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Electrophoresis–A new approach for the determination of organic matters adsorption on irradiated TiO_2

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Abstract

The application of electrophoretic analysis for monitoring the adsorption of organic onto TiO_2 and for detecting the formation of adsorbed organic species during the photocatalytic reactions has been successfully demonstrated. When highly adsorbed organic compounds such as maleic acid, oxalic acid and 1,2,3-THB interacted with TiO_2 surface at pH 3, the zeta potential of TiO_2 exhibited a negative shift. On the contrary, no apparent change in zeta potential of TiO_2 was recorded from the interaction of weakly adsorbed organic compounds such as methanol, sucrose, glucose and resorcinol. The electrophoretic analysis showed that during photocatalytic reaction, the weakly adsorbed resorcinol formed intermediate species that were highly adsorbing onto TiO_2, while no change in TiO_2 zeta potential during the photocatalytic reaction of methanol. The removal kinetics of adsorbed organic species during the photocatalytic reaction of resorcinol and 1,2,3-THB can be easily followed by monitoring the change in zeta potential of TiO_2. As the adsorbed organic compounds were progressively removed from the irradiated surface of photocatalyst, the zeta potential of TiO_2 gradually shifted to a more positive value and finally restored to the zeta potential of bare TiO_2 when complete removal of adsorbed organic was achieved.

Keywords: Electrophoresis; Photocatalyst; Adsorption; Irradiation

1. Introduction

The application of TiO_2 semiconductor as an environmental photocatalyst has been intensively studied. It has been envisaged that the mechanistic of TiO_2 photocatalysis involved the integration of different interface transfer processes, which included (1) the generation and migration of electron–hole pairs and their recombination, (2) reactive oxygen species and (3) adsorption/desorption of organic pollutants.

To date, extensive studies have been focused on the fate of electron–hole pairs and the mechanism of reactive oxygen species in a photocatalytic reaction. Only fewer emphases have concentrated on the adsorption/desorption of organic pollutants generated during the photocatalytic reaction. Several researchers have demonstrated that a well-adsorbed organic pollutant is most probable to be oxidised via the direct electron transfer between the substrates and positive holes, whereas the hydroxyl radicals mediated reaction pathway is favourable for organic pollutants that do not adsorb well [1,2]. Hence, this indicates a link between the mechanistic role of photoactive species and the adsorption property of the organic pollutants and their intermediate species.

Vast ranges of techniques have been developed to study the interaction between the adsorbed organic compounds with the surface of TiO_2 [3–5]. Some of these methods (e.g. FTIR, XPS, HPLC and GC) required pre-treatment processes such as solvent extraction and/or drying prior to the analysis. Under certain circumstances, these pre-treatment processes could be undesirable as they may potentially change the surface property of TiO_2, as well as the interaction between the organic matters and TiO_2. Therefore, it becomes the aim of this work to develop a technique that allows a direct monitoring of adsorption behaviour

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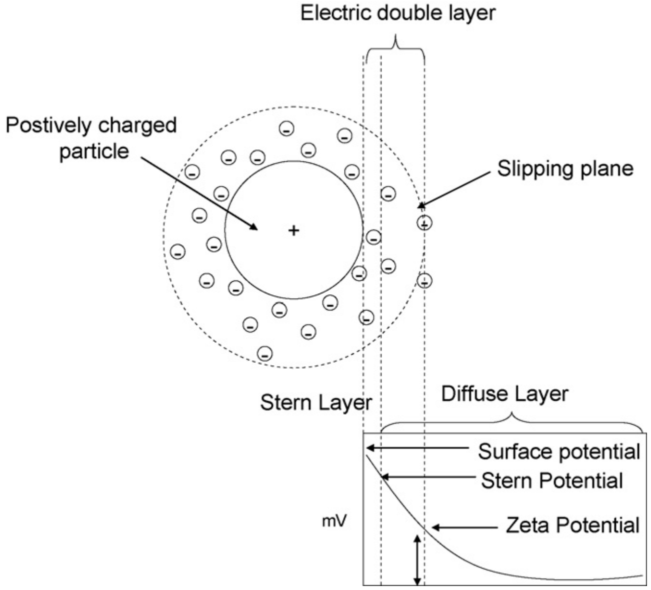

Fig. 1. Electric double layer and zeta potential.

of organic compounds generated during the photocatalytic reaction.

