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TiO₂-Based Photocatalytic Degradation of 2-Chlorophenol Adsorbed on Hydrophobic Clay

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The combination of adsorption and heterogeneous photocatalysis has been investigated as a promising technology for the removal of organic water pollutants. A laboratory study of the removal and decomposition of 2-chlorophenol (2-CP) as a toxic organic pollutant was carried out under various conditions with an organophilized clay mineral (hexadecylpyridinium chloride-modified montmorillonite; HDPM) as adsorbent and Degussa P25 TiO₂ as photocatalyst. Three different oxidation processes leading to the degradation of 2-CP were compared: direct photolysis, heterogeneous photocatalysis in a TiO₂ suspension, and the decomposition of substrate adsorbed on HDPM in the presence of TiO₂. Both the degradation of 2-CP and the formation of intermediates were analyzed by HPLC, the total organic carbon content and the total organic and inorganic chloride contents were measured to monitor the mineralization process, and X-ray diffraction and thermoanalytical measurements were made to characterize the hydrophobic clay adsorbent. The heterogeneous photocatalytic degradation of dissolved (2-CP/UV/TiO₂) and desorbed 2-CP (2-CP/HDPM/UV/TiO₂) appeared to be equally efficient, whereas direct photolysis of 2-CP was far less efficient in the oxidative destruction. HDPM proved to be a suitable adsorbent, capable of adsorbing toxic organics from water. It was demonstrated that the adsorbent (at relatively high concentration) did not decrease the rate of mineralization of 2-CP. The results confirmed that the adsorbent retains its structure and composition during the mineralization process, and thus it can be reused without regeneration. The combination of adsorption and heterogeneous photocatalysis studied may be an efficient and economical means of accumulating, removing, and oxidizing organic water contaminants, and its application is in accordance with the growing environmental demands.

Introduction

Although most effluent-water is nowadays purified with adequate effectiveness by traditional biological and/or physicochemical methods, the presence in such water of compounds formed by the chlorination of water with high organic matter contents poses an ever increasing problem, particularly as these compounds are often mutagenic or carcinogenic in nature (e.g. chlorinated phenol derivatives). This has led to an expanding demand for efficient and economical water treatment procedures. A group of methods have been developed in the past 20 years and are already widely utilized: the advanced oxidation processes (*1−5*). These new technologies involve the degradation of organic components in water by oxidation based on the generation of very reactive free radicals. One of the most dynamically developing of these new methods is heterogeneous photocatalysis, which has already produced results that are profitably applicable in practice (*6−15*). The experimental evidence that has accumulated to date unambiguously shows that, under suitable conditions, semiconductors (e.g. TiO₂) may be efficiently employed both in the conversion of solar to chemical energy and in the degradation of organic pollutants. To resolve the environmental problems outlined above successfully, it is therefore necessary to develop still further the existing chemical water purification technologies. The new procedures are expected to use relatively simple techniques with low energy consumption and to be effective against a very wide range of organic pollutants. Elimination of pollutants not disposable by straightforward physical removal (e.g. oil residues in seawater, or contaminants in polluted soil) may pose further problems. In such cases, the concomitant or successive application of adsorption (nondestructive) and oxidative (destructive) techniques may be one of the possible solutions (*16−22*). A combination of these procedures allows the extraction of pollutants from water by a suitable adsorbent, their enrichment, removal and efficient and economical degradation.

The suitable adsorbent should efficiently adsorb the pollutants to be removed and/or degraded; not deactivate the photocatalyst to be applied; and be easily removable (e.g. by sedimentation) from the purified water.

Certain hydrophobized clay minerals meet all of these requirements. Clay minerals are soil components capable of binding organic compounds, in consequence of their large specific surface areas and ion-exchange capacities. The adsorption properties of modified clay minerals are conveniently controlled by the length of the carbon chain of the modifier and the extent of surface coverage (*23−25*).

Selective adsorption of various organic compounds from aqueous solutions has been extensively studied; on the basis of these results, the adsorption of organic compounds on clay minerals may be determined (*26−29*). A wide range of organic components are very efficiently adsorbed on clay minerals hydrophobized with cationic surfactants: the organophilic bentonites (*30−33*). The amount of organic molecules bound within the space enclosed by the silicate lamellae, the interlamellar space, may be calculated from the adsorption excess isotherm. Changes in basal spacing, i.e., the distance between the lamellae of the clay mineral, may be monitored by means of X-ray diffraction measurements; thus, the binding of an organic pollutant may be followed by an independent investigation method.

In line with current environmental problems, we chose to study the heterogeneous photocatalytic degradation of organic pollutants represented by the model compound 2-chlorophenol (2-CP), adsorbed on montmorillonite modified with hexadecylpyridinium chloride (HDPM), in TiO₂ semiconductor suspensions irradiated by UV light.

