# Immobilization of Palladium Phthalocyaninesulfonate onto Anionic Clay for Sorption and Oxidation of 2,4,6-Trichlorophenol under Visible Light Irradiation

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Layered double hydroxide (LDH) and dodecyl sulfonate-intercalated layered double hydroxide (SDS-LDH) with an Mg/Al ratio of 3.0 were studied as a support of anionic photosensitizer, palladium phthalocyaninesulfonate (PdPcS). The composite clays were synthesized by two different routes: (i) PdPcS intercalation into the clay galleries via direct coprecipitation and (ii) PdPcS adsorption on the clay external surface via ion exchange. Under visible light irradiation ($\lambda > 450$ nm), all the PdPcS-containing solids were effective for the sensitized oxidation of 2,4,6-trichlorophenol (TCP) in an aerated aqueous solution. But the reaction efficiency was notably different from one catalyst to another, because of different location and arrangement of the immobilized PdPcS. Among the samples studied, the highest activity was observed with the immobilized PdPcS in the SDS-LDH interlayers, where the sorbed TCP is located via partition mechanism. It was further observed that the reaction rate increased with the initial amount of TCP adsorption and with the amount of PdPcS (0.4−2.2 wt %) present in the clay. Recycling experiments demonstrated that the composite clay was relatively stable and could be repeatedly used for TCP removal only with visible light and molecular oxygen.

## Introduction

Layered double hydroxide (LDH), also known as anionic clay, constitutes a class of host−guest materials that have gained great attention recently.[1−9] Through the incorporation of an anionic guest species into the layered host, a novel material can be produced with desirable physical and chemical properties.[3,10] For example, the anionic clays intercalated with hydrophobic surfactant such as dodecyl sulfate are good sorbents for removal of nonpolar organic pollutants from water.[5−7] The intercalated LDH with metalloporphyrins and metallophthalocyanines exhibits enhanced stability and catalytic activity for organic oxidation by $O_2$ or $H_2O_2$.[1,11−14]

A typical formula of a LDH is $[M_{1-x}^{2+}M_x^{3+}(OH)_2]$-$A_{x/n}^{n-}\cdot zH_2O$, where $M^{2+}$ and $M^{3+}$ are divalent and trivalent metal cations, $x$ is equal to the ratio $M^{3+}/(M^{3+} + M^{2+})$, and $A^{n-}$ is the interlayer anion with charge $n-$. The octahedrally coordinated units, $M(OH)_6^{4-}$, share edges to form infinite two-dimensional sheets, and the sheets stack together via hydrogen bonding between the hydroxyl groups of adjacent layers, where the charge-balancing anions and water molecules are located. Clearly, the anion-exchange capacity is determined by $M^{2+}/M^{3+}$ ratio present in the phase-pure LDH. The guest anions can be introduced into the LDH interlayers through ion exchange, direct coprecipitation, thermal reaction, and reconstruction of a calcined LDH precursor.[1−4] Depending on the synthesis conditions and the guest size, the intercalated anions may take a parallel, perpendicular, or tilted orientation to the hydroxide sheets. All these features make it possible to construct the composite materials with tunable and novel properties.

Metal phthalocyanines (MPc) are a class of macrocyclic complexes that have been widely studied as the photosensitizer for singlet oxygen generation.[15−19] Singlet oxygen is approximately 1 V more oxidizing than ground (triplet) oxygen, and thus it can react rapidly with many unsaturated and electron-rich compounds. For example, chlorophenol, a

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representative of toxic and recalcitrant pollutants, can be completely degraded into carbon dioxide and chloride in an aerated aqueous solution of metal phthalocyaninesulfonate (MPcS) under visible light irradiation.[16−18] In comparison with other advanced oxidation methods, such as $TiO_2$ photocatalysis[20] and photo-Fenton reactions,[21] the photosensitization system can collect up 50% of the solar spectrum and only utilize zero-cost molecular oxygen as an oxidant for pollutant degradation. However, the system efficiency is greatly limited by the dye aggregation, due to enhanced self-quenching of the excited complex. In this regard, incorporation of MPcS species into a restricted space like LDH[14,22] may be a good idea to retard the dye aggregation and, consequently, accelerate the photosensitized reaction. To the best of our knowledge, not much work on this subject has been published in the literature.