In this study, electrophoretic analysis is investigated as a simple approach to determine the adsorption of organic matters during the photocatalytic reaction. In comparison to most of the conventional methods, this technique does not require any pre-treatment process. It measures the movement of a charged particle relative to its suspended aqueous solution under the influence of applied electric field. As the charged particles are dispersed in solution, each particle will be surrounded by oppositely charged ions, resulting in the development of a net charge and subsequently, an electric double layer around each particle.

Several models have been developed to describe the structure of the electrical double layer [6]. The current classic model or commonly known as the Gouy–Chapman–Stern model combined the Helmholtz single adsorbed layer with the Gouy–Chapman diffuse layer. The electrical double layer is divided into compact and diffuse layers. The compact layer is called the Stern layer, in which the ions are strongly bounded and next to the Stern layer is the diffuse layer (see Fig. 1). Within the diffuse layer, there is a conceptual slipping plane at which the ions and particles form an electric neutral region. When a particle moves, ions within the slipping plane move with it. Beyond the slipping plane, the ions do not travel with the particle. The zeta potential, which is calculated from the electrophoretic mobility, is defined as the electric potential of the Stern layer including the conceptual slipping plane.

In the past, the electrophoretic analysis has been widely used to monitor the stability of the colloids and emulsion including TiO_2 suspension. For example, Fernandez-Nieves and Nieves [8] monitored the electrophoretic mobilities of TiO_2 under the influence of different flocculants and found that at $pH < 5.5$, the Na^+ and the $SO_4{}^{2-}$ ions are better flocculant agents than the Ca^{2+} and the Cl^- or $NO_3{}^-$. The study which combines UV radiation and electrophoresis is rather limited. Boxall and Kelsall [7] developed a second-order kinetic model to describe the time dependant changes in electrophoretic mobilities of aqueous dispersion of TiO_2 particles when irradiated with photons of energy corresponding to greater than their band gap (3.2 eV), in the absence of hole and electron scavengers. In the present work, a new application of electrophoresis to study the interaction of organic species with TiO_2 surface during illumination is presented. A range of organic compounds having different adsorption behaviours on TiO_2, were used to illustrate its application.

2. Experimental

2.1. Chemicals

Degussa P25 TiO_2 (80% anatase, 20% rutile) was used as the photocatalyst, since it has been renowned as the benchmark photocatalyst for comparison [9–10]. Analytical grade chemicals were used without further purification in all experiments. All solutions were prepared using Millipore Milli-Q water.

2.2. Adsorption studies

The adsorption of organic compounds, including resorcinol, 1,2,3-THB (1,2,3-trihydroxybenzene), oxalic acid, maleic acid, methanol, glucose and sucrose, onto TiO_2 without illumination was first carried out. The experiments were performed in a 100 mL glass bottle. The initial concentration of organic matters was set at 13 mg of Carbon/L. A loading of 1 g/L photocatalyst was used. The suspension was allowed to mix at a constant stirring rate for 24 h such that the system established adsorption equilibrium before a sample was collected.