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Experimental Section

Materials. The 2-CP/HDPM system was chosen for the study of the photodegradation of an adsorbed model pollutant. The original montmorillonite sample (Mád, Tokaj Hills, Hungary, cation-exchange capacity (CEC) $= 8.51 \times 10^{-4}$ mol g^{-1}) was organophilized at 338 K by addition of the cationic surfactant hexadecylpyridinium chloride in a 1.5-fold amount relative to the CEC in a suspension of montmorillonite. The ion-exchange period was 48 h. The sample was then washed with a 1:1 propanol—water mixture, dried, and pulverized. The 2-CP was adsorbed onto the resulting HDPM from aqueous solution, after which the suspended clay mineral was centrifuged, dried, and pulverized. The amount of 2-CP adsorbed was calculated by using the previously determined adsorption isotherm of 2-CP. The 2-CP (Fluka Chemica, purum) was used as received. The water was purified with a Milli-Q water ion-exchange system (Millipore Co.) to give a resistivity of 1.8×10^7 Ω cm. Degussa P25 TiO$_2$ was used without further purification.

Methods. Photocatalytical Experiments. In the initial experiments, the photoreactor (100 cm^3) used was an open Pyrex glass tube with double walls, surrounded by a thermostating jacket at 25 ± 0.5 °C, into which 100 cm^3 of the suspension to be studied was poured. The tube reactor was surrounded and irradiated by six medium-pressure Hg-vapor lamps (6 W power, radiation maximum at 365 nm) providing a radiation intensity of $I = 9.1 \pm 0.1 \times 10^{-6}$ einstein dm^{-3} s^{-1}.

In the subsequent experiments, a thermostated reactor (25 ± 0.1 °C) equipped with an immersion-type UV lamp (high-pressure mercury lamp, 150 W) was used. The radiation emitted by the lamp was mainly in the range 240—366 nm (maxima at 254, 265, 302, 313, and 366 nm; rate of photon emission of the lamp 8.33, 3.06, 4.72, 11.39, 19.72 × 10^{-6} einstein s^{-1}, respectively (manufacturer's specification)). In our experiments the surrounding of the lamp with a glass filter allowed a considerable proportion of the high-energy photons (λ < 310 nm) to be filtered out, and conditions resembling natural UV radiation close to the surface of the Earth could be created. Air was bubbled through the stirred suspension (375 cm^3) in the reactor continuously, ensuring a constant dissolved oxygen concentration (2.5×10^{-4} mol dm^{-3}).

Samples were taken from the irradiated suspension at predetermined intervals and were subjected to analysis as described below.

Determination of the Adsorption Excess Isotherm. A saturated solution of 2-CP was made at 20 ± 0.5 °C by the addition of 2-CP to Milli-Q water under continuous mechanical shaking for a suitable saturation time. The adsorption excess isotherm was determined by the immersion method (*34*) in the concentration range $x_{2-CP, \, rel} = 0-1$ ($x_{2-CP,saturation} = 0.2167$ mol dm^{-3} at 20 °C). Adsorbent (0.03—0.3 g) was added to a known volume (9 cm^3) of 2-CP solution, which was then allowed to stand for 48 h at 20 ± 0.1 °C until adsorption equilibrium had been established. The clay mineral suspension was next centrifuged, and the concentration of the supernatant was determined by using a Zeiss liquid interferometer.

Analysis. The concentrations of 2-CP and its degradation products were measured by means of HPLC, with a Merck-Hitachi L-4250 UV detector and an L-7100 pump. Aromatic components were separated on a LiChrospher 100 RP-18 column with methanol/water (28:72) as eluent; their absorbance was measured at 210 nm. Aliphatic intermediates (mainly carboxylic acids) were quantitated after elution on a Grom Resin ZH ion-exchange column with sulfuric acid as eluent, at 206 nm. All compounds were identified and quantitated by chromatographing standard samples of known concentrations and determining retention times and peak sizes.
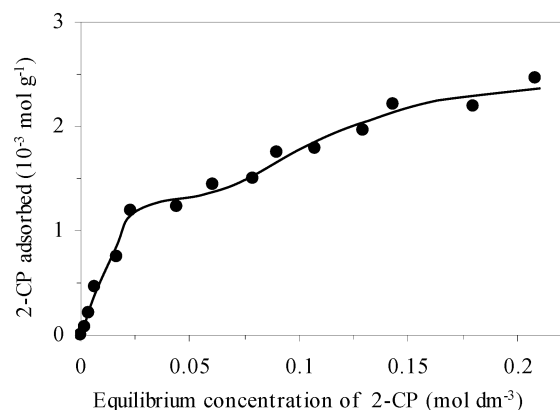

FIGURE 1. Adsorption excess isotherm of 2-CP from water on HDPM at 20 °C.

The degradation process could also be followed by measuring the total organic carbon (TOC) content in the suspension. The measurement was carried out in a Euroglas TOC 1200 apparatus (Delft, The Netherlands). The TOCs of suspensions were determined directly by injecting samples of 100 μL; for solid materials, samples of 3—10 mg were combusted at 1000 °C in an oxygen—argon mixture and the produced CO$_2$ was analyzed. Standard solutions of potassium hydrogenphthalate were used for calibration.