In this work, we have investigated $Mg_3Al$-LDH as a support of PdPcS, which is the best photosensitizer known in the MPc family.[18] The composite materials were synthesized with two different routes: the intercalation of PdPcS into LDH interlayers via direct coprecipiation and the adsorption of PdPcS onto the LDH external surface via so-called ion exchange. Moreover, the LDH pillared with anionic dodecyl sulfonate (SDS-LDH) was also examined as a support for improvement of PdPcS dispersion and organic pollutant adsorption. The physical states of the immobilized PdPcS were characterized by X-ray diffraction (XRD) and diffuse reflectance spectroscopy. The material's photoactivity was evaluated by the photosensitized oxidation of 2,4,6-trichlorophenol (TCP) in water under visible light irradiation ($\lambda > 450$ nm). The results showed that the immobilized PdPcS was well dispersed onto the clay precursor, with an obviously increased portion of monomer to the aggregate. All the composites were effective to initiate the photosensitized degradation of TCP. However, the efficiency varied notably from one catalyst to another, due to different location and aggregation degree of the immobilized PdPcS. Among the catalysts studied, the intercalated PdPcS in the interlayers of SDS-LDH displayed the highest activity. Eight consecutive experiments demonstrated that this catalyst could be repeatedly used, without significant loss both in the adsorption capacity and in the photosensitization activity for removal of toxic TCP.

## Experimental Section

**Materials.** Palladium(II) phthalocyanine sulfonate (PdPcS) was synthesized as previously described.[23] Magnesium chloride, aluminum chloride, TCP, and dodecyl sulfonic acid in sodium form (SDS, $C_{12}H_{25}NaO_3S$) were purchased from Shanghai Chemicals and used directly without further purification. Deionized and doubly distilled water was used throughout this study. The solution pH was adjusted by concentrated NaOH solution.

**Synthesis of LDH and SDS-LDH.** The blank supports were both prepared at an Mg/Al molar ratio of 3.0 through a direct coprecipitation method.[4,7] Three separate solutions were first prepared with carbonate-free water. Solution A was a mixed solution of 1.5 M $MgCl_2$ and 0.5 M $AlCl_3$. Solution B was 4.0 M NaOH. Solution C was water at pH 10.5. Then, 50 mL of solution A and 50 mL of solution B were simultaneously and slowly added dropwise into 150 mL of solution C, under a nitrogen atmosphere in a three-neck round-bottom flask. The suspension was further stirred for 24 h at 90 °C under nitrogen. After separation, the white precipitate was washed extensively with water and dried at 65 °C overnight. The resulting product was denoted as LDH. The support SDS-LDH was prepared with similar procedures, except that solution C was 0.17 M SDS dissolved previously in water at pH 10.5.

**Synthesis of Immobilized PdPcS.** Two types of the catalysts were prepared. The first was the intercalation of PdPcS into the interlayers of LDH or SDS-LDH, via in situ coprecipitation method as described by Carrado and co-workers.[14] The synthesis route was essentially the same as that used above for blank support synthesis, but in solution C was also dissolved a certain amount of PdPcS. The resultant products were denoted as LDH-($x$ PdPcS)$_{\text{int}}$ or SDS-LDH-($x$ PdPcS)$_{\text{int}}$, where $x$ was the weight percentage of PdPcS. The second was the adsorption of PdPcS on the external surface of LDH or SDS-LDH, via an ex situ ion exchange method.[14] First, 1.00 g of LDH or LDH-SDS was dispersed and sonicated in water (25 mL). Then, 25 mL of PdPcS solution was added dropwise, and the blue mixture was stirred for 24 h. After filtration, the blue product was repeatedly washed with water and dried at 60 °C overnight. The final samples were denoted as LDH-($x$ PdPcS)$_{\text{ads}}$ or SDS-LDH-($x$ PdPcS)$_{\text{ads}}$, where $x$ was the weight percentage of PdPcS.

Note that after the synthesis, no PdPcS was left in the filtrate, as detected by absorption spectroscopy. Also no PdPcS was leached off from the solid into water, even through vigorous stirring overnight. This indicated that all the added PdPcS was completely loaded onto the clay, and the loaded PdPcS was firmly immobilized on the support.

**Instrumentation.** The powder XRD patterns were recorded on a D/max-2550/PC diffractometer (Rigaku), operated at 40 kV and 300 mA. The visible diffuse reflectance spectrum was recorded on an Agilent 8453, equipped with an attachment of Labsphere RSA-HP-53. The organic concentration was analyzed on a Dionex P680 HPLC, equipped with an Apollo C18 reverse column. The eluent was $CH_3OH-H_2O$ (8:2, v/v), acidified previously with 0.1% acetic acid, and the flow rate was set at 1 mL/min.

**Sorption Isotherms.** The sorption isotherms of TCP on catalyst in water were carried out using the batch slurry method.[24] The slurry containing 50 mg of catalyst and 50 mL of TCP solution at various concentrations was stirred overnight for achievement of adsorption equilibrium. After the suspension was filtered through a membrane (0.45 $\mu$m), the concentration of TCP in the filtrate was determined by a standard HPLC method. The amount of TCP sorption, $q_e$, was calculated by the equation, $q_e = (C_0 - C_e)V/m$, where $C_0$ and $C_e$ were the initial and equilibrium concentrations of TCP in solution, $V$ was the suspension volume (50 mL), and $m$ was the amount of catalyst (50 mg).