The amount of organic carbon adsorbed onto the surface TiO_2 was evaluated using a total organic carbon analyser (TOC, Shimadzu T-VCSH). The sample was filtered through 0.45 μm PTFE filters prior to TOC measurement. Fourier Transform Infrared spectroscopy (FTIR, AVATAR 320) equipped with a smart diffuse reflectance was used to study the interaction of organic matters adsorbed on the surface of photocatalyts. Spectra were taken at mid-infrared range (i.e. $1000–4000\,cm^{-1}$) with a resolution of $4\,cm^{-1}$ and 200 scans. The particles were recovered by centrifugation. To avoid heat treatment, the particles (i.e. the powder which has been filtered from the suspension) were dried under vacuum in a desiccator prior to the FTIR analysis. Zeta potential analysis was also carried out to investigate the surface charge of TiO_2 before and after adsorption of organic compounds. For all experiments, the suspension was adjusted to pH 3 ± 0.5. Under this condition, the TiO_2 surface is highly positive. Hence, this allows the change in zeta potential to be easily deduced when the organic compounds interact with the TiO_2 surface.

2.3. Photoactivity studies

A volume of 500 mL photocatalyst suspension (0.1 g/L) with an initial pH adjusted to 3.0 ± 0.5 using perchloric acid was

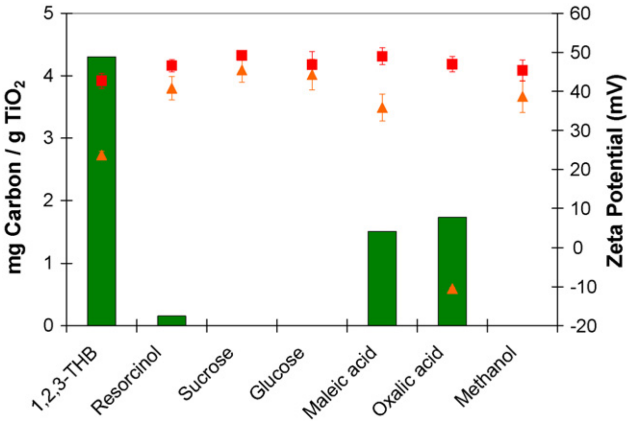

Fig. 2. The relation between zeta potential and adsorption of organic substrates. Conditions: $[TiO_2] = 1$ g/L, $[\mathrm{Organic}]_0 = 13$ mg/L Carbon, $pH_0 = 3 \pm 0.5$, (■) zeta potential of TiO_2 prior to adsorption (▲) zeta potential of TiO_2 after adsorption (■) amount of organic substrates adsorbed per gram TiO_2.

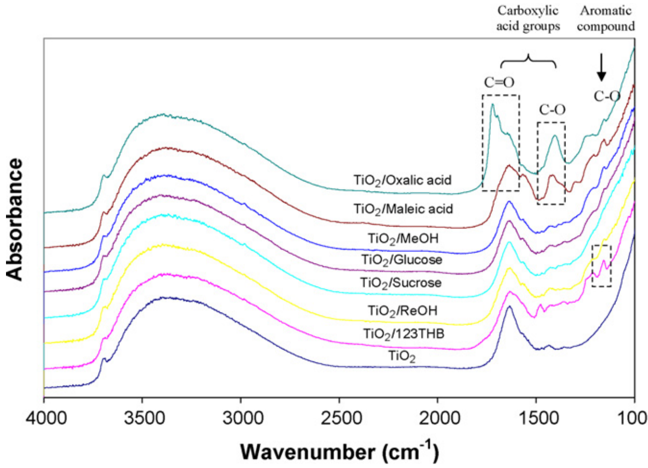

Fig. 3. FTIR spectrum of TiO_2 after in contact with various organic compounds. Conditions: $[TiO_2] = 1$ g/L, $[\mathrm{Organic}]_0 = 13$ mg/L Carbon, $pH_0 = 3 \pm 0.5$.

circulated through a cylindrical annular-type photoreactor. The suspension was illuminated for 30 min in order to remove any residual organic matters, and subsequently 100 mL of the prepared organic stock solution (i.e. resorcinol, methanol, 1,2,3-THB) was added into the system to give an initial organic concentration of 13 mg/L of carbon. The suspension was mixed for 15 min in the dark to attain good mixing prior to UV illumination. The photocatalytic activity experiment was carried out for up to 4 h. A 20 W blacklight blue fluorescent tube with an emission range of 300–400 nm was used as the lamp source. Purified air was also introduced continuously into the system at 100 mL/min. An online pH meter was used to monitor the pH change. Samples were withdrawn intermittently and filtered through 0.45 μm PTFE filters prior to analyses. The total dissolved organic carbon was monitored using a total organic carbon analyser (TOC, Shimadzu T-VCSH). For zeta potential analysis, samples were measured directly using a Brookhaven ZetaPALS system. Control experiment was also conducted in the absence of organic compounds in order to assess the effect of illumination on the zeta potential of photocatalyst.