The Euroglas TOC 1200 apparatus is equipped with an optional unit for the determination of adsorbable organohalide (AOX) content, based on the conversion of the halogens in organic compounds into halides by combustion. The halides formed are led through a scrubber into a titration cell, for a coulometric titration with silver ion. Thus, the chloride and chlorine contents could be determined both in the suspensions studied and in their separate liquid and solid phases. For measurement of the concentration of chloride ion, 100 μL samples of the clear solution (supernatant) were injected directly into the microcoulometric cell. The total chlorine contents of solid samples were measured after the combustion of 10 mg samples at 1000 °C.

The XRD experiments were carried out in a Philips X-ray diffractometer (PW 1930 generator, PW 1820 goniometer) with CuK-α radiation (λ = 0.15418 nm) at 2Θ = 1—15°. To prevent evaporation of the investigated wet samples, the hydrophobic clay suspensions were coated with a thin Mylar foil. The basal spacing (d_L) was calculated from the (001) reflection via the Bragg equation.

The HDPM adsorbent polluted with 2-CP and the adsorbent-catalyst air-dry powder samples recovered from the irradiated suspension were studied by thermal analysis with a MOM Q-1500 D Derivatograph. The measurements were made under air, in the temperature range 25—1000 °C, at a heating rate of 5 °C min^{-1}.

Results and Discussion

Adsorption of 2-CP on HDPM. The adsorption of an organic component from aqueous solutions onto a clay mineral is influenced significantly by the surface polarity of the adsorbent. Since water is preferentially adsorbed on hydrophilic Na- and Ca-montmorillonites (*33*), the surface of the clay mineral has to be hydrophobized. 2-CP molecules are positively adsorbed on HDPM in the full composition range, i.e., the surface of the adsorbent and the interlamellar space of the clay mineral are enriched in aromatic molecules. The adsorption excess isotherm of the 2-CP/water system on HDPM at 20 °C is presented in Figure 1. The specific adsorption excess of 2-CP is plotted as a function of the equilibrium concentration.
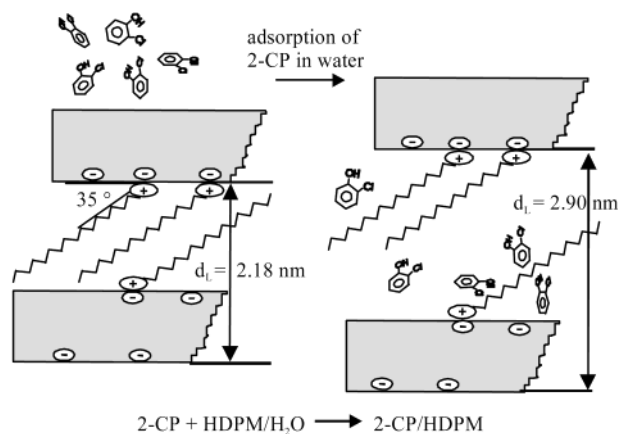
FIGURE 2. Preparation of 2-CP/HDPM organocomplex by adsorption of 2-CP in water.
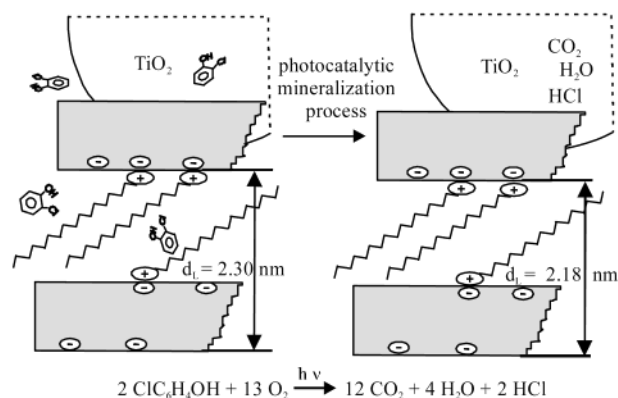

FIGURE 3. Desorption of 2-CP in 2-CP/HDPM/TiO$_2$ aqueous suspension and complete mineralization of 2-CP by heterogeneous photocatalysis.

It can be seen from the isotherm that approximately $2.0-2.5 \times 10^{-3}$ mol g^{-1} of 2-CP is adsorbed by HDPM in the concentration range $0.15-0.2$ mol dm^{-3}. On the basis of the adsorption isotherm, a concentration range was chosen in which the equilibrium concentration of 2-CP in water is relatively low ($\sim$0.02 mol dm^{-3}), and the amount of 2-CP adsorbed falls within the early saturation region of the isotherm. After adsorption, the interlamellar space of hydrophobic HDPM is enriched in the pollutant to be degraded (Figure 2). The polluted adsorbent is then mixed with TiO$_2$, and the mixture is dispersed in water to produce a composite suspension (Figure 3). Finally, the desorbing component is photocatalytically oxidized by irradiating the suspension with UV light.

These results confirm that HDPM is suitable for the accumulation by preferential adsorption of 2-CP from water.