**Photoreactions**. The photosensitized oxidation of TCP was carried out in an open thermostated vessel. First, the suspension containing 50 mg of catalyst and 50 mL of TCP solution was stirred in the dark overnight. Then the slurry was irradiated with a Halogen lamp (500 W) through a glass filter ($\lambda \geq 450$ nm). At a given time interval, small aliquots were withdrawn by syringe, filtered through a membrane (0.45 $\mu$m), and analyzed by HPLC. The kinetic data

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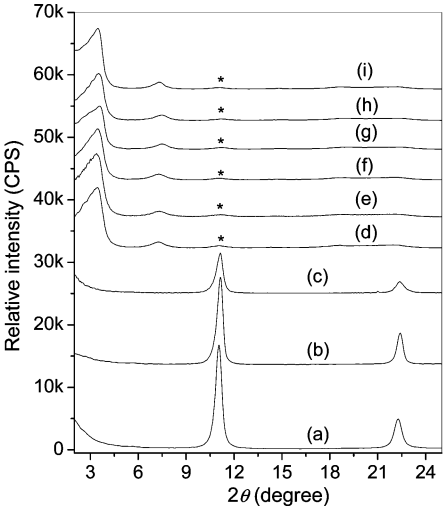

**Figure 1.** XRD patterns of (a) LDH, (b) LDH-(0.8 PdPcS)$_{ads}$, (c) LDH-(0.8 PdPcS)$_{int}$, (d) SDS-LDH, (e) SDS-LDH-(0.8 PdPcS)$_{ads}$, (f) SDS-LDH-(0.4 PdPcS)$_{int}$, (g) SDS-LDH-(0.8 PdPcS)$_{int}$, (h) SDS-LDH-(1.5 PdPcS)$_{int}$, and (i) SDS-LDH-(2.2 PdPcS)$_{int}$. The asterisks represent the LDH phase present in the sample.

was well fitted into the pseudo-first-order rate equation, $\ln(C/C_e) = -k_{obs}t$, where $C$ and $C_e$ are the concentration of TCP in bulk solution at irradiation times $t = 0$ and $t = t$, respectively, and $k_{obs}$ is the apparent rate constant.

Recycle experiments were performed for assessment of catalyst stability. The suspension containing 50 mg of catalyst and 50 mL of TCP (0.11 mM) was first stirred in the dark for 1 h, then irradiated, and analyzed as described above. When TCP in the solution phase almost completely disappeared, the irradiation stopped. Then, 4.00 mL of TCP stock solution (1.35 mM) was added into the irradiated suspension, so as to restore the initial concentration of TCP at about 0.11 mM. The new suspension was stirred again for 1 h in the dark, followed by light irradiation and HPLC analysis. Such procedure was repeated from one run to another, and the total number of runs was eight as a result of the limit in time and in the catalyst concentration. Note that the adsorption equilibrium of TCP over the catalyst was fast and could be established in less than 1 h.

## Results and Discussion

**XRD Analysis.** The blank clay LDH showed a sharp and symmetric peak at $2\theta = 11.06$ ° (Figure 1a). This was equal to the basal spacing of $d_{003} = 8.0$ Å, typical of chloride-LDH.[7] When the clay was synthesized in the presence of the anionic surfactant SDS, the basal spacing was increased to 25.6 Å (Figure 1d). This indicates that SDS has been inserted into the LDH interlayers. By subtracting the hydroxide plate thickness (4.8 Å), the gallery height of SDS-LDH was estimated to be 20.8 Å. These data are almost the same as the length of the alkyl chain of SDS (20.8 Å),[25] suggesting that the intercalated surfactant is perpendicularly oriented to the clay layers.[3,7] However, there also appeared a weak reflection at $2\theta = 11.06°$ (Figure 1, asterisk). It indicates that the final product still contains a trace amount of chloride-LDH, probably a result of an insufficient amount of SDS used during the sample synthesis.

After the blank LDH or SDS-LDH was loaded with 0.8 wt % PdPcS, via ex situ ion exchange at 25 °C, the resulting composite showed a pattern similar to that of the parent clay. The basal spacing was 8.0 Å for PdPcS-loaded LDH (Figure 1b) and 25.7 Å for PdPcS-loaded SDS-LDH (Figure 1e). Similar results are also reported for CuPcS loading onto LDH via ion exchange at 25 °C[14] or at 80 °C.[26] It means that PdPcS is only adsorbed on the external surface of LDH or SDS-LDH. This is ascribed to the size of the MPcS anion (M = Cu, Pd), which is too large to be inserted into the LDH interlayers only through so-called ion exchange. Thus, the samples prepared by this method are denoted here as LDH-($x$ PdPcS)$_{ads}$ or SDS-LDH-($x$ PdPcS)$_{ads}$.