3. Results and discussion

3.1. The change in zeta potential of photocatalyst versus the extent of adsorption of organic compounds

Fig. 2 shows the relationship between the change in the zeta potential of TiO_2 and the extent of organic adsorption on TiO_2 surface in the dark. Prior to the adsorption studies, the zeta potential of TiO_2 was found to be +48 mV. When organic compounds such as 1,2,3-THB, maleic acid and oxalic acid adsorbed onto the surface of TiO_2, the zeta potential of TiO_2 exhibited a negative shift. It is anticipated that the interaction between the adsorbed organic compounds with the TiO_2 surface neutralised the positive surface charge of photocatalyst, and thus a drop in the zeta potential of TiO_2.

As can be seen from Fig. 2 also, the magnitude of change in zeta potential of TiO_2 varied with organic compounds. With oxalic acid, the drop in zeta potential of TiO_2 was observed to be greater than that with maleic acid. The oxalic acid has pK_a values of 1.92 and 4.2. At pH 3 ± 0.5, oxalic acid exists as $(OH)OC–COO^-$ (82%) and $C_2O_4^{2-}$ (16%). By contrast, maleic acid has pK_a values of 1.83 and 6.07. Hence, at pH 3 ± 0.5, maleic acid undergoes partial deprotonation to form mainly $(OH)OC–C{=}C–COO^-$ (98%). Since the dissociated species of oxalic acid has higher charge than that of maleic acid, this explains the greater drop in zeta potential in the oxalic acid/TiO_2 system.

For 1,2,3-THB, it has a pK_a value of 11.34. As such, 1,2,3-THB will remain as neutral species at pH 3 ± 0.5. Previously [11], we have demonstrated that the 1,2,3-THB molecules bound to the surface of TiO_2 via an inner-sphere complex mechanism. The hydroxyl group in ortho position of the 1,2,3-THB molecules provided fixation sites to the photocatalyst, which then allowed 1,2,3-THB to complex with the Ti center [12–14]. As neutral species are accumulated at the Stern layer, it is not surprised that the decrease in the zeta potential of TiO_2 to be rather small.

The presence of adsorption of 1,2,3-THB, oxalic acid or maleic acid onto the TiO_2 surface was further confirmed by the FTIR spectroscopy. It was detected that the FTIR spectra obtained from the interaction of oxalic acid and maleic acid with TiO_2 were similar to those reported by Weisz et al. [15] and Arana et al. [16], respectively. The signal due to stretching of carboxylic acid groups, ν(C–O) (1350–1450 cm^{-1}) and ν(C=O) (1650–1800 cm^{-1}) were clearly illustrated in Fig. 3. Similarly, the signal from the stretching of the aromatic compound, ν(C–O) (1200–1300 cm^{-1}) [17], resulting from the adsorption of 1,2,3-THB, was also demonstrated in Fig. 3. On the other hand, the spectrum of resorcinol, sucrose, glucose or methanol after in contact with TiO_2 was essentially identical to that of the bare TiO_2, implying that the organic compounds could have been loosely bound to the surface of TiO_2. Evidence in support of the lack of contact between resorcinol, sucrose, glucose or methanol with the TiO_2 surface is also provided in Fig. 2. Negligible amount of organic matters have found to adsorb onto the TiO_2 surface.