Photocatalytic Degradation of 2-CP. Low-Intensity Irradiation ($\lambda_{irr} = 365$ nm). One of the most important goals of applying heterogeneous photocatalysis can be the possibility of utilizing solar energy for the destruction of organic pollutants. Applying near UV irradiation with relatively low intensity, we wanted to collect data of the degradation under conditions resembling natural UV radiation. In the first phase of the experiments, the "mild" degradation of 2-CP was studied: the suspension was irradiated with low-intensity light ($I = (9.1 \pm 0.1) \times 10^{-6}$ einstein dm^{-3} s^{-1}) for 18 h. The suspension contained 5.0 g of 2-CP/HDPM (the adsorbent contained 9.65×10^{-4} mol 2-CP g^{-1}) and 1.0 g of TiO$_2$ per liter. Samples were withdrawn from the irradiated reaction mixture at different time intervals and analyzed. The results of HPLC measurements revealed that nearly half of the adsorbed 2-CP is desorbed into the aqueous phase almost
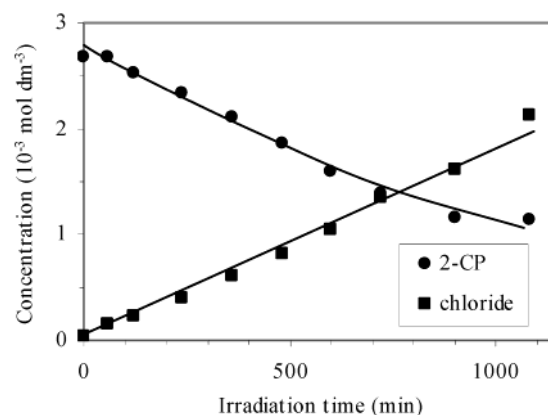
FIGURE 4. Kinetics of disappearance of 2-CP and resulting formation of chloride ions ($\lambda_{irr} = 365$ nm).

TABLE 1. Basal Distances of Different HDPM Systems, Determined from the X-ray Diffraction Patterns of Wet Paste and Air-Dry Powder Samples

sample	d_L (nm)
HDPM, air-dry powder	1.75 ± 0.01
HDPM, wet paste	2.18 ± 0.01
2-CP/HDPM organocomplex, air-dry powder	2.55 ± 0.01
2-CP/HDPM organocomplex + TiO$_2$ suspended in water, original state (nonirradiated)	2.90 ± 0.01
2-CP/HDPM organocomplex + TiO$_2$ suspended in water, after an 18-h irradiation	2.30 ± 0.01

instantaneously. As illustrated in Figure 4, the decrease in the equilibrium concentration of 2-CP ($\Delta c_{2-CP} = 1.53 \times 10^{-3}$ mol dm^{-3}) is significantly lower than the increase in the concentration of chloride ion ($\Delta c_{Cl^-} = 2.13 \times 10^{-3}$ mol dm^{-3}). This clearly shows that 2-CP undergoes continuous desorption from the adsorbent. (At the first stage of the degradation of 2-chlorophenol the rate of formation of chloride ions in the solution phase is only slightly higher than the apparent rate of degradation of dissolved 2-chlorophenol. The presence of intermediates containing chlorine results in lower difference between the rate of disappearance of 2-chlorophenol and the rate of formation of chloride ions. After longer irradiation time the degradation of these intermediates becomes significant, the rate of formation of chloride ions will be higher, and the difference becomes marked.)

The HPLC analysis demonstrated that aromatic intermediates such as chlorohydroquinone ($c_{max} \approx 4 \times 10^{-4}$ mol dm^{-3}), catechol ($c_{max} \approx 5 \times 10^{-5}$ mol dm^{-3}), and traces of hydroquinone ($c_{max} < 10^{-5}$ mol dm^{-3}) appear in the liquid phase in the initial phase of conversion. After longer irradiation times, aliphatic carboxylic acids also appear in the solution; acetic acid and formic acid could be identified (concentration range $1-3 \times 10^{-4}$ mol dm^{-3}). In addition, the presence of oxygen-containing aliphatic degradation products was shown by liquid chromatographic analysis. The TOC content remained practically unchanged during the 18-h irradiation. This means that complete degradation to CO$_2$ did not take place under the given conditions.