When the LDH clay was synthesized in the presence of 0.8 wt % PdPcS, via direct coprecipitation at 90 °C, the resulting sample also gave a pattern similar to that of the parent clay, with $d_{003} = 7.9$ Å (Figure 1c). This was somewhat unexpected, since the same method was successfully used for the intercalation of CuPcS into the LDH ($d_{300} = 23$ Å).[14] It is unlikely that PdPcS is significantly different from CuPcS[14,26] and CoPcS[12,13] in size and negative charges. Only the difference was the amount of MPcS used for the synthesis. In those reports, about 50 wt % CuPcS or CoPcS was used, whereas in the present work only 0.8 wt % PdPcS was added. For this concern, the LDH sample containing 56.2 wt % PdPcS was prepared via direct coprecipitation. XRD analysis showed that the basal spacing was 22.7 Å, larger than the parent LDH (Figure S1 in Supporting Information). Similar to those reported for the intercalated CuPcS and CoPcS, it could be concluded that PdPcS is indeed intercalated in the LDH interlayers, probably with a perpendicular orientation to the hydroxide layers.[14,26] As a result of very low loading of PdPcS (0.8 wt %), the XRD pattern of LDH-(0.8 PdPcS)$_{int}$ is similar to that of blank LDH.

The same conclusion could also be made for the samples, PdPcS-loaded SDS-LDH, prepared by direct coprecipitation. The basal spacing was 26.0 Å, for all the samples containing 0.4−2.2 wt % PdPcS (Figure 1f−i). During the synthesis, all the anions ($Cl^-$, $SDS^-$, and $PdPcS^{4-}$) present in the reaction suspension could interact with the positively charged interlayer surface of LDH. But PdPcS would prefer to occupy the clay interlayers, because of its strongest interaction among the anions.[3] The dimension of MPcS[14] is about 19.9 × 17.3 × 5.5 Å,[3] smaller than the gallery height of SDS-LDH (20.8 Å). Thus the PdPcS anion could be accommodated in the SDS-LDH interlayers, with no change in the $d$-spacing (it was also true for the sample containing 41.4% PdPcS, see Figure S1 in the Supporting Information). In other words, both SDS and PdPcS anions are located in the LDH interlayers, probably all with a perpendicular arrangement to the clay layers. Thus, the samples prepared by direct coprecipitation are denoted here as LDH-($x$ PdPcS)$_{int}$ or SDS-LDH-($x$ PdPcS)$_{int}$.

**Visible Reflectance Spectra.** Great difference among the samples was observed by visible diffuse reflectance spectra (Figure 2). In aqueous solution, PdPcS was highly aggregated. Its aggregate band at 613 nm was higher than the monomer band at 646 nm (Figure 2a). After PdPcS was

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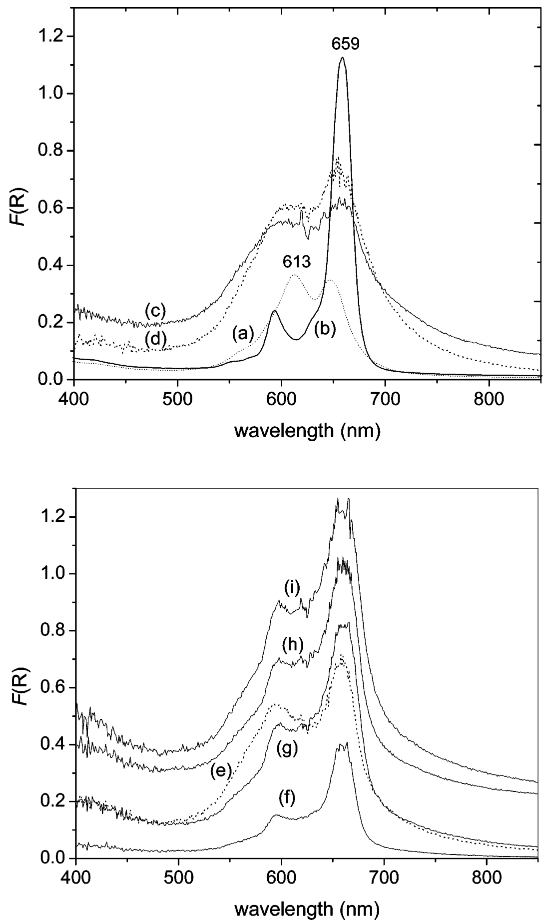

**Figure 2.** Visible absorption spectra of (a) PdPcS in water, (b) PdPcS in *N*,*N*-dimethylformamide, (c) LDH-(0.8 PdPcS)$_{\mathrm{int}}$, (d) LDH-(0.8 PdPcS)$_{\mathrm{ads}}$, (e) SDS-LDH-(0.8 PdPcS)$_{\mathrm{ads}}$, (f) SDS-LDH-(0.4 PdPcS)$_{\mathrm{int}}$, (g) SDS-LDH-(0.8 PdPcS)$_{\mathrm{int}}$, (h) SDS-LDH-(1.5 PdPcS)$_{\mathrm{int}}$, and (i) SDS-LDH-(2.2 PdPcS)$_{\mathrm{int}}$. The *y*-axis for parts a and b is the absorbance (0−1.9), whereas the *y*-axis for parts c−i is expressed by *F*(*R*).

immobilized onto the clay, it existed predominately in a form of monomer (Figure 2c−i). The monomer band was red-shifted to 660 nm, suggesting a strong interaction between PdPcS and clay. Because of that, the $\pi-\pi$ interaction between PdPcS species is greatly minimized,[27] consequently resulting in significant enhancement in the dye disassociation.

