

Photochemical behaviour of phenylbenzoquinone at the surface of the clays: Kaolinite, bentonite and montmorillonite

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ABSTRACT

The kinetics of direct photochemical transformation of phenylbenzoquinone (PhQ) was studied at the surface of clays, light absorbing and scattering supports. When compared to the spectrum in solution, the UV absorption of PhQ on clays shows a hyperchromic as well as a solvatochromic effects. In kaolinite, bentonite and montmorillonite, the shift was about $\Delta\lambda = 30$ nm and the molar absorption coefficient was roughly three times higher. For various layers of clays, the disappearance of PhQ, followed a pseudo-first order kinetics. The diffusion of the compound from the lower part to the illuminate one was found to be low toward photolysis within the range 15–70 μm . In these conditions, the first order rate constant at the surface of kaolinite, k^0 , was found equal $2.3 \times 10^{-2} \text{ min}^{-1}$ in aerated conditions. This was roughly constant for the two other tested clays, bentonite and montmorillonite, where k^0 was estimated to be $2.1 \times 10^{-2} \text{ min}^{-1}$ and $1.8 \times 10^{-2} \text{ min}^{-1}$, respectively. The photocyclization was found to be oxygen concentration dependent: $k_{\text{vacuum}}^z/k_{\text{air}}^z = \Phi_{\text{vacuum}}/\Phi_{\text{air}} \approx 3.5$. Diffuse-reflectance experiments clearly show the implication of the triplet state excited state in the photolysis of PhQ.

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1. Introduction

The increasing use of pesticides has led to high concentrations of those in water as well as in soil. Their negative ecological consequences are often assigned to their persistence in these media. The interest in these environmental effects leads to an increase of the research activities toward the methods which could help for the study of the behaviour and fate of such non-desired substrates. The principal degradation pathways for these pollutants involve photolysis, hydrolysis, oxidation and dehalogenation when halogenated products are concerned [1,2]. Many of these organic chemicals can undergo photochemical transformations with sunlight via direct or indirect photoreactions [1–4]. Their photolytic degradation has been intensively studied in aqueous solutions [1] and has led in many cases to a better knowledge of their life time and fate. In contrast, for the photolysis at the surface of soils, there is a lack of studies more probably owing to the complexity of the medium. Most studies at the surface of soils were devoted to the detection of possible toxic byproducts that can be generated under excitation by solar light [5,6] or to kinetic studies that cannot be easily used for comparison purposes [7]. Among the factors that make the photochemical studies on soil very complex, several parameters are of great importance: the chemical composition of the soil, pH,

the penetration of light, the spectroscopic properties of the organic substrate deposited on soil, the determination of kinetic constant that accounts for the photolytic disappearance of the substrate at the surface of the soil without taking into account the depth of the support. These aspects, which have to be taken into account, for the kinetic study of photolytic degradation of pesticides in soils were recently and deeply presented at the surface of clays as a first approach [8–11]. In these works, these aspects were developed with the aim of evaluating the disappearance quantum yields of pesticides at the surface of clays.

In the present work, special efforts have been directed toward the determination of the first order kinetic constant at the surface of various clays as well as the elucidation of the mechanism of transformation in these solid supports. For this purpose, we have chosen a model molecule, phenylbenzoquinone, for which the photolysis mechanism in solution is well described [12–14]. The goal of the paper is to compare the photoreactivity of phenylbenzoquinone in solution with that in porous systems such as clays which are light absorbing and scattering media.

2. Experimental

Phenylbenzoquinone was obtained from Eastman as the purest grade available. It was used without further purification. Since 2-hydroxydibenzofuran is not a commercial compound. In order to make standardization possible, it was collected from irradiated solutions of phenylbenzoquinone in methanol. Several milligrams

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were obtained using preparative HPLC as described in the literature [12]. Kaolinite was obtained from Fluka. Bentonite and montmorillonite were purchased from Aldrich. The three clays were used as received. All other reactants were of the highest grade available and were used without further purification.