The changes in the basal spacing (d_L, see Figures 2 and 3) of HDPM in different states were followed by X-ray diffraction measurements at different stages of the experiments. The data in Table 1 demonstrate that the basal spacing of the HDPM increases upon the adsorption of 2-CP. The interlamellar distance of the adsorbent containing 2-CP suspended in water is further increased as water molecules stream into the interlamellar space and a new equilibrium is established (34). After an 18-h irradiation, the basal spacing is significantly decreased, indicating that a considerable
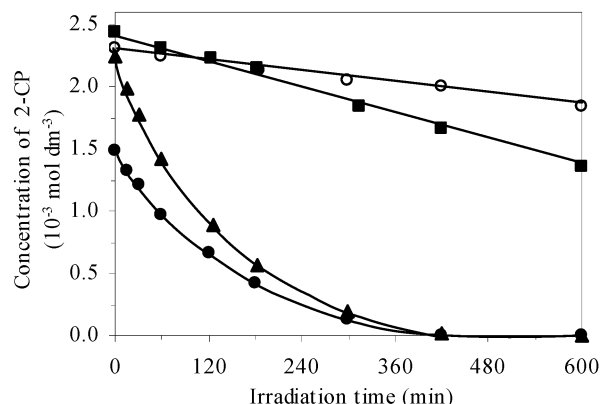
FIGURE 5. Kinetics of 2-CP removal under different experimental conditions ($\lambda_{irr} = 310-370$ nm): in air-purged 2-CP solution without UV-irradiation (○), with irradiation (■: 2-CP/UV), in a suspension of TiO$_2$ (▲: 2-CP/UV/TiO$_2$, 1.0 g dm^{-3}) and in a complex suspension (●: 2-CP/HDPM/UV/TiO$_2$, 1.0 g dm^{-3} TiO$_2$ and 5.0 g dm^{-3} organocomplex).

FIGURE 6. Changes in TOC content during photodegradation of 2-CP in the suspension containing TiO$_2$ (▲: 2-CP/UV/TiO$_2$, 1.0 g dm^{-3}) or TiO$_2$ and the organocomplex (●: 2-CP/HDPM/UV/TiO$_2$, 1.0 g dm^{-3} TiO$_2$ and 5.0 g dm^{-3} organocomplex) under UV irradiation ($\lambda_{irr} = 310-370$ nm). The disappearance of the carbon content of the UV-irradiated 2-CP solution is also registered in the Figure (■: 2-CP/UV, $c_{0,2-CP} = 2.5 \times 10^{-3}$ mol dm^{-3}).

proportion of the 2-CP is desorbed from the interlamellar space into the solution.

High-Intensity Irradiation: Complete Mineralization of 2-CP. In the subsequent kinetic experiments, we aimed at complete degradation of the pollutants (probably to CO$_2$, H$_2$O, and HCl). To achieve this, the light intensity was increased considerably (high-pressure mercury vapor lamp) and a different experimental setup was used.

We first studied the direct photolysis of 2-CP solution (2-CP/UV), then the conversion of 2-CP in irradiated suspensions containing TiO$_2$ (2-CP/UV/TiO$_2$), and finally the degradation of 2-CP adsorbed on HDPM in irradiated suspensions containing TiO$_2$ (2-CP/HDPM/UV/TiO$_2$). The mixture of 2-CP/HDPM and TiO$_2$ powder was suspended in Milli-Q water to yield a suspension containing 5.0 g dm^{-3} with respect to 2-CP/HDPM and 1.0 g dm^{-3} with respect to TiO$_2$. The 2-CP content of the organocomplex in these experiments was 5.33×10^{-4} mol g^{-1}. The preparation of a homogeneous suspension in systems containing HDPM was promoted by sonication for ca. 30 min. After addition of the suspension into the reactor, a constant dissolved oxygen concentration (2.5×10^{-4} mol dm^{-3}) was maintained by continuous purging with air. (The effect of purging air through a 2-CP solution was checked in a control experiment, discussed below.) In the experiments with the 2-CP/HDPM/UV/TiO$_2$ system, the initial equilibrium concentration of 2-CP dissolved in the liquid phase was about 1.5×10^{-3} mol dm^{-3}. The total concentration of 2-CP in the system was about 2.6 $\times 10^{-3}$ mol dm^{-3}, and therefore an initial 2-CP concentration of 2.5×10^{-3} mol dm^{-3} was chosen for the experiments on systems containing no adsorbent. The measurements depicted in Figure 5 indicate that after 10 h of purging with air about 18% of the 2-CP dissolved in water is removed from the solution. In aerated 2-CP solutions, only irradiated with near-UV light, photochemical reactions likewise take place. The concerted action of purging and irradiation decreased the amount of 2-CP in the solution by ca. 45% after 10 h. When TiO$_2$ was also present in the irradiated suspension, the 2-CP concentration was reduced to the same extent (by 45%) within 1 h, and after a 7-h irradiation practically all the 2-CP in the solution was converted. When the same amount of 2-CP (corresponding to a concentration of 2.5×10^{-3} mol dm^{-3}) adsorbed by the HDPM was added to the TiO$_2$-containing suspension, the 2-CP was converted during the same length of irradiation time (about 7 h), even though its concentration in the water was lower.