Rincon et al. [12] reported that the poor adsorption of resorcinol onto TiO_2 was due to the absence of hydroxyl group in the ortho-position of benzene ring. Previous work by Vamathevan et al. [18] and Tan et al. [19] showed that the adsorption of sucrose onto the surface of TiO_2 was negligible. Tan et al. [19] also observed an insignificant amount of methanol adsorbed onto the surface of TiO_2. By means of a Raman spectroscopy, Lana-Villarreal et al. [20] found that aqueous methanol did not interact strongly with the TiO_2 surface. Wang et al. [21,22] reported that when a relatively large amount of water vapour was introduced into the system consisting of methanol vapour, the surface methoxy signal (i.e. at 2828 cm^{-1} and 2935 cm^{-1}) became undetectable. They concluded that the methoxy species on TiO_2 was hydrolysed by water addition. Due to the competitive adsorption between the water and methanol, the contact between methanol and the TiO_2 surface was hindered. Christensen et al. [23] developed an in-situ FTIR to study the photochemical behaviour of thermal TiO_2 film in aqueous methanol. They found that the methanol was chemisorbed onto the TiO_2 surface at 10 °C; however, a significant of reduction in the methanol adsorption was recorded at 50 °C. When increasing the potential from 0 to 1.2 V, they observed a band formation at 1015 cm^{-1} in the IR spectra of $NaClO_4$/methanol electrolyte, which was collected from the in-situ FTIR spectroscopy. They assigned the signal to the C–O stretching of methanol, possibly could be caused by the desorption of chemisorbed methanol from the TiO_2 surface (which consisted of mainly amorphous TiO_2 with some rutile crystalline). As shown in Fig. 3, the signals due to the interaction of methoxy species, molecular methanol or C–O stretching of methanol were unidentified in our system. Correspondingly, this confirmed the absence of interaction between methanol and TiO_2.

The zeta potential of TiO_2 upon mixing with resorcinol, sucrose, glucose and methanol was also evaluated and was found to be unaffected. These observations can be associated to the absence of surface interaction between the organic compounds and the photocatalyst. Based on these findings, it is established that there exists a correlation between the change in zeta potential and the adsorption behaviour of organic compounds onto TiO_2 surface.

3.2. *Zeta potential in the application for identifying the mechanistic degradation pathway of different organic matters*

Fig. 4 depicts the effect of illumination on the zeta potential profile of TiO_2 at pH 3.0 ± 0.5. In the absence of organic compounds, the UV photons had an insignificant impact on the zeta potential of TiO_2, similar to that reported by Nagasaki et al. [5].

In the presence of resorcinol and/or 1,2,3-THB, as the photocatalytic reactions proceeded, the zeta potential of TiO_2 changed progressively with illumination time. Figs. 5 and 6 present the change in the zeta potential of TiO_2 during the photocatalytic oxidation of resorcinol and 1,2,3-THB, respectively.

As illustrated in Figs. 5 and 6, the zeta potential profile of TiO_2 can be divided into three sections. At the beginning of the photocatalytic reaction, the zeta potential of TiO_2 dropped

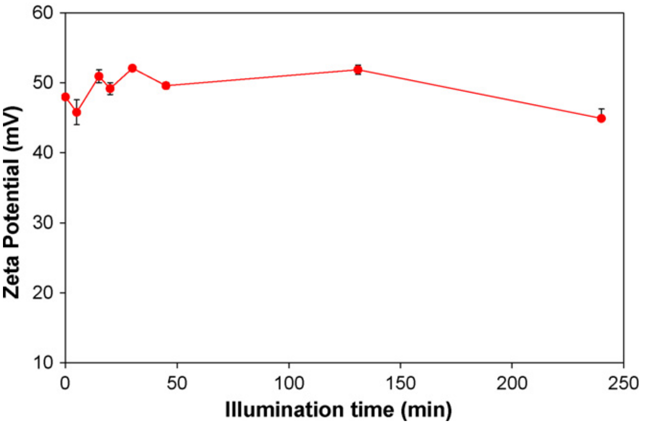

Fig. 4. Effect of illumination on the zeta potential of TiO_2 in the absence of organic compounds. Conditions: $[TiO_2] = 0.1$ g/L, $pH_0 = 3 \pm 0.5$, airflow rate = 100 mL/min.