The preparation of the clay layer (2.5 cm × 1.5 cm) was performed on a Pyrex glass as described in the literature [8]. In our case, the clay slurry with the desired amount of clay and defined concentration of phenylbenzoquinone was prepared in methanol. After deposition of a known volume on the Pyrex glass, the slurry was allowed to dry overnight at room temperature. The layer thickness of the sample was determined by knowing the dry amount of kaolinite deposited on the pyrex plate, the surface area and the bulk density, ρ_{bulk} , of the layer ($\rho_{\text{bulk kaolinite}} = 1.8$; $\rho_{\text{bulk bentonite}} \approx \rho_{\text{bulk montmorillonite}} \approx 1.7$ [10]). With this procedure, layers of various thickness were obtained: from 15 μm to 200 μm . It has to be pointed out that the irradiation of the dry sample was performed by using a Pyrex tube (roughly 20 cm³) as a reactor. This permitted the study of the effect of oxygen concentration. The medium was deoxygenated by vacuum for 1 day then the reactor was tightly closed. After procedure, the analysis of the sample did not show any degradation of phenylbenzoquinone.

For each irradiation time, two different sample plates were used. The layer was quantitatively collected and mixed with 2 ml of methanol. The mixture was gently agitated for 10 min at room temperature. After centrifugation at 3500 rpm for 10 min, the HPLC analysis showed that more than 95% of product recovery was obtained.

For kinetic as well as analytical purposes, the irradiations of the plates at 365 nm were conducted with a high pressure mercury lamp (Osram HBO, 125 W) equipped with a grating monochromator. The beam was parallel. The incident light intensity was determined by chemical actinometry with ferrioxalate ($I_0 = 2.4 \times 10^{15}$ photons cm⁻² s⁻¹).

Diffuse-reflectance experiments in the 200 ns to 400 μs time scale were carried out using a nanosecond laser flash photolysis spectrometer from Applied Photophysics (LKS.60). The excitation ($\lambda = 355$ nm) was from the third harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser (pulse width ≈ 9 ns). The excitation beam was used in a right-angle geometry with respect to the monitoring light beam to prevent specular reflexion of the laser light to enter into the monochromator. The area irradiated on the quartz cuvette cell was approximately 1 cm². The cell was moved after each shot in order to irradiate a new area. The obtained signal was the result of an average of more than 5 shots. The signal at preselected wavelength

was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator, and a 1P28 photomultiplier. The signal from the photomultiplier was digitized by a programmable digital oscilloscope (HP54522A). A 32 bits RISC-processor kinetic spectrometer workstation was used to analyse the digitized signal.

Diffuse-reflectance and transmittance of clay layers were recorded with a Cary 300 scan (Varian) equipped with integrating sphere (DRA-CA-30I; 70 mm; Varian). The spectra were recorded within the range 230–800 nm. The recorded reflectance was corrected by using Spectralon's (Labsphere) absolute reflectance.

The consumption of phenylbenzoquinone and the formation of the byproduct, 2-hydroxydibenzofuran, were monitored by analytical HPLC using a Waters apparatus equipped with a 996-photodiode array detector. The experiments were performed by UV detection at either 365 nm or 290 nm for phenylbenzoquinone and 290 nm for the formation of the byproduct. The HPLC analysis were conducted by using a reverse phase Merck column (Spherisorb ODS-2, 250 mm × 4.6 mm, 5 μm). The flow rate was 1.0 mL min⁻¹ and the injected volume was 50 μL . The elution was accomplished with acidified water (acetic acid 0.01%) and acetonitrile (7/3 by volume).

3. Results and discussion

The diffuse-reflectance spectrum of phenylbenzoquinone (PhQ) at different concentrations on kaolinite layer of 200 μm together with that of kaolinite alone are given in Fig. 1a. They clearly show that the percentage of reflected light within the range 230–700 nm decreased when the concentration of PhQ increased. By subtracting the spectrum due to kaolinite, the maximum was found to be roughly at 395 nm (Fig. 1b). When compared to the UV-vis absorption spectrum recorded in aqueous solution [12,13], $\lambda_{\text{max}} = 365$ nm, a similar shape is obtained for wavelengths over 290 nm with a significant bathochromic shift, $\Delta\lambda = 30$ nm. This is more likely related to the interaction of PhQ with the surface of kaolinite. Moreover, it is worth noting that the reflexion bands appeared wider more likely to the presence of several shoulders. This is in agreement with the fact that PhQ molecules are inserted in various sites of kaolinite. Similar results were obtained when bentonite and montmorillonite were employed.