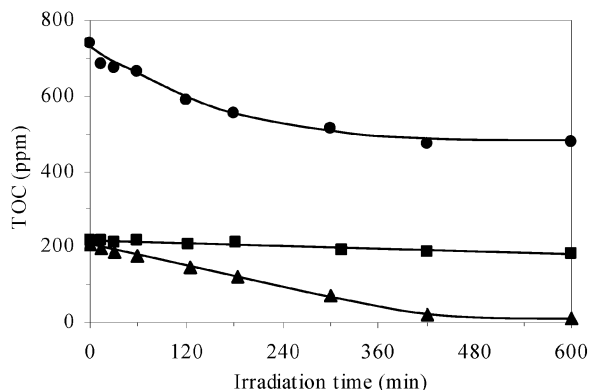Comparison of the experiments on 2-CP/HDPM/UV/TiO$_2$ and 2-CP/UV/TiO$_2$ reveal how insignificant the shielding effect of montmorillonite present as a highly concentrated suspension really is. It may be assumed that the establishment of dynamic desorption equilibrium is rapidly followed by the conversion of 2-CP in water, so that the rate-limiting step is probably the oxidation of 2-CP.

The aromatic intermediates observed in these experiments were chlorohydroquinone, pyrocatechol, and hydroquinone, as in the case of low-intensity irradiation described above. As regards these aromatic intermediates, significantly less chlorohydroquinone ($c_{max} \approx 3.5 \times 10^{-5}$ mol dm^{-3}) and slightly more pyrocatechol ($c_{max} \approx 4 \times 10^{-5}$ mol dm^{-3}) were formed than in the system containing the photocatalyst. In the experiment on 2-CP/UV/TiO$_2$, the change in composition was observable visually in the samples withdrawn, as the stability of the suspension was reduced by surface adsorption of the reaction products. Samples exposed to long irradiation, and containing low concentrations of intermediates, were slowly sedimenting suspensions, whereas after total degradation of the intermediates the TiO$_2$ suspension regained its original hydrophilicity.

The results of TOC measurements are summarized in Figure 6. Even though 2-CP is continuously converted in the UV irradiated solution lacking the catalyst, there is little decrease in TOC (altogether ca. 18% after 10 h), its extent being practically identical with the decrease in chlorophenol concentration caused by aeration, i.e., in this case the conversion does not lead to complete mineralization, even after relatively long irradiation times.

The TOC content is reduced continuously and more markedly during the photocatalytic decomposition of 2-CP. Comparison of the decrease in 2-CP (shown in Figure 5) with the change in TOC content reveals that the TOC is reduced at a lower rate than is the 2-CP concentration, in accordance with the observed appearance of intermediates. All the product formation and decomposition profiles (for both the aromatic and aliphatic compounds) exhibited quite similar trends either in the presence or in the absence of HDPM (chlorohydroquinone ($c_{max} \approx 2 \times 10^{-4}$ mol dm^{-3}), hydroquinone ($c_{max} \approx 7 \times 10^{-5}$ mol dm^{-3}), pyrocatechol ($c_{max} \approx 3 \times 10^{-5}$ mol dm^{-3}), and aliphatic compounds).

Comparison of the results of TOC content analysis with those of HPLC measurements in the 2-CP/HDPM/UV/TiO$_2$ system reveals that the TOC content decreases simultaneously with the disappearance of 2-CP and its degradation products, after ca. 7 h of irradiation. It should be stressed that the carbon content remains unchanged from this time on, i.e., it may be assumed that the HDP cation modifying
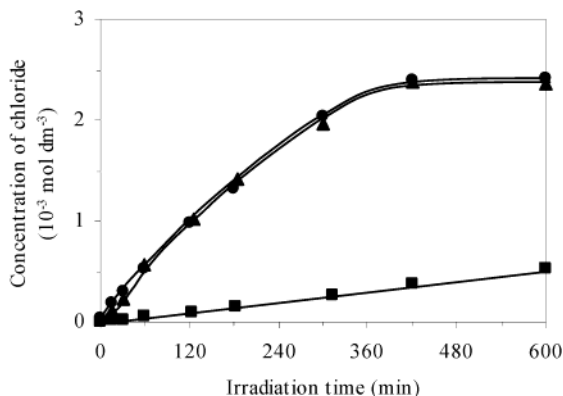
FIGURE 7. Changes in chloride concentration in UV-irradiated 2-CP solution (■: 2-CP/UV, $c_{0,2-CP} = 2.5 \times 10^{-3}$ mol dm^{-3}), and in the irradiated suspension containing TiO$_2$ (▲: 2-CP/UV/TiO$_2$, 1.0 g dm^{-3}) or TiO$_2$ and the organocomplex (●: 2-CP/HDPM/UV/TiO$_2$, 1.0 g dm^{-3} TiO$_2$ and 5.0 g dm^{-3} organocomplex) under UV irradiation (λ_{irr} = 310−370 nm).

FIGURE 8. Changes in H$^+$ concentration in UV-irradiated 2-CP solution (■: 2-CP/UV, $c_{0,2-CP} = 2.5 \times 10^{-3}$ mol dm^{-3}), and in the irradiated suspension containing TiO$_2$ (▲: 2-CP/UV/TiO$_2$, 1.0 g dm^{-3}) or TiO$_2$ and the organocomplex (●: 2-CP/HDPM/UV/TiO$_2$, 1.0 g dm^{-3} TiO$_2$ and 5.0 g dm^{-3} organocomplex) under UV irradiation (λ_{irr} = 310−370 nm).

