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Effect of surfactant microstructures on photocatalytic degradation of phenol and chlorophenols

*D. Fabbri, A. Bianco Prevot and E. Pramauro**

Dipartimento di Chimica Analitica, Università di Torino

Via P.Giuria 5 – 10125 Turin, Italy.

e-mail: edmondo.pramauro@unito.it

Abstract

The effect of hexadecyltrimethylammonium bromide (HTAB) on the photocatalytic degradation of phenol (Phe), 2,5-dichlorophenol (2,5-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP) in the presence of aqueous TiO₂ suspensions at pH ca. 5 was investigated using a laboratory photoreactor equipped with a medium-pressure mercury lamp. Inhibition of substrate decomposition was observed for phenol, both below and above the surfactant critical micellar concentration, whereas a more complex behaviour was exhibited by chlorophenols. It was found that adsorption of these compounds onto the surfactant-modified semiconductor particles facilitates their faster decomposition, but the competitive partition of substrates between adsorbed surfactant structures and micellar aggregates tends to limit the beneficial kinetic effects at higher amphiphile concentrations. The crucial influence of surfactant adsorption was clearly evidenced in some runs performed at pH 3. Relevant inhibition of chloride release from chlorophenols, observed in the presence of HTAB, indicates a higher persistence of reaction

intermediates in the reaction media, suggesting the need for a careful investigation of surfactant effects on all the degradation steps of the process.

KEYWORDS

Photocatalysis, phenol, chlorophenols, surfactants, microstructures

INTRODUCTION

Chlorophenols belong to a class of toxic organic compounds listed by EPA as priority pollutants [1]. They are introduced in the environment mainly during the manufacturing of various products, including pesticides, pharmaceuticals and dyes, during the chlorination of municipal waters and through the degradation of other chemicals. Due to their resistance to usual biological treatments and to their slow or ineffective removal from contaminated water streams using physical methods, the application of destructive oxidation techniques has been considered.

Heterogeneous photocatalysis is one of the more promising advanced oxidation processes (AOP) developed in the past twenty years in alternative to conventional water and wastewater treatments. This process allows to perform the efficient degradation and in most cases the complete mineralization of a variety of organic pollutants present at low concentration levels in aqueous wastes [2-8]. Since the early report on photocatalytic degradation of 4-chlorophenol [9], it was demonstrated in several studies that chlorophenols are among the great number of aromatic pollutants which can be efficiently removed from aqueous wastes using this approach.

As was already reported in the literature, the primary step of the photocatalytic treatment involves the irradiation of suitable semiconductor particles with light energy greater than the band-gap, with the production of charge carriers (electrons and holes) which can either recombine or migrate to the particle surface where various redox reaction can occur with different species (adsorbed substrates, oxygen and hydroxyl groups, water and dissolved molecules, etc.). These reactions give rise to the production of highly reactive oxidizing or reducing products, in turn capable of attack the organic pollutants. Among

the reactive species produced, hydroxyl radicals play a crucial role as oxidants in the destruction of organic compounds, as pointed out in the literature [5, 10-14]. For aromatic molecules the $\bullet\text{OH}$ attack occurs mainly through its addition to the ring [15], although hydrogen and electron abstraction [16, 17] may play a significant role. On the other hand, reductive pathways may be also present in some cases [18].

Concerning the various semiconductors examined, polycrystalline TiO_2 particles mainly composed of the anatase phase have been largely employed due to various favourable factors including low costs, safety (toxic products are not released from the irradiated semiconductor) and good photostability [19].

In recent years increased attention has been focused on possible applications of photocatalysis to treat complex aqueous wastes, including those containing dissolved surfactants. This could be of particular interest in view of the potential coupling of these treatments with prior extraction/washing steps performed with micellar solutions, largely applied to remove organic contaminants from solid phases such as soils or sediments.

It must be recalled that photocatalysis leads to the complete degradation of different types of surfactants [20], which can compete with the target substrate for active sites of the semiconductor. In previous studies we found that the degradation of some aromatic pollutants in the presence of surfactants bearing alkyl chains is possible, although at relatively low reaction rates [21, 22]. In other reported investigations the possible beneficial effects arising from surfactant adsorption in photocatalysis were examined [23] and the use of peculiar amphiphiles, resistant to the radicals attack, has also been proposed [24, 25]. More recently we investigated the influence of SDS on photocatalytic decomposition of 2,4,5-trichlorophenol, evidencing a neat inhibitory effect exerted by the amphiphile on the reaction kinetics and on the formation of main aromatic intermediates [26].

The aim of the present work was to study more in detail the influence of surfactant adsorption, surfactant microstructures formation and substrate hydrophobicity on the photocatalytic degradation of phenol and two chlorophenolic derivatives in aqueous TiO_2 dispersions containing HTAB, looking mainly at the evolution of the primary process. The release of chloride ion was also monitored in order

to ascertain the amphiphile effects on formation and fate of reaction intermediates originated from chlorinated substrates.

EXPERIMENTAL SECTION

Reagents and Materials.

High-purity (99%) 2,4,5-trichlorophenol (2,4,5-TCP), 2,5-dichlorophenol (2,5-DCP), phenol (Phe), purchased from Aldrich, and the analytical-grade surfactant N-hexadecyl-N,N,N-trimethylammonium bromide (HTAB, Merck) were used as received.

For all the photodegradation experiments polycrystalline TiO₂ Degussa P25 (composed of c.a. 80% anatase and 20% rutile) was employed. In order to remove any organic impurity this oxide was washed with water and irradiated with simulated solar light for about 12 h. The washed semiconductor was then dried in the oven at 80°C. The resulting powder was resuspended in water by sonication immediately before use.

Acetonitrile (Lichrosolv, Merck), H₃PO₄ and NaOH (Merck) were used to prepare the LC eluents. Na₂CO₃ and NaHCO₃ solutions (Merck) were used as eluents for the IC measurements. Pure water was produced using a Milli-Q™ system (Millipore).

Instruments.

The following instruments were used: HPLC Merck-Hitachi, equipped with L-6200 pumps and a UV-VIS L-4200 detector; IC Dionex DX 500 equipped with a gradient pump GP-40 and electrochemical detector ED 40 (Dionex).

Degradation Experiments.

The degradation experiments were carried out in a photochemical stirred batch reactor from Helios-Italquarz (Milan), equipped with a medium pressure mercury lamp (125 W). **The reported transmitted**

photon flux within this reactor, determined by using radiometric measurements, is around 10 mW cm⁻² [27].

Degradations were performed both in pure water and in the presence of the cationic surfactant HTAB in the concentration range 6×10^{-5} to 1.5×10^{-3} M. All the experiments were performed employing 500 mL of aqueous solutions containing 2.0×10^{-4} M phenol (or chlorophenols), 500 mg L^{-1} of TiO_2 and the proper amount of surfactant. The temperature was kept at 25 °C. The starting pH of the irradiated suspensions was in most cases around 5, but some experiments were also performed at pH 3 for 2,4,5-TCP.

Analytical Determinations.

In order to follow the degradative process, dispersion samples (2-5 mL) were manually taken from the reactor at different irradiation time; all the analytical determinations were performed after filtration through a 0.45 μm Millex-LCR hydrophilic PTFE membranes (Millipore).

The substrate degradation was monitored using HPLC, working with a column RP-C18 Lichrospher 10 mm (4 mm i.d. x 125 mm long, from Merck). The eluent was acetonitrile/phosphate buffer (1.11×10^{-2} M, pH=3) 15/85 % v/v for Phe, 45/55 % v/v for 2,5-DCP, 50/50 % v/v for 2,4,5-TCP; flow rate 1 mL min^{-1} . The detector wavelength was 220 nm. In order to recover quantitatively the 2,4,5-TCP adsorbed on TiO_2 an equal volume of CH_3CN was added to the suspension samples before filtration.

In order to recover quantitatively the analytes adsorbed on TiO_2 an equal volume of CH_3CN was added to the suspension samples before filtration. This procedure must be in particular applied before the HPLC measurements for 2,5-DCP and 2,4,5-TCP, whereas the observed recovery of phenol was not significantly different in the presence or in the absence of the added solvent.

Addition of acetonitrile to the samples before the HPLC runs is also necessary in order to avoid sensitization effects due to the presence of surfactants. Acetonitrile was added after the filtration in preliminary studies performed in the dark to estimate the substrate adsorption.

The formation of chloride was followed by a suppressed ion chromatography; the elutions were performed with a solution containing K_2CO_3 (10 mM) and $NaHCO_3$ (4 mM) at 30 °C, at a flow rate of 1.0 mL min⁻¹.

RESULTS AND DISCUSSION

Preliminary experiments on substrate adsorption

Adsorption of phenol on TiO_2 in the dark was found to be negligible in the absence of added HTAB, whereas a slight decrease of substrate concentration (<3%) was measured in the presence of surfactant.

The behaviour of chlorophenols is different: the measured adsorption of 2,5-DCP (5-6 %) and 2,4,5-TCP (14-16%) on TiO_2 is significant and becomes higher in the presence of HTAB, reaching its maximum for measurements performed with HTAB $6.0 \times 10^{-4} M$ (concentration not far from the c.m.c.) where the measured adsorptions for 2,5-DCP and 2,4,5-TCP were 28-30% and 35-38%, respectively.

Measurements performed at higher HTAB concentration ($1.5 \times 10^{-3} M$) showed a decrease of adsorption (ca. 50% for 2,5-DCP and ca. 60% for 2,4,5-TCP) in respect to the reported maximum, which can be attributed to micellar solubilization.

The addition of acetonitrile allowed us to recover more than 97% of the analytes initial concentration, with a loss within the usual precision of the kinetic measurements performed in the examined heterogeneous systems.

Effect of HTAB on the primary process

As previously found in most similar experiments, the photocatalytic degradation of examined substrates in water obeys to a pseudo-first order kinetic law described by the equation:

$$-\ln(C/C_0) = k_{obs} C_{sub} \quad (\text{Eq.1})$$

Significant variations of the reaction rate, largely dependent on surfactant concentration, were observed in the presence of added HTAB.

i) Surfactant concentrations lower than the critical micellar concentration (c.m.c.) .

Photocatalytic degradation of phenol in aqueous solutions containing HTAB at concentrations below the c.m.c. value becomes slower than in water (see Figure 1). It must be noted that, due to the presence of other solutes, the c.m.c. value for HTAB is expected to be lower than that reported in literature in pure water (around 9×10^{-4} M).

A similar kinetic behaviour, although less evident in the first part of the reaction, is shown by 2,5-dichlorophenol in the presence of very low HTAB concentrations (6.0×10^{-5} M). Under these conditions the relatively scarce surfactant adsorption onto the TiO_2 particles seems to be inadequate to ensure a relevant substrate binding, as confirmed by the non negligible amounts of this compound still found after 3 hours irradiation (see Figure 2). For HTAB 6.0×10^{-4} M, just below the c.m.c., the observed neat increase of the degradation rate could be attributed to the facilitated accumulation of 2,5-DCP on adsorbed surfactant layers. In this later case the measured reaction rate was higher than that observed in water.

A different behaviour is exhibited by 2,4,5-TCP, for which a neat increase of degradation rate with respect to water is observed even at lower HTAB concentrations (6.0×10^{-5} M) (see Figure 3). By increasing the HTAB concentration until 6.0×10^{-4} M, the reaction rate continuously increases. Also for this compound the degradation was monitored for 3 hours, being the complete removal observed after 90 min irradiation in water and after lower irradiation times in the presence of HTAB.

Due to the very fast decay of 2,4,5-TCP., the fit of kinetic data according to Eq. (1) has been performed up to ca. 70% degradation.

In order to explain the above mentioned effects on the investigated substrates, both processes occurring in the bulk solution and at the semiconductor/solution interface have to be carefully analyzed. In particular, when the surfactant concentration is below the c.m.c., adsorption of surfactant molecules on the TiO_2 particles must be considered. The interactions between the solid surface and the surfactant

ionic heads justify the usual adsorption mode [28, 29]. Moreover, the attraction strongly depends on the semiconductor surface charge, which is in turn dependent on the solution pH. In fact, previous studies on adsorption of HTAB and SDS on metal oxides, performed using IR spectroscopy [30], demonstrated the influence of pH on surfactant adsorption.

Taking into account that the **initial** pH of the examined aqueous solutions is not far from the isoelectric point of anatase [31], negligible or low repulsive effects due to the surface charge of TiO₂ can be expected **at the beginning of the treatment**.

The pH of aqueous TiO₂ dispersions containing HTAB, monitored during the experiments, showed negligible variations after 30, 60 and 90 min irradiation, whereas a pH in the range 3.8 - 4.0 was measured after 180 min irradiation. On these basis, a nearly constant surfactant absorption can be assumed during the primary process involving 2,4,5-TCP and 2,5-DCP at higher HTAB concentrations, whereas partial desorption of HTAB from positively charged semiconductor particles cannot be excluded after long term irradiation, when the degradation of phenol and 2,5-DCP (at the lowest HTAB concentration) are still in progress.

Hydrophobic interactions between the hydrocarbon chains of adjacent adsorbed surfactant molecules are also important and they become dominant for surfactants bearing longer hydrocarbon tails. These interactions lead to the formation of typical admicellar structures when the surfactant concentration increases.

As a consequence, the solutes present in the system tend to be involved in various partition equilibria: adsorption onto TiO₂ (or surfactant-modified TiO₂) surface, adsolubilization in the hemimicelle layers and micellar solubilization (above the c.m.c), as shown in Figure 4. The increased concentration of substrate molecules near to the active sites of the semiconductor surface could justify the observed increase in the degradation rate. Previous studies, in fact, supported the favourable influence of substrate adsorption on photocatalytic degradation [32, 33], although the contribution of reaction paths involving the bulk solution cannot be completely excluded in these cases.

In previous investigations concerning the degradation of 2,4,5-TCP in the presence of SDS no beneficial effects were observed [26] and this can be explained taking into account that SDS adsorption onto TiO₂ is much lower than HTAB adsorption. In fact differences in Langmuir constants by about two orders of magnitude were observed [31]. Thus, adsorption of SDS becomes significant only at relatively high surfactant concentrations (around the c.m.c.) and under these conditions micellar solubilization can effectively compete with adsolubilization, decreasing the substrate availability near the semiconductor surface.

Another evidence of the stronger adsorption of HTAB onto TiO₂ comes from the observation of partial disaggregation of semiconductor microparticles due to the formation of charged bilayers onto the semiconductor. This phenomenon increases the surface area of the catalyst, giving rise to a corresponding increase of the degradation rate. It was observed at very low HTAB concentrations, whereas the same effect can be seen in the presence of higher concentrations (near the c.m.c. range) of SDS.

Although there is a lack of informations about the partition equilibria of the investigated solutes between the bulk solution and the admicellar structures, comparison of micellar binding constants (K_B) could be useful in order to hypothesize the adsolubilization tendency of the investigated compounds. In a previously published work [34] K_B values of 120 M⁻¹, 3,200 M⁻¹ and 15,600 M⁻¹ for phenol, 2,5-DCP and 2,4,5-TCP, respectively, were reported in HTAB micellar solutions. On these basis a lower tendency of phenol to bind to the adsorbed surfactant layer could be expected, whereas adsolubilization should be much more important for the more hydrophobic chlorinated derivatives. This assumption is sustained by recently published studies on adsolubilization of chlorophenols in SDS-alumina admicelles, where the crucial influence of substrate hydrophobicity was evidenced [35].

For 2,4,5-TCP the degradation rate measured in the presence of adsorbed HTAB was significantly higher than that observed in pure water, in agreement with the expected higher tendency of this compound to interact with the adsorbed surfactant structures.

ii) Surfactant concentrations higher than the c.m.c.

For phenol, the presence of HTAB micelles still decreases the degradation rate (see Figure 1) and this can be attributed to a further reduction of substrate concentration at the semiconductor-solution interface due to micellar solubilization.

On the contrary, the degradation of 2,5-DCP in the presence of micellar HTAB is faster than in water, probably because adsolubilization still plays a favourable role, whereas it is slower in respect to the runs performed below the c.m.c. due to the expected partial solubilization of the substrate into the micellar aggregates.

From the insets in Figures 1 and 2, it can be observed that, for phenol and 2,5-DCP, the degradation kinetics follows well Eq. (1) along the process.

For 2,4,5-TCP a similar trend was observed: the degradation rate is lower than that measured at HTAB concentrations below the c.m.c, but always much higher in respect to that determined in pure water (see Figure 3). For this very hydrophobic compound, a slow direct release from micelles to the surfactant-modified TiO₂ particles probably occurs [36].

The evolution of k_{obs} as a function of HTAB (see Figs. 2-3) exhibits a maximum for the examined chlorophenols at concentrations near the c.m.c., in agreement with the surfactant adsorption trend. However, it must be recalled that the observed degradation behaviour reflects the complexity of the investigated system, where various partition equilibria simultaneously exert their influence on the photocatalytic treatment and where surfactant desorption and surfactant degradation could also play a role at longer irradiation times.

Moreover, the pK_a decrease of phenols in the presence of cationic micellar aggregates, more noticeable for hydrophobic substrates, is another factor which can influence their reactivities in the microheterogeneous system.

Effect of HTAB on chloride evolution

The effect of HTAB on the release of chloride, the only end-product which can be conveniently monitored under the examined conditions, has been investigated. It is worth to mention that the measurement of TOC (or DOC) is precluded due to the fact that also the surfactant molecules are degraded.

Before to start with the Cl⁻ determination in the irradiated solutions, several IC measurements were performed on filtered blank samples containing TiO₂, HTAB at various concentrations and known amounts of chloride up to 6.0x10⁻⁴ M. No interferences from the matrix components were observed on Cl⁻ determination.

For 2,5-DCP the chloride formation becomes slower than that observed in water for HTAB concentrations below the c.m.c., and even much slower above this value (see Figure 5). After 3 hours irradiation the stoichiometric chloride concentration was not attained, suggesting the possible presence of persistent chlorinated intermediates. About 70% of stoichiometric chloride was released in solutions containing 1.0x10⁻⁴ M HTAB, whereas only ca. 21% of total chloride was measured in the presence of HTAB 1.5x10⁻³ M. Since in the later case the primary process is much faster than in water (complete degradation of 2,5-DCP occurs after ca. 80 min), this implies that relevant concentrations of chlorinated reaction products are present well after the time required for the substrate abatement.

A similar behaviour has been exhibited by 2,4,5-TCP, for which the chloride release at HTAB concentrations below, around and above the c.m.c. limit is shown in Figure 6. Also here the adsorbed surfactant, which largely favours the primary process, in some way hinders the successive decomposition of chlorinated intermediates, probably because they are more hydrophilic than the initial substrate and tend to be less bound to the adsorbed surfactant layer. In this light, the examination of transient products fate becomes an important aspect of the study since accumulation of these species in the reaction media occurs after the complete destruction of the target compound.

Studies concerning these peculiar aspects of surfactant-assisted photocatalysis are actually under study in our laboratory.

Effect of pH on surfactant adsorption

In order to confirm the influence of surfactant adsorption on the degradation reaction some photocatalytic runs were performed at pH 3 (value well below the isoelectric point of TiO₂) on 2,4,5-TCP, the substrate which appeared more sensitive to the surfactant effects.

In the absence of HTAB, the reaction rate is slightly faster at pH 3, reflecting the increased adsorption of 2,4,5-TCP onto the positively charged TiO₂ particles. On the contrary, adsorption of HTAB becomes negligible at pH 3 due to the relevant electrostatic repulsion between the surfactant molecules and the positively charged semiconductor particles. Only negative effects on the degradation rate due to surfactant competition were observed in this case, with a further significant inhibition upon micellization. Figure 7 shows the evolution of the calculated k_{obs} under the investigated experimental conditions; the corresponding kinetic data at pH 5 is also shown for comparison purposes.

The above results suggest that surfactant-assisted adsorption of **hydrophobic** substrate molecules plays an important role, facilitating the initial degradation steps.

CONCLUSIONS

Provided a proper selection of the amphiphiles used, the presence of such components in wastes to be treated by photocatalysis do not stop the degradation process, although surfactant molecules themselves are degraded. When surfactant adsorption is high and substrates are hydrophobic (as for chlorophenols in the present study), a beneficial kinetic effect on the primary process is expected on the basis of admicellar structures formation onto the semiconductor particles. The increase of surfactant concentration above the c.m.c. significantly reduces the substrate degradation rate by introducing competitive partitioning between adsorbed surfactant and micellar aggregates.

The effect of amphiphilic microstructures on further degradation steps, in particular on the evolution of more hydrophilic intermediate products, is less favourable since the persistence of such products tends to increase. In order to avoid potential risks a careful analytical control of the treatment, even after the complete destruction of the target pollutant, is necessary.

Acknowledgements

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FIGURE CAPTIONS

Figure 1 Photocatalytic degradation of phenol (initial concentration: 2×10^{-4} M) in water (\circ) and in the presence of 1×10^{-4} M (\square), 6×10^{-4} M (\diamond) and 1.5×10^{-3} M (\blacktriangle) HTAB. TiO_2 : 400 mg L^{-1} .

Figure 2 Photocatalytic degradation of 2,5-dichlorophenol (initial concentration: 2×10^{-4} M) in water (\circ) and in the presence of 6×10^{-5} M (\star), 6×10^{-4} M (\diamond) and 1.5×10^{-3} M (\blacktriangle) HTAB. TiO_2 : 400 mg L^{-1} .

Figure 3 Photocatalytic degradation of 2,4,5-trichlorophenol (initial concentration: 2×10^{-4} M) in water (\circ) and in the presence of 6×10^{-5} M (\star), 1×10^{-4} M (\square), 6×10^{-4} M (\diamond) and 1.5×10^{-3} M (\blacktriangle) HTAB. TiO_2 : 400 mg L^{-1} .

Figure 4 Partition equilibria of solutes between: a) solution and TiO_2 ; b) solution and admicelles; c) solution and micelles (above c.m.c. concentration); d) admicelles and micelles.

Figure 5 Chloride evolution during the 2,5-DCP degradation (initial concentration: 2×10^{-4} M): water (\bullet), HTAB 6×10^{-5} M (\blacksquare) and HTAB 1.5×10^{-3} M (\blacklozenge). Dashed line: stoichiometric chloride concentration.

Figure 6 Chloride evolution during the 2,4,5-TCP degradation (initial concentration: 2×10^{-4} M): water (●), HTAB 6×10^{-5} M (■), HTAB 1×10^{-4} M (▼), HTAB 6×10^{-4} M (◆), HTAB 1.5×10^{-3} M (★).

Dashed line: stoichiometric chloride concentration.

Figure 7 Surfactant effect on the degradation kinetics of 2,4,5-TCP at pH = 3 (initial substrate concentration: 2×10^{-4} M).

Figure 1

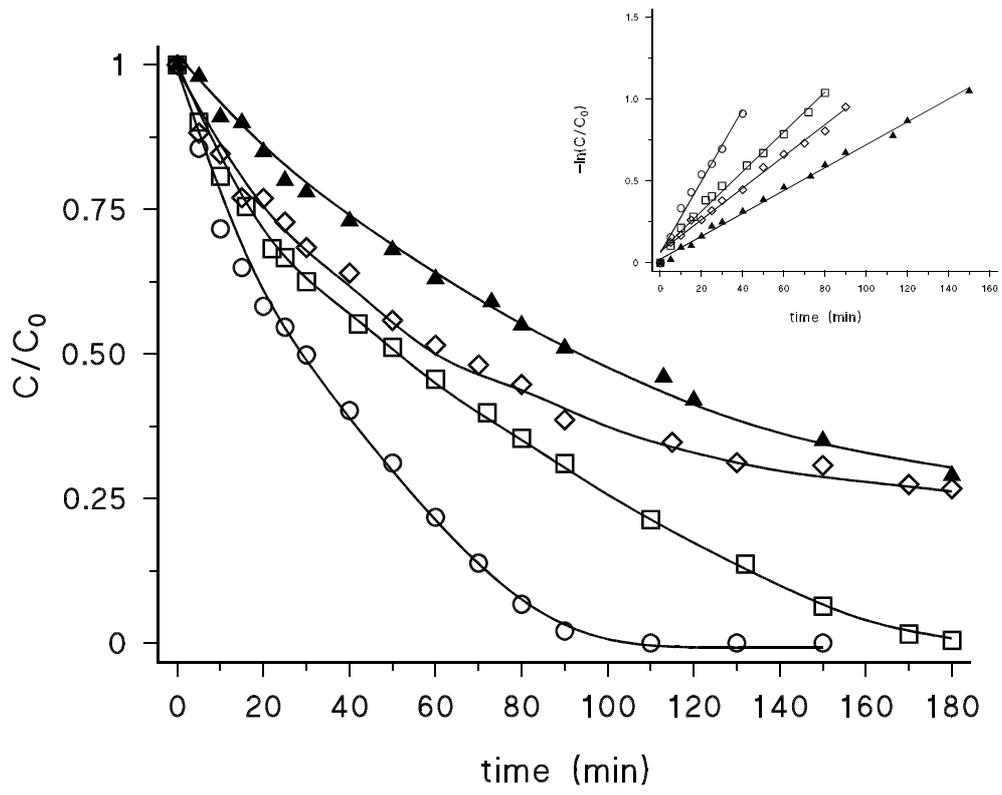


Figure 2

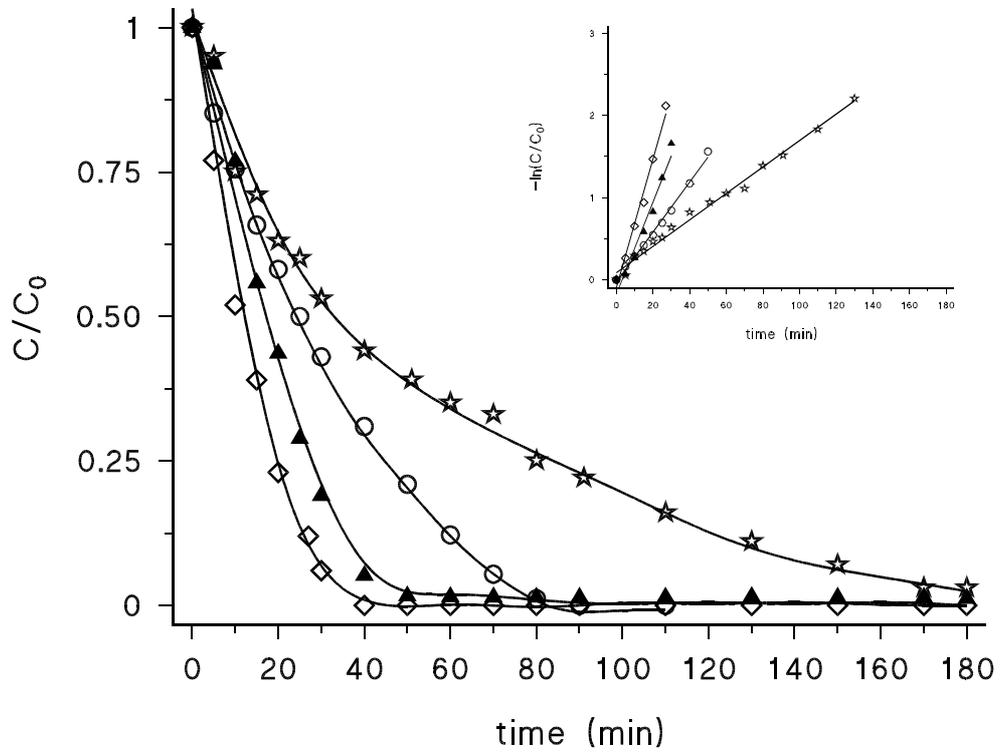


Figure 3

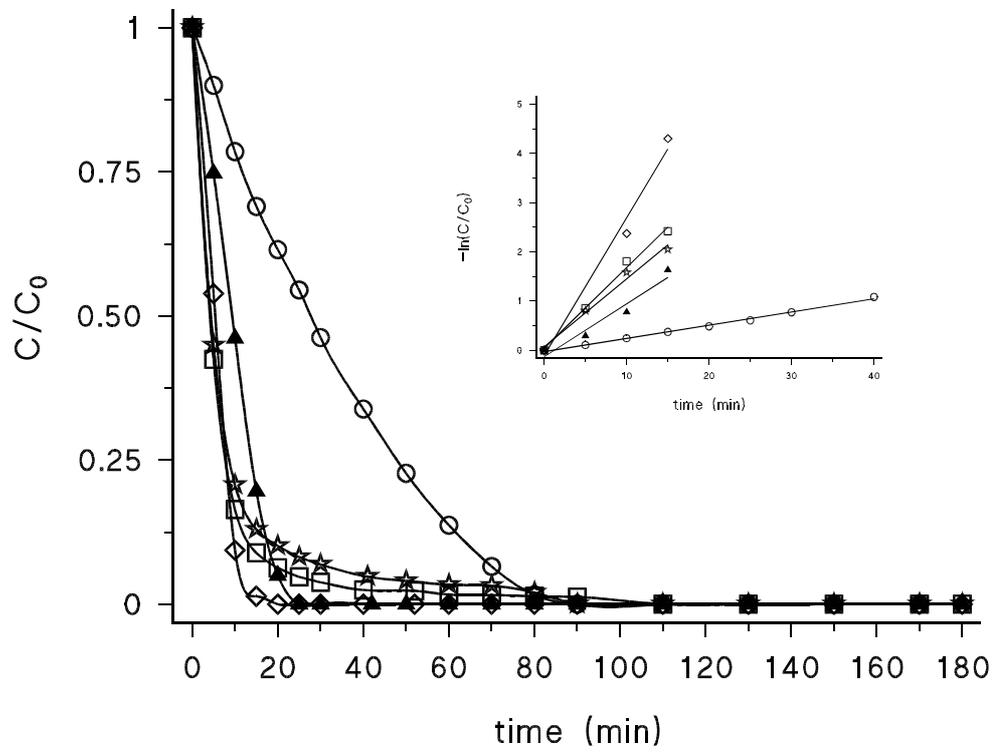


Figure 4

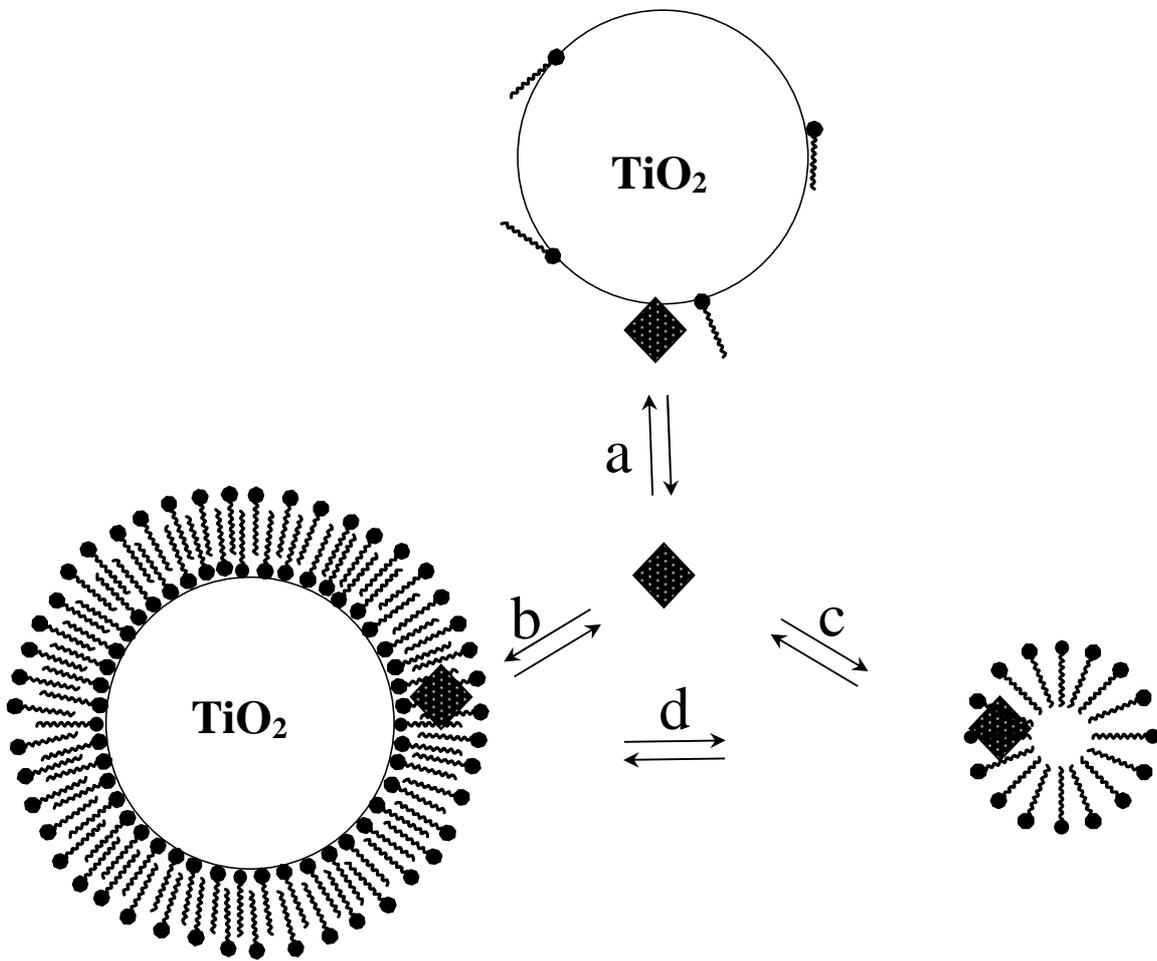


Figure 5

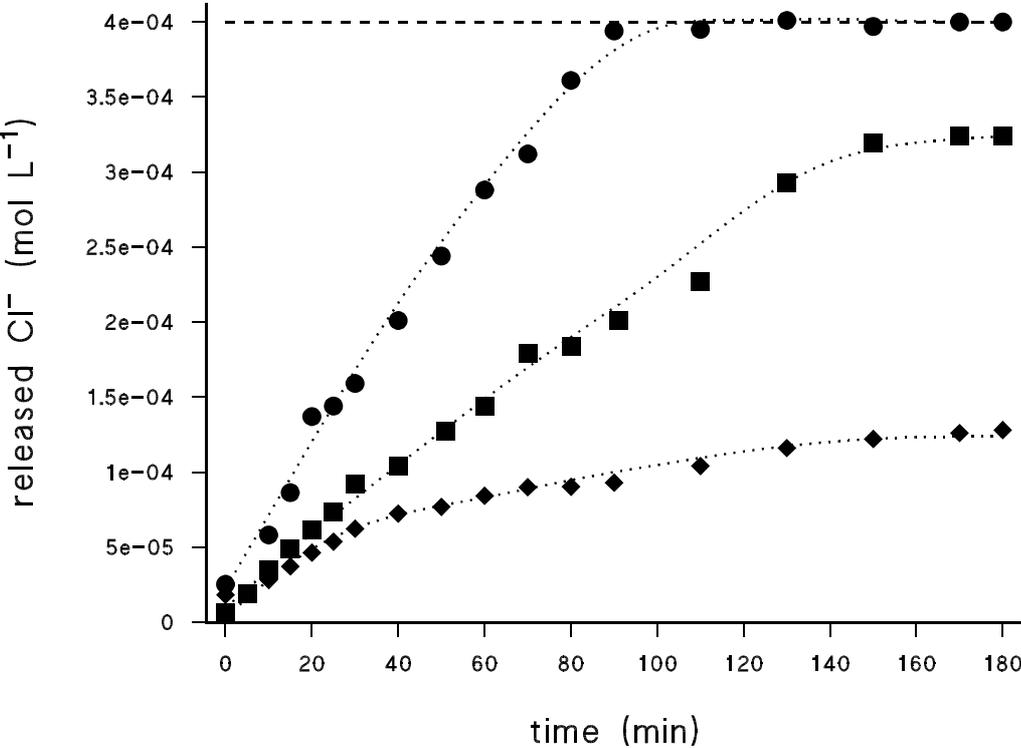


Figure 6

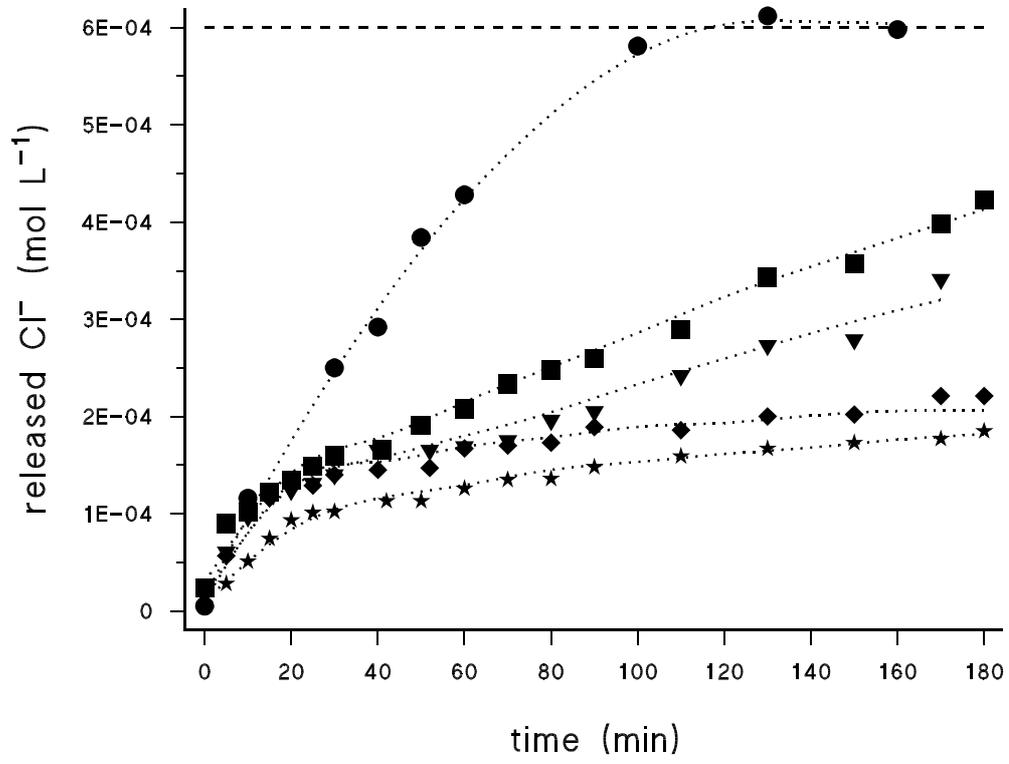


Figure 7