Among the solid samples, the degree of dye disassociation was also different, implying different macrocycle interaction between the immobilized PdPcS species. First of all, the adsorbed PdPcS on LDH (Figure 2d) was less aggregated than the corresponding intercalated PdPcS (Figure 2c). This means that the macrocycle interaction between the flat-lying oriented PdPcS species on the LDH external surface is weaker than the interaction between the perpendicularly oriented PdPcS species in the LDH interlayers. This observation was similar to those reported for CuPcS[26] and CoPcS.[28] However, when SDS-LDH was used as the support, the adsorbed PdPcS (Figure 2e) was more aggregated than the corresponding intercalated PdPcS (Figure 2f), opposite to the LDH case presented above. It seems that the intercalated SDS surfactant functions as a dispersing reagent so that the macrocycle interaction between the intercalated PdPcS species is minimized. Such a dispersing effect of the intercalated SDS would not significantly affect the adsorbed PdPcS on the clay external surface. Thus the adsorbed PdPcS on SDS-LDH (Figure 2e) displays a similar absorption spectrum, as compared to the adsorbed PdPcS on LDH (Figure 2d).

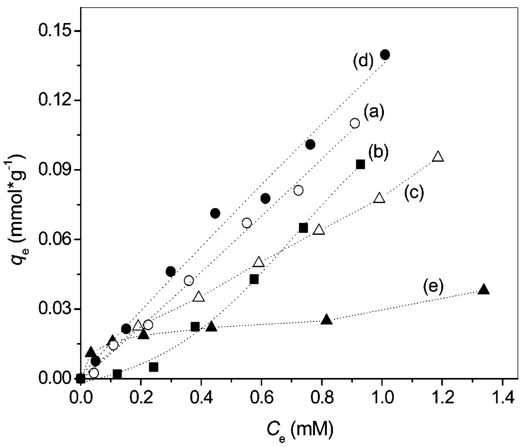

**Figure 3.** Adsorption isotherms of TCP from aqueous solution on the solid of (a) $Cl^-$-LDH, (b) $CO_3^{2-}$-LDH, and (c) SDS-LDH at pH 6 and on the solid of (d) $Cl^-$-LDH and (e) SDS-LDH at pH 12.

The result above shows that water-soluble PdPcS could be firmly immobilized and well dispersed into/onto anionic clay. For high dispersion of PdPcS in a monomeric form, SDS-LDH appears to be a better support than LDH, when the composite catalyst is prepared via a direct coprecipitation method. However, the degree of dye aggregation also slightly increases with the amount of PdPcS loaded (0.4−2.2 wt %), as evidenced from Figure 2f to Figure 2i. Such dye aggregation would lead to decreased photosensitization efficiency, as a result of self-annihilation of the excited states. This information will serve as guidance to the following photoactivity study.

**Sorption Isotherms of TCP.** The composite catalyst has a considerable adsorption capacity toward TCP in aqueous solution. Thus, it is first necessary to investigate how the substrate is transferred into the catalyst from solution. Figure 3 shows the sorption isotherms of TCP onto three blank supports ($Cl^-$-LDH, $CO_3^{2-}$-LDH, and SDS-LDH) in water at pH 6 or pH 12. Two types of isotherms were observed, implying different mechanisms of adsorption.

The adsorption isotherms on $Cl^-$-LDH at pH 6 and at pH 12 were all linear. The slope was estimated to be 0.120 L/g at pH 6 (Figure 3a) and 0.134 L/g at pH 12 (Figure 3d). Because TCP is a weak acid (p$K_a = 6.23$),[29] it suggests that the adsorption of TCP on LDH proceeds via ion exchange. This was further supported by the isotherm on $CO_3^{2-}$-LDH at pH 6 (Figure 3b). The isotherm was essentially linear at $C_e > 0.25$ mM, with a slope (0.125 L/g) very close to that on $Cl^-$-LDH at pH 6 (0.120 L/g). The isotherm at $C_e < 0.25$ mM was somewhat right-shifted, probably as a result of $CO_3^{2-}$ anions difficult to be displaced by TCP, as compared to $Cl^-$ anions in the LDH interlayers.[4]

