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The removal and photodecomposition of *n*-nonylphenol using hydrophobic clay incorporated with copper-phthalocyanine in aqueous media

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Abstract

In order to achieve the effective removal and decomposition of *n*-nonylphenol (Np), an endocrine disruption chemical with poor solubility, tenuously dispersed in environmental water, the synthesis and characterization of a hydrophobic clay (HpC) with copper-phthalocyanine (CuPC) were investigated. The HpC powders were prepared by intercalating the cetyltrimethylammonium cations (CTA^+) into montmorillonite (