FIGURE 9. Thermogravimetric curves of different powder samples containing HDPM: the organocomplex with 2-CP mixed with TiO$_2$ powder mixture before (2-CP/HDPM+TiO$_2$ (5:1)) and after UV irradiation (2-CP/HDPM/UV/TiO$_2$/600 min), the powder mixture without 2-CP (HDPM + TiO$_2$ (5:1)) and the original HDPM powder sample.

the adsorbent is not broken down within the time period of the study. To decide whether HDP is detached from the adsorbent in the course of the conversion (e.g. whether the HDP cations on the montmorillonite are exchanged for hydrogen ions in the acidifying medium), in the case of 2-CP/HDPM/UV/TiO$_2$ the carbon content was also measured in the supernatant. After the mineralization of 2-CP and its degradation products is completed, the only carbon-containing molecules in the system are HDP cations bound to or desorbed from the adsorbent. After about 7 h of irradiation, the carbon content of the suspension does not decrease any further, indicating that HDP cations are not oxidized. At the same time, the carbon content of the solution (supernatant) is altogether 5−10 ppm. These data suggest that sonication results in the desorption of a small amount of HDP, but there is no question of considerable amounts of the cation getting into the solution.

The end-products of the photooxidation of 2-CP are mainly CO$_2$, H$_2$O, and HCl. Accordingly, the chloride ion concentration of the suspension increases continuously, as shown in Figure 7.

In the experiments on 2-CP/UV/TiO$_2$ and 2-CP/HDPM/ UV/TiO$_2$ the rates of accumulation of chloride ions are practically the same; the accumulation of chloride ions is much slower during the direct photolysis of 2-CP. The pH of the liquid phase decreases during the photolytic and photocatalytic conversion of 2-CP, as shown in Figure 8. The hydrogen and chloride ion concentrations in the solution increase in a nearly identical fashion. Slight differences are observed only in the systems containing suspended material, and these are accounted for by the adsorption of hydrogen ions by montmorillonite.

It is important to emphasize that the intermediates formed in the course of the reaction are rapidly converted further until mineralization is complete. The end-products of degradation are probably environmentally harmless inorganic compounds (CO$_2$, H$_2$O, and HCl). It is noteworthy that the presence of a relatively high concentration of adsorbent in the course of the heterogeneous photocatalytic degradation of 2-CP does not reduce the efficiency of mineralization. The concentrations of both 2-CP and the products formed from it and also the TOC content change similarly in time both in the presence and in the absence of the adsorbent.

Analysis of the Adsorbent after Photochemical Conversions. To compare the initial adsorbent with that exposed to UV light, the sediment (TiO$_2$ + HDPM) was separated from the liquid phase by centrifugation and dried at room temperature. The air-dry powder obtained was subjected to
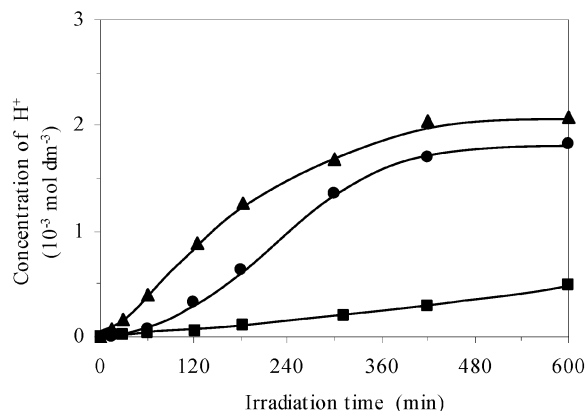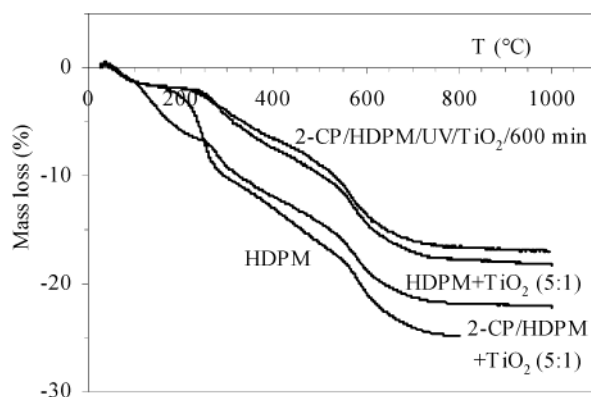
thermoanalytical and X-ray diffraction measurements, and its chlorine content was determined by combustion. Thermogravimetric curves are presented in Figure 9.