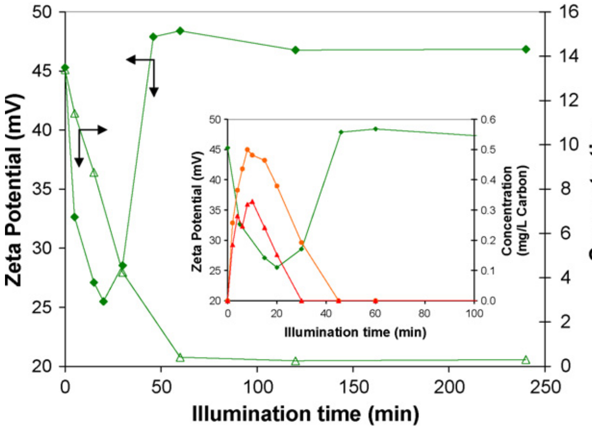

Fig. 5. The relation between the zeta potential of TiO_2 (♦) and the mineralisation of resorcinol (△), as well as the net production of 1,2,3-THB (●) and 1,2,4-THB (▲) during the photocatalytic oxidation of resorcinol at pH 3.0 ± 0.5. Conditions: $[TiO_2] = 0.1$ g/L, $[Resorcinol]_0 = 13$ mg/L Carbon, $pH_0 = 3 \pm 0.5$, airflow rate = 100 mL/min.

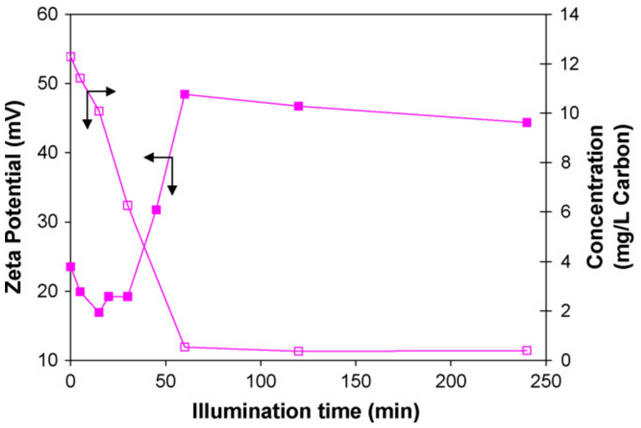

Fig. 6. The relation between the zeta potential of TiO_2 (■) and the mineralisation of 1,2,3-THB (□) Conditions: $[TiO_2] = 0.1$ g/L, $[1,2,3\text{-THB}]_0 = 13$ mg/L Carbon, $pH_0 = 3 \pm 0.5$, airflow rate = 100 mL/min.

with illumination time, and reached an optimum change before it was restored to a zeta potential value of ∼+48 mV. Earlier, we observed that the zeta potential of TiO_2 was shifted negatively when the organic matters were adsorbed onto the photocatalyst surface. Taking this into account, the negative shift in the zeta potential of TiO_2 in Figs. 5 and 6 is regarded as the rapid formation of adsorbed intermediate products on the TiO_2 surface, and the positive shift as the gradual removal of adsorbed intermediate products from the surface of TiO_2. The plateau region can then be referred as the complete removal of adsorbed species.