The changes in the optical properties of the medium may be used for the calculation of the molar absorption coefficient, ϵ , of PhQ deposited on kaolinite as proposed by Ciani et al. [9]. The method which is employed for thick enough samples is based on the Kubelka-Munk Model. In these conditions the Kubelka-Munk

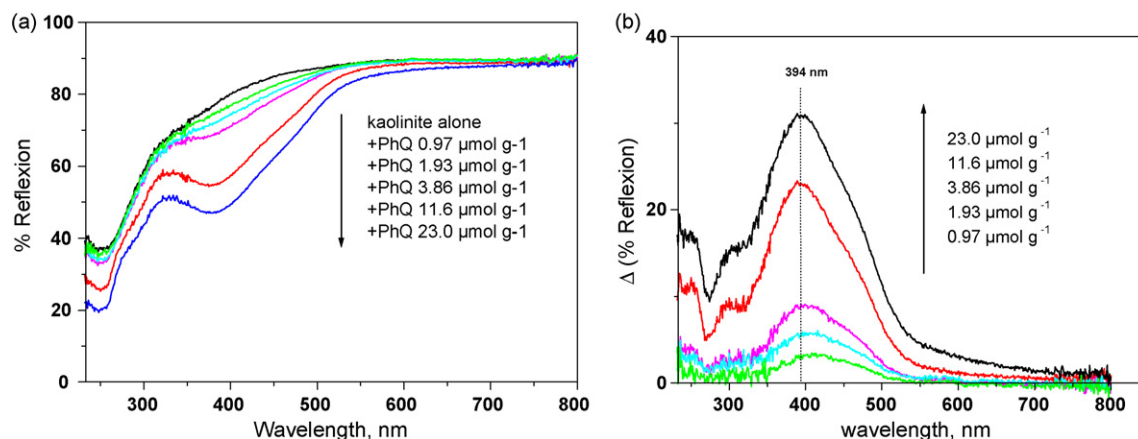


Fig. 1. (a) Diffuse-reflectance spectra of the mixture phenylbenzoquinone/kaolinite deposited on Pyrex glass (thickness of 200 μm) at various concentrations of PhQ. (b) Reflexion spectra of PhQ in kaolinite.

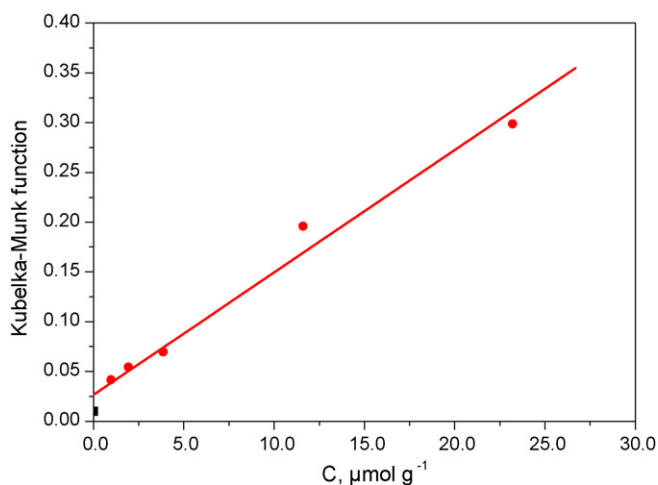


Fig. 2. Kubelka-Munk function at 395 nm as a function of adsorbed concentration of PhQ (layer thickness: 200 μm). (■): Such data for $C_i = 0$ was calculated using the published values of k and s ($k = 13.5 \text{ cm}^2 \text{ g}^{-1}$ and $s = 2500 \text{ cm}^2 \text{ g}^{-1}$ at 400 nm [10]).

function for kaolinite mixed with PhQ may be written as follows:

$$f(R_{\infty,i}) = \frac{k}{s} + \frac{2 \ln(10) \varepsilon_i(\lambda) C_i}{s}$$

where k and s are respectively the absorption coefficient and the scattering coefficients of kaolinite; $\varepsilon_i(\lambda)$ is the molar absorption coefficient of PhQ at a given wavelength; C_i is the deposited concentration of PhQ (mol cm^{-3}).