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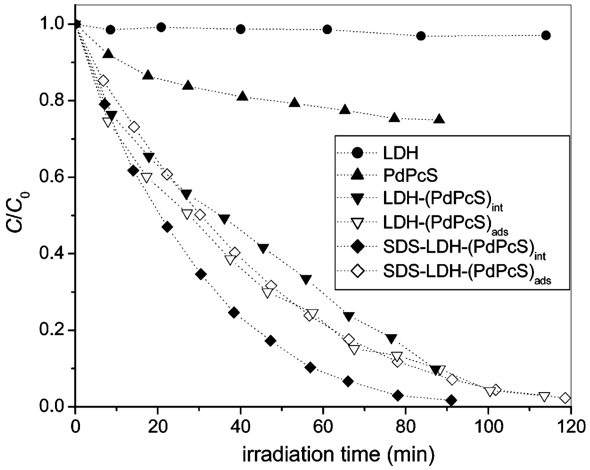

**Figure 4.** Photosensitized oxidation of TCP in water at pH 6 over different catalysts, as indicated by the legend. The initial concentration of TCP was 0.31 mM, and the catalyst was 50 mg/50 mL. In a homogeneous solution, PdPcS was set at 0.4 mg/50 mL.

**Table 1. Dark Adsorption of TCP and Rate Constants of TCP Oxidation over Different Catalysts**

| sample | $q_e$ (mmol·g$^{-1}$) | $k$ (min$^{-1}$) |
|---|---|---|
| PdPcS | | 0.00645 |
| LDH-(0.8 PdPcS)$_{ads}$ | 0.0350 | 0.0258 |
| LDH-(0.8 PdPcS)$_{int}$ | 0.0336 | 0.0198 |
| SDS-LDH-(0.8 PdPcS)$_{ads}$ | 0.0219 | 0.0255 |
| SDS-LDH-(0.8 PdPcS)$_{int}$ | 0.0202 | 0.0392 |

The isotherm on SDS-LDH was somewhat complicated. The amount of TCP adsorption at pH 6 (Figure 3c) was higher than that at pH 12 (Figure 3e), in contrast to the adsorption on LDH. The surfactant SDS is located in the LDH interlayers, and consequently it can create a hydrophobic zone for uptake of TCP molecules from aqueous phase. It means that the adsorption of TCP on SDS-LDH at pH 6 occurs via partition mechanism.[7] In an alkaline solution, TCP completely dissociated into the corresponding anion. Then, the adsorption at pH 12 was rather weak, approaching a limit at $C_e > 0.20$ mM (Figure 3e). Interestingly, such a limit was almost the same as the intercept (0.075 mmol/g), resulted from the isotherm at pH 6 (Figure 3c). If the partition mechanism is in operation at pH 6, the isotherm would be linear with a zero intercept. The positive intercept observed at pH 6 then suggests some additional adsorption also involved. Recall that there exists a trace amount of LDH in the sample SDS-LDH (Figure 1). Therefore, such additional adsorption at pH 6 and the observed adsorption at pH 12 are due to the mechanism of ion exchange on $Cl^-$-LDH.

The loading of PdPcS (0.4−2.2 wt %) onto the clay did not show significant effect on the TCP adsorption, only with a slight decrease of a few percentages. It implies that the observed adsorption of TCP over the PdPcS-loaded clay is almost entirely contributed from the adsorption on the blank clay. Whatever the adsorption occurs via ion exchange or partition mechanism, the adsorbed TCP is located in the interlayers of LDH or SDS-LDH. Such an arrangement of the adsorbed TCP will facilitate its oxidation by singlet oxygen, generated from the intercalated PdPcS species upon visible light irradiation, as will be shown below.

**Photosensitized Oxidation of TCP.** The catalyst photoactivity was evaluated by TCP oxidation in an aerated aqueous solution at pH 6 under visible light irradiation ($\lambda >$ 450 nm). As a result of dark adsorption of TCP, all the photoreactions were performed only after the adsorption equilibrium was reached. Figure 4 shows the time profiles of TCP oxidation over different catalysts. All PdPcS-containing composites were effective to initiate the photoreaction, whereas the clay itself was not active under similar conditions. The disappearance of TCP with irradiation time was well fitted into the pseudo-first-order kinetics, from which the apparent rate constant, $k_{app}$, was obtained. Table 1 summarizes the apparent rate constant of TCP, determined over different catalysts, and the corresponding initial amount of TCP adsorption, measured before the photoreaction.

All the heterogeneous reactions over immobilized PdPcS catalysts were faster than the homogeneous reaction in an aqueous solution of PdPcS (0.4 mg/50 mL). It has been proved that the photosensitized oxidation of TCP in solution is essentially initiated by singlet oxygen ($^1O_2$), generated via energy transfer from the excited PdPcS into ground state oxygen ($^3O_2$).[18] Two important factors are responsible for the observed difference in the reaction efficiency between free and immobilized PdPcS sensitizers. The first is the dye aggregation, which in general enhances self-annihilation of the excited dye, consequently leading to great decrease in the photosensitization efficiency. Free PdPcS in solution mainly exists in a form of aggregate (Figure 2a), whereas the immobilized PdPcS predominantly exists in a form of monomer (Figure 2c−i). Because of higher degree of disassociation, the immobilized PdPcS is more photoactive than the unsupported free PdPcS, in the generation of $^1O_2$ and consequently in the oxidation of target substrate TCP. The second factor is the adsorption of TCP on the solid catalyst (Figure 3). Singlet oxygen, once formed upon light excitation, would not diffuse too far away from where it was produced, as a result of limited lifetime. Then, enrichment of TCP onto the catalyst would accelerate its oxidation by singlet oxygen, generated nearby in situ. Separate experiment about the effect of adsorption confirmed that the rate of TCP oxidation increased indeed with the initial amount of TCP adsorption (Figure S2 in the Supporting Information), similar to the case previously reported with the PdPcS-loaded organobentonite.[29]