The curve obtained for the sample containing HDPM + TiO$_2$ (5:1 (w/w) powder mixture) demonstrates that up to 200 °C the mass of the organophilic clay hardly decreases at all (there is little adsorbed water, Δm_{25-150} = 1.7%), whereas a very significant change in mass occurs between 200 and 750 °C ($\Delta m_{200-750}$ = 15.7%). It is within this temperature range that the total amount of HDP cation is burnt off. The decrease in mass associated with the dehydroxylation of montmorillonite (an endothermic process between 550 and 650 °C) also falls within this range and results in a loss in mass of a few percent (typically 3−4% for Na-montmorillonite) (35, 36). Thus, the bulk of the change in mass observed is due to the burning-off of organophilizing cations (corresponding to a cation exchange of ca. 6.0×10^{-4} mol HDP$^+$ g^{-1} hydrophilic Na-montmorillonite). The TG curve of the sample from the experiment on 2-CP/HDPM/TiO$_2$ (5:1 (w/w) powder mixture) displays a marked stepwise decrease in mass in the range 100−225 °C ($\Delta m_{100-225} \approx 5\%$), characteristic of the thermal desorption of adsorbed 2-CP (5.0 $\times$ 10^{-4} mol 2-CP g^{-1} organocomplex = 6−7% 2-CP content). The TG curve obtained for the air-dry adsorbent recovered after an UV irradiation of 600 min deviates only slightly from that for the original adsorbent (the loss in mass was 6.8%
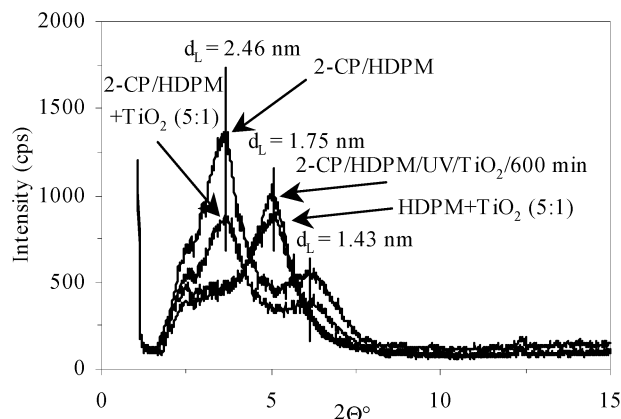
FIGURE 10. X-ray diffraction patterns of air-dry powder samples containing HDPM: the organocomplex with 2-CP mixed with TiO₂ powder mixture before (2-CP/HDPM+TiO₂ (5:1)) and after UV irradiation (2-CP/HDPM/UV/TiO₂/600 min), the powder mixture without 2-CP (HDPM + TiO₂ (5:1)) and the original 2-CP/HDPM powder sample.

TABLE 2. Total Chlorine Contents in Basic Materials and Photocatalytically Treated Powder Samples ($\lambda_{irr} = 310-370$ nm)

sample	total chlorine content (10^{-6} mol g^{-1})
TiO₂	30 ± 1
HDPM	24 ± 1
HDPM/TiO₂	25 ± 1
2-CP/HDPM	556 ± 5
2-CP/HDPM/TiO₂/UV (600 min irradiation)	32 ± 1

less). (The thermogravimetric curve labeled HDPM depicts the changes in mass characteristic of the original industrial product, prior to extraction purification, corresponding to a cation exchange of about 8.3×10^{-4} mol HDP$^+$ g^{-1} hydrophilic Na-montmorillonite.)

X-ray diffractograms of the air-dry samples are presented in Figure 10.

The reflection at around 5° (2Θ) ($d_L = 1.75$ nm), characteristic of the original HDPM, is shifted toward smaller angles after the adsorption of 2-CP, indicating that the lamellae of the organophilic clay mineral are swollen by 2-CP molecules ($d_L = 2.46$ nm). Another reflection is also apparent in the diffractogram of the 2-CP/HDPM sample, which is probably due to hydrophilic surfaces preserved in the Na$^+$ state bending together ($d_L = 1.43$ nm). The X-ray diffractogram of the adsorbent recovered after an irradiation of 600 min hardly differs from that of the original HDPM.

The total chlorine contents of the solid samples were determined by combustion. As shown in Table 2, the chlorine contents of the samples were very low (except for that of the 2-CP/HDPM sample).

The chlorine content in the 2-CP/HDPM sample (before the photocatalytic treatment) was practically equivalent with the amount of Cl$^-$ formed in the suspension after irradiation for 600 min. The photocatalytic treatment decreased the chlorine content to the level of the original adsorbent.

To demonstrate that during the oxidation run no modifications occur to the sorbent, the sediment was added again to a 2-chlorophenol solution. Applying identical conditions, after adsorption equilibrium had been established, the 2-chlorophenol decrease in the solution phase was determined. We found that within the experimental error (10%) the amount of adsorbed 2-chlorophenol was the same as before the treatment. This fact indicates that the adsorbent practically retained its adsorption capacity.

The simultaneous application of heterogeneous photocatalysis and adsorption methods offers a promising alternative in water purification. The combination of these procedures allows the enrichment, removal and effective and economical degradation of pollutants, in compliance with the increasingly strict environmental requirements. Our results verify that the modifier HDP cation is not detached from the surface of the clay mineral in the course of the heterogeneous photocatalytic degradation of 2-CP, and the recovered adsorbent may be reused practically without regeneration (37).

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