consumption via the photoreduction of O_2 to produce super oxide ion) rate must balance. However, in the later case, the observed rates are slightly higher, presumably due to either diffusion effect or inhibition of electron–hole recombination in the photo-process. Because in this later case, O_2 sensor probe is directly coated with TiO_2, hence, no gap exists between the interface and the detector electrode. This facilitates immediate monitoring of any change in $[O_2]$ before it diffuses. Whereas, in case of employing bare O_2 electrode, due the noticeable gap between the TiO_2 coated glass slide/interfacial zone and the detector probes, the photoproduct and reactant gets enough time to diffuse before reaching at the detector electrodes.

Additionally, since in the later case oxygen undergoes reduction reaction more promptly due to the close/direct contact of TiO_2 with the oxygen electrode, photogenerated electron gets less chance to recombine with the holes in this case. Thus, more electrons are captured by dissolved oxygen in the reduction process, which indicates higher consumption of photogenerated holes in the anodic process as well. Hence, the production of $^{\bullet}OH$ increases in the process, which ultimately enhances the oxidation of 4-CP, giving a higher rate of Cl^- formation.

It is informative to estimate the quantum efficiency of $[O_2]$ consumption and $[Cl^-]$ production in the preceding photomineralization process. The apparent quantum efficiency for both cases can be derived via the following equation:

$$\text{quantum efficiency},\ \Phi = \frac{\text{rate} \times N_A}{\text{intensity}} q^{-1} \qquad (6)$$

where, N_A is the Avogadro number $= 6.022 \times 10^{23}$ mol^{-1} [23].

Clearly, the extent of $[O_2]$ consumption, with that of $[Cl^-]$ formation during the photodegradation process described in this study correspond to reasonable values of quantum yields 0.1–0.2%. These values match with the range of quantum yields 0.1–1.0%, reviewed by Mills et al. [3]. However, the rate of the photomineralisation process is strongly dependent on a variety of factors as described by Mills and Le Hunte [2], it is evident from the observed quantum efficiencies of this present study that the validity of this approach adapted herein, is very promising.

Table 2
Rates of $[O_2]$ disappearance and $[Cl^-]$ production, measured employing TiO_2 coated O_2 electrode and Ag/AgCl electrode, respectively

[4-CP] (mol dm^{-3})	O_2 depletion rate (mol cm^{-3} s^{-1}) ($\times10^{-11}$)	$[Cl^-]$ formation rate (mol cm^{-3} s^{-1}) ($\times10^{-11}$)
2.0×10^{-4}	3.55	3.26
5.0×10^{-4}	4.61	4.44
1.0×10^{-3}	4.82	4.89

5. Conclusion

The consumption of dissolved oxygen concentration with the formation of Cl^- from TiO_2-sensitised photocatalysis of 4-CP have been successfully correlated which provided information that the photomineralisation process is ultimately an *electrochemical process*, in which the anodic (photo-oxidation of organic pollutants via h^+ consumption) and cathodic (photoreduction of O_2 via e^- consumption) rates must balance. The observed quantum yields for 4-CP degradation match with the values obtained previously employing suspended [3] and supported [16,17] TiO_2 photocatalyst, indicated that the sensing capability of the electrochemical sensor probes does not appear to be hampered due to direct illumination.

Further investigations will be explored employing TiO_2 coated microelectrodes in case of a variety of environmental problems, which should allow the associated mass transport properties to be studied and modelled.

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