In order to validate the above interpretation, the formation and disappearance of adsorbed intermediates products generated from the photocatalytic degradation of resorcinol was followed and compared to the recorded zeta potential of TiO_2. Previously [11], we have found that resorcinol was converted into two highly adsorbed intermediate products, 1,2,3-THB and 1,2,4-THB, upon illumination. From Fig. 5 (inset), it can be seen that as resorcinol was converted into 1,2,3-THB and 1,2,4-THB, the zeta potential of TiO_2 decreased with increasing THBs concentration. It then attained an optimum change at the highest THBs concentration. As THBs were gradually removed, the zeta potential of TiO_2 shifted to a more positive value, and it was finally restored to the initial value of +48 mV when THBs were completely removed from the system. Hence, this indicated that there is a strong correlation between the net production of adsorbed intermediate products and the zeta potential profile of TiO_2. Moreover, it also supported the notion that the drop in zeta potential of TiO_2 was resultant from the interaction between the adsorbed organic compounds with the surface of photocatalyst.

From Figs. 5 and 6 also, it was evidenced that the zeta potential of TiO_2 was restored to that of bare TiO_2 as soon as the system reached complete mineralisation This reflected the absence of accumulation of persistent adsorbed intermediate products on the TiO_2 surface. It is suggested that the existence of surface poisonous effect can be easily deduced by simply comparing the zeta potential profile of TiO_2 with the removal kinetics of organic compounds.

In the presence of methanol, the zeta potential of TiO_2 remained unaffected throughout the photocatalytic reaction (see Fig. 7). Chen et al. [24] detected the formation formic acid and formaldehyde in the photocatalytic oxidation of methanol. Lana-Villarreal et al. [20] showed that the formic acid interacted strongly with the TiO_2 surface. However, Tran et al. [25] reported that the photocatalytic oxidation of formic acid proceeded much faster than that of methanol oxidation. Correspondingly, the constant zeta potential observed during the photocatalytic oxidation of methanol may be associated to the rapid disappearance of its intermediate products.

In the present study, it was found that not only that the zeta potential analysis can be used to study the removal kinetic of adsorbed intermediate products generated during the photocatalytic reaction, it also help to provide an insight into the active species involved in a photocatalytic reaction. The fact that the zeta potential of TiO_2 remained unchanged during the photocatalytic oxidation of methanol, it implies that the hydroxyl radical ($^{\bullet}OH$) is the key species involved in the photocatalytic reaction. For resorcinol and 1,2,3-THB, since a drastic shift in zeta potential of TiO_2 was observed, both holes and $^{\bullet}OH$ could have been responsible for the photocatalytic reaction. In summary, it is concluded that the disappearance of organic compounds in solution via adsorption during the photocatalytic reaction can be distinguished by means of zeta potential analysis.

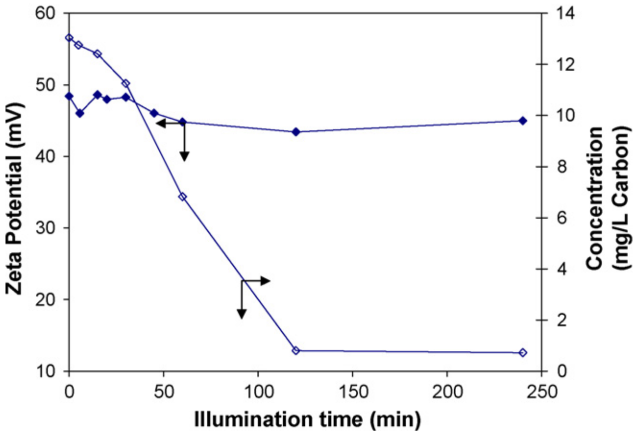

Fig. 7. The relation between the zeta potential of TiO_2 (♦) and the mineralisation of methanol (◊) Conditions: $[TiO_2]$ = 0.1 g/L, $[Methanol]_0$ = 13 mg/L Carbon, $pH_0 = 3 \pm 0.5$, airflow rate = 100 mL/min.