However, the photosensitization activity also was notably different from one catalyst to another (Table 1). Among four immobilized catalysts, which contained similar amounts of PdPcS (0.8 wt %), the sample SDS-LDH-(0.8 PdPcS)$_{int}$ was the best, and LDH-(0.8 PdPcS)$_{int}$ was the poorest for the photosensitized oxidation of TCP. This trend in photoactivity is in agreement with the order in the degree of dye aggregation (Figure 2). The intercalated PdPcS in SDS-LDH (Figure 2g) has the highest degree of dye dissociation, whereas the intercalated PdPcS in LDH (Figure 2c) is the lowest among four catalysts. The result demonstrates again that the dye aggregation is an important factor in controlling the photosensitization efficiency. This is also illustrated by two catalysts, LDH-(0.8 PdPcS)$_{ads}$ and SDS-LDH-(0.8 PdPcS)$_{ads}$, which have a similar spectrum (Figure 2d,e) and thus a similar activity for the photosensitized oxidation of TCP (Table 1).

Among the catalysts, there are some differences in the initial amount of TCP adsorption (Table 1). The adsorption

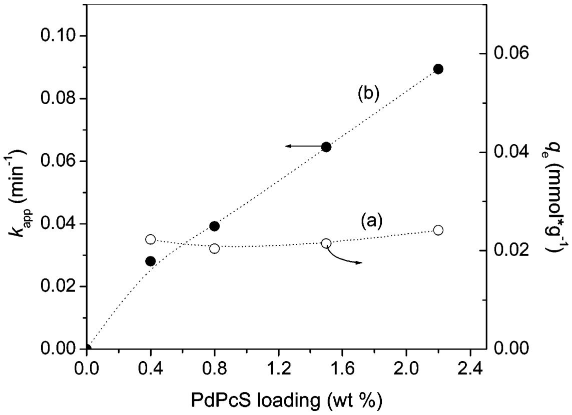

**Figure 5.** Effect of PdPcS loading into SDS-LDH on (a) TCP sorption and (b) TCP photooxidation in aqueous suspension at pH 6. The catalyst was prepared by co-precipitation method. The initial concentrations of TCP were 0.31 mM, and the catalyst at 50 mg/50 mL.

on the intercalated PdPcS was slightly smaller than that on the adsorbed PdPcS. Since the adsorbed TCP is located in the clay interlayers (Figure 3), the observed decrease in the initial amount of adsorption is evidence that PdPcS is indeed located in the interlayers of LDH and SDS-LDH, as discussed above by XRD and spectral analysis. The intercalated PdPcS would block the entrance of TCP into the layers, consequently leading to the decreased adsorption. Although the rate of TCP oxidation is proportional to the initial amount of TCP adsorption (Figure S2 in the Supporting Information), the reaction rate is first determined by the rate of $^1O_2$ generation, which is closely related to the degree of dye aggregation. Thus, for the photosensitized oxidation of TCP (Table 1), SDS-LDH-(0.8 PdPcS)$_{int}$ is more active than SDS-LDH-(0.8 PdPcS)$_{ads}$, whereas LDH-(0.8 PdPcS)$_{int}$ is less active than LDH-(0.8 PdPcS)$_{ads}$. In other words, the immobilized PdPcS, which possesses a high degree of dye disassociation and a high capacity of TCP adsorption, would display a high activity for the photosensitized oxidation of TCP. Therefore, the intercalated PdPcS in the SDS-LDH interlayers is the best among four catalysts studied.

**Effect of PdPcS Loading.** The intercalated PdPcS in SDS-LDH has shown its excellent activity for the photosensitized oxidation of TCP. Then, it is necessary to examine the effect of PdPcS loading both on the sorption and on the oxidation of TCP. Figure 5 shows the results determined at pH 6 over the SDS-LDH loaded with different amount of PdPcS. While the adsorption of TCP remained almost the same (Figure 5a), the rate of TCP oxidation increased with the amount of PdPcS present in the catalyst interlayers (Figure 5b). The latter is in agreement with the general law of photoreaction that the reaction rate is proportional to the concentration of light-absorbing species, under the condition that the incident photons are sufficient enough. However, the plot of rate constant versus PdPcS loading was not exactly linear (Figure 5b). Instead, it first increased quickly and then slowly with PdPcS loading. This is due to the degree of dye aggregation that increases slightly with the PdPcS loading (Figure 2f−i). The result confirms again that the photosensitized oxidation of TCP is essentially initiated by the PdPcS species in a monomeric form.