According to the previous expression the slope of the plot $f(R_{\infty,i})$ as a function of C_i permits the direct determination of the molar absorption coefficient. As clearly shown in Fig. 2, there is a linear relationship between the Kubelka-Munk function at 395 nm and the used concentration of PhQ within the range 1–23 $\mu\text{mol g}^{-1}$. Under these conditions it is clear that phenylbenzoquinone is distributed homogeneously within the kaolinite layer and without significant interactions between the organic molecules.

It has to be pointed out that the obtained intercept k/s shows, within the experimental errors, a perfect agreement with that found theoretically by using the published values of k and s [10]. The molar absorption coefficient at 395 nm was evaluated to $6.7 \times 10^6 \text{ mol}^{-1} \text{ cm}^2$ which is three times greater than that obtained in aqueous solution, namely $2.0 \times 10^6 \text{ mol}^{-1} \text{ cm}^2$ [12]. This is, once again, in complete agreement with the presence of great interactions between phenylbenzoquinone and the surface of kaolinite.

In order to study the photodegradation of phenylbenzoquinone on kaolinite, layers of various thickness were exposed to a monochromatic light at 365 nm. Dark control experiments were carried out with samples kept in the dark and at room temperature.

As shown in Fig. 3, the irradiation of PhQ deposited on kaolinite (thickness 54 μm and 28 μm) led to an important decrease in the concentration of PhQ. For the 28 μm layer, the total disappearance was observed within 10 h irradiation time. The experimental data were perfectly fitted using a pseudo-first order law. The observed rate constant was evaluated to $7.3 \times 10^{-3} \text{ min}^{-1}$. In the case of 54 μm , it is clear that the disappearance followed a two steps

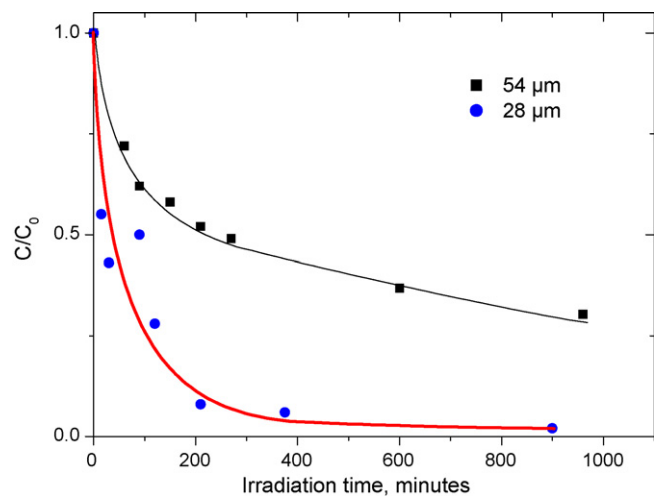


Fig. 3. Transformation of phenylbenzoquinone at the surface of kaolinite in aerated conditions under continuous irradiation ($\lambda_{\text{excitation}} = 365 \text{ nm}$).

process: a fast step at the early stages of the irradiation (up to 200 min) and a slower one for prolonged irradiation. The first part which permitted 50% conversion of phenylbenzoquinone followed a pseudo-first order process with an observed rate constant of $3.8 \times 10^{-3} \text{ min}^{-1}$. The second step is owing to the diffusion kinetics of the organic compound from the bottom part of the clay to the illuminated one as clearly explained by Balmer et al. [8]. In order to study such effect, the determination of the observed first order rate constant corresponding to the first step, was undertaken with various layer thickness (Table 1). As clearly seen, the rate constant appeared to be roughly inversely proportional to the layer thickness when $z \leq 70 \mu\text{m}$. For higher values of z , the observed rate constant decreased drastically due to a very low diffusion process when compared to the photolysis. This aspect can be highlighted by calculating the value $k^Z \times Z$. This appeared to be constant within the layer thickness range 15–70 μm and roughly equal to $0.20 \text{ min}^{-1} \mu\text{m}$. Such conclusion is in complete agreement with the expression described in the literature [8]:

$$k^Z Z = 1.443(Z_{0.5} k^0)$$

where k^Z is the observed rate constant obtained for a given layer thickness, k^0 is the photolysis first order rate constant at the surface of the clay layer and $Z_{0.5}$ is the depth at which the light intensity is reduced to 50%. The two former values are considered constant and depend on the clay and the substrate. In the case of kaolinite, $Z_{0.5}$ was estimated to be equal to 6.0 μm [8,10]. By taking into account the range 15–70 μm , the photolysis first order rate constant at the surface of kaolinite layer, k^0 , was then evaluated to $2.3 \times 10^{-2} \text{ min}^{-1}$.

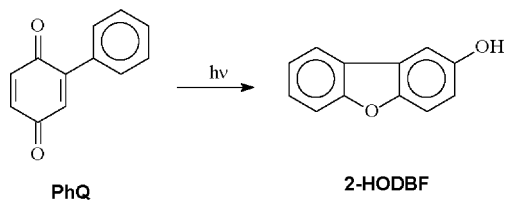
Similar experimental studies were also undertaken in bentonite and montmorillonite where k^0 was estimated to be $2.1 \times 10^{-2} \text{ min}^{-1}$ and $1.8 \times 10^{-2} \text{ min}^{-1}$, respectively. This shows that for these three clays, the interactions of PhQ with the solid support are similar and do not have significant effect on the photochemical process.

Table 1

Effect of the layer thickness of kaolinite on the observed first order rate constant of phenylbenzoquinone disappearance upon monochromatic excitation at 365 nm.

Layer thickness, Z (μm)	k^Z ($\times 10^3$) (min^{-1})	$k^Z \times Z$ ($\text{min}^{-1} \mu\text{m}$)	Layer thickness, Z (μm)	k^Z ($\times 10^3$) (min^{-1})	$k^Z \times Z$ ($\text{min}^{-1} \mu\text{m}$)
15	14	0.21	70	3.0	0.21
20	9.2	0.18	120	1.4	0.17
28	7.0	0.20	150	0.6	0.09
54	3.8	0.20	200	0.3	0.06

From the analytical point of view, the HPLC chromatogram showed the presence of one byproduct, 2-hydroxydibenzofuran (2-HODBF), with a retention time higher than that of phenylbenzoquinone. The selectivity of the reaction was demonstrated by injecting a standard solution of 2-HODBF. Whatever the layer thickness, the observed first order rate constant for the formation of such product was similar to that obtained from the degradation of phenylbenzoquinone indicating an efficient and selective photocyclization process as observed in water, acetonitrile or methanol [12,13].

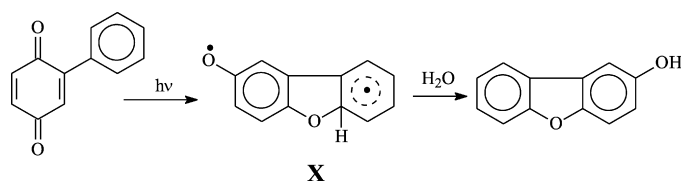


Such photocyclization reaction at the surface of kaolinite was further studied in the absence of oxygen. A 40 μm film of kaolinite with 10 $\mu\text{mol g}^{-1}$ of phenylbenzoquinone was photolysed at 365 nm in deaerated as well as in aerated medium. The phototransformation of PhQ was efficiently inhibited by molecular oxygen. This was also observed by following the formation of 2-HODBF.

The observed first order rate constant was evaluated to $5.5 \times 10^{-3} \text{ min}^{-1}$ and $1.9 \times 10^{-2} \text{ min}^{-1}$ in aerated and in oxygen free media, respectively. Since both experiments were performed within the same conditions, the ratio $k_{\text{vacuum}}^z/k_{\text{air}}^z \approx 3.5$ can be taken as equal to the ratio of quantum yields ($\Phi_{\text{vacuum}}/\Phi_{\text{air}}$). Such value is comparable with those reported in the literature in methanol or acetonitrile solutions (3.8 and 4.2, respectively) [12,13]. These results show that the photocyclization of phenylbenzoquinone at the surface of kaolinite proceeds via the triplet excited state. The involvement of such excited state was confirmed by using diffuse-reflectance laser flash photolysis. For such experiments, a quartz cell filled with phenylbenzoquinone ($\approx 50 \mu\text{mol g}^{-1}$) mixed with kaolinite as powder was used. Owing to the weak signal, the recorded trace was the result of several individual shots (see Section 2). When PhQ at the surface of kaolinite was flash photolysed at 355 nm a transient absorption was recorded after the pulse (Fig. 4). Its maximum is located at 535 nm. It was easily assigned to the triplet-triplet absorption of PhQ by comparison with that already published in the literature [13,14]. Under aerated conditions, the decay followed a first order kinetics with an observed rate constant

of $9.1 \times 10^5 \text{ s}^{-1}$. Due to the low intensity of the signal we were not able to detect any other species after the complete decay of the triplet excited state.

From the results obtained under continuous irradiation at 365 nm, it appears clearly that PhQ undergoes a photocyclization process at the surface of kaolinite as it does in some solvents such as water, acetonitrile, methanol, etc. [12,14]. No evidence for the formation of the phenylsemiquinone radical was obtained. The reaction proceeds through the triplet excited state as clearly demonstrated by laser flash photolysis experiments. In aqueous as well in some organic solutions, it is suggested that the conversion of the triplet state to a triplet biradical species, X, is the key for the photocyclization process [13,14]. Such reaction appeared to be also operating at the surface of kaolinite even though we are in a completely different medium. X may be, with the assistance of small amounts of adsorbed water or even kaolinite, converted to give 2-HODBF.



As clearly shown in this study, the photochemical behaviour of phenylbenzoquinone at the surface of the three different clays was similar to that in pure solvents. This could be owing to the occurrence of a monomolecular process. The situation can be different when reactions such as dimerization, homolytic scission are involved and also when highly polar molecules are involved.

4. Conclusion

The photochemical behaviour of phenylbenzoquinone was deeply studied at the surface of clays. The process efficiently leads to the formation of 2-hydroxydibenzofuran as the only byproduct. The first order rate constant was found to be roughly constant by using kaolinite, bentonite and montmorillonite as solid supports. As it does in solutions, the reaction is efficiently inhibited by molecular oxygen in complete agreement with the involvement of the triplet excited state. Through the presence of water molecule or the clay, the latter species may lead to the formation of a triplet biradical that can be successively protonated and deprotonated giving rise to the formation of the final product.

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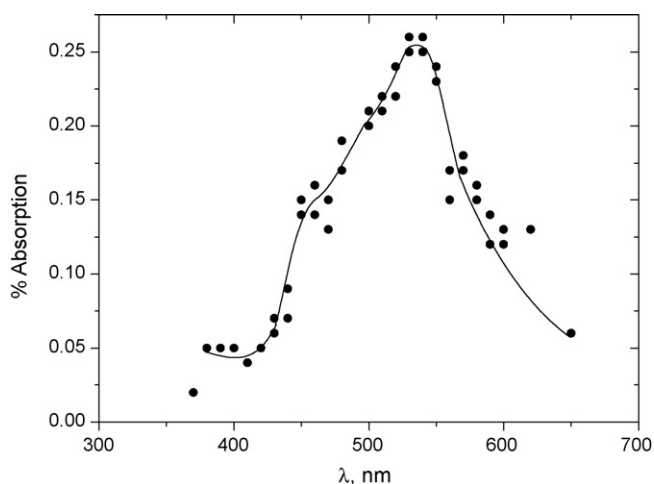


Fig. 4. Transient absorption, after the laser pulse, of phenylbenzoquinone at the surface of kaolinite (powder of kaolinite with 50 $\mu\text{mol g}^{-1}$ of PhQ).

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