4. Conclusion

The zeta potential analysis is a useful tool to study the interaction of organic compounds with the TiO_2 surface as well as to detect the formation of adsorbed intermediate products during the photocatalytic reactions. It was established that in the presence of poorly adsorbed organic compounds or intermediate products (e.g. methanol, glucose, sucrose and resorcinol), the zeta potential of photocatalysts remained unchanged. On the other hand, a drastic negative shift was seen when highly adsorbed organic compounds such as oxalic acid, maleic acid, 1,2,3-THB were formed or/and adsorbed on the photocatalysts surface. Although the electrophoresis technique cannot provide any information on the quantity and type of adsorbed organic compounds formed on the photocatalyst surface, it has been demonstrated that the zeta potential analysis has the advantage of providing a direct monitoring of the removal kinetics of adsorbed organic intermediates generated by photocatalytic reactions.

References

[1] K. Chiang, T.M. Lim, L. Tsen, C.C. Lee, Appl. Catal. A 261 (2004) 225.
[2] Y. Chen, S. Yang, K. Wang, L. Lou, J. Photochem. Photobiol. A 172 (2005) 47.
[3] D. Jiang, H. Zhao, S. Zhang, R. John, J. Catal. 223 (2004) 212.
[4] K.D. Dobson, A.J. McQuillan, Spectrochim. Acta A 55 (1999) 1395.
[5] A. Nagasaki, H. Sakai, M. Shimazaki, T. Kakihara, T. Kono, N. Momozawa, M. Abe, Shikizai Kyokaishi 72 (1999) 665.
[6] K. Bourikas, C. Kordulis, J. Vakros, A. Lycourghiotis, Adv. Colloid Interf. Sci. 110 (2004) 97.
[7] C. Boxall, G.H. Kelsall, J. Chem. Soc. Faraday Trans. 87 (1991) 3547.
[8] A. Fernandez-Nieves, F.J. de las Nieves, Colloid Surf. Physiochem. Eng. Aspect 148 (1999) 231.
[9] N. Serpone, J. Photochem. Photobiol. A 104 (1997) 1.

[10] N. Serpone, G. Sauve, R. Koch, H. Tahiri, P. Pichat, P. Piccinini, E. Pelizzetti, H. Hidaka, J. Photochem. Photobiol. A 94 (1996) 191.
[11] S.W. Lam, K. Chiang, T.M. Lim, R. Amal, G.K.-C. Low, Appl. Catal. B 55 (2005) 123.
[12] A.G. Rincon, C. Pulgarin, N. Adler, P. Peringer, J. Photochem. Photobiol. A 139 (2001) 233.
[13] R. Rodriquez, M. Blesa, A.E. Regazzoni, J. Colloid Interf. Sci. 177 (1996) 122.
[14] D. Vasudevan, A.T. Stone, Environ. Sci. Technol. 30 (1996) 1604.
[15] A.D. Weisz, L.G. Rodenas, P.J. Morando, A.E. Regazzoni, M.A. Blesa, Catal. Today 76 (2002) 103.
[16] J. Arana, O.G. Daiz, M.M. Saracho, J.M.D. Rodriguez, J.A.H. Melian, J.P. Pena, Appl. Catal. B 34 (2002) 113.
[17] P.Z. Araujo, P.J. Morando, M.A. Blesa, Langmuir 21 (2005) 3470.
[18] V. Vamathevan, R. Amal, D. Beydoun, G. Low, S. McEvoy, Chem. Eng. J. 98 (2004) 127.
[19] T. Tan, D. Beydoun, R. Amal, J. Photochem. Photobiol. A 159 (2003) 273.
[20] T. Lana-Villarreal, J.M. Perez, R. Gomez, C.R. Acad. Sci. Chimie 9 (2006) 860.
[21] C.-Y. Wang, H. Groenzin, M.J. Shultz, J. Am. Chem. Soc. 127 (2005) 9736.
[22] C.-Y. Wang, H. Groenzin, M.J. Shultz, J. Am. Chem. Soc. 127 (2004) 8094.
[23] P.A. Christensen, J. Eameaim, A. Hamnett, Phys. Chem. Chem. Phys 1 (1999) 5315.
[24] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, Water Res. 33 (1999) 661.
[25] H. Tran, K. Chiang, J. Scott, R. Amal, Photochem. Photobiol. Sci. 4 (2005) 565.