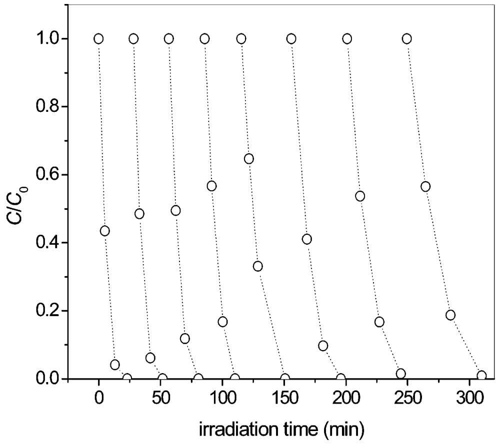

**Figure 6.** Recycling experiment for TCP oxidation in aerated aqueous solution at pH 6 over SDS-LDH-(0.8 PdPcS)$_{int}$.

It is worthy of noting that the present result is notably different from that obtained with the PdPcS intercalated in organobentonite.[29] The latter catalyst exhibits an optimal loading of PdPcS at 1.0 wt % for the photosensitized oxidation of TCP under similar conditions (Figure 5, in ref 29), due to the adsorption sites of TCP blocked partially by the intercalated PdPcS (0.1−1.6 wt %). In the organobentonite, the intercalated surfactant and the intercalated PdPcS are both horizontally oriented to the clay plates.[29] But in the present support of organo-LDH, both the intercalated SDS and the intercalated PdPcS are present in a perpendicular orientation. Such structural arrangement would favor the uptake of TCP. In this regard, organo-LDH is a superior support to organo-bentonite for PdPcS loading and thus for the photosensitized oxidation of TCP.

**Recycling Experiment.** For practical use in water purification, the stability of the catalyst is also an important factor to be considered. For this concern, recycling experiments were performed for the photosensitized oxidation of TCP over the catalyst, SDS-LDH-(0.8 PdPcS)$_{int}$ (see the experimental section for details). The result (Figure 6) showed that composite clay was recyclable for consecutive sorption and oxidation of TCP. The catalyst activity was still excellent even after eight runs. However, it was obvious that the reaction rate gradually decreased from one run to another. Two factors are responsible for such decrease in the reaction rate. First, the catalyst concentration was gradually decreased from one run to another, due to the sample analysis (1 mL of the suspension was taken out for each analysis). Such decrease in the catalyst concentration would decrease the rate of the photosensitized reaction.[29] It was verified here that the rate constant was indeed in a linear decline with the number of runs during the first five recycles. Second, some intermediates were formed from the oxidation TCP, which were light-pink in color. Such colorful intermediates would decrease the light intensity reaching on the catalyst, consequently decreasing the rate of TCP oxidation. Note that the degradation of the pillared SDS by $^1O_2$ was impossible, since $^1O_2$ is kinetically inert to saturated hydrocarbons under the present conditions. Possible leaching of the intercalated SDS into solution was not observed, since the amount of TCP adsorption was almost the same during the first two recycles.

The result shows that the catalyst has a high stability during the recycling experiments.

## Conclusions

The photosensitizer PdPcS has been firmly immobilized and highly dispersed onto the anionic clay (LDH and SDS-modified LDH). Depending on the method of synthesis, the immobilized PdPcS can be present on the external surface or in the interlayer space of clay. Although these catalysts are all effective for the photosensitized oxidation of TCP, the activity was notably different from one to another. For dispersion of monomeric sensitizer, which is much more photoactive than the aggregate, SDS-LDH is a better support than LDH, as a result of the intercalated SDS preventing the intercalated PdPcS from detrimental aggregation. Because of that as well as the hydrophobic zone created, the intercalated PdPcS in SDS-LDH exhibits the highest activity among solid catalysts for the oxidation of TCP at pH 6. The recycle experiment shows that this catalyst can be repeatedly used for the sorption and oxidation of TCP, without significant loss in the activity. As compared to cationic clay, the anionic clay LDH provides a large interlayer space for the intercalation of both surfactant and sensitizer in a perpendicular arrangement. It deserves further investigations for improvement of its sorption, photosensitization and recycling stability, and efforts are underway in this laboratory.

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**Supporting Information Available:** XRD patterns of LDH, LDH-(56.2 PdPcS)$_{\text{int}}$, and SDS-LDH-(41.4 PdPcS)$_{\text{int}}$ and effect of initial amount of TCP concentration on the initial rate of TCP oxidation sensitized by SDS-LDH-(0.8 PdPcS)$_{\text{int}}$ in an aerated aqueous suspension at pH 6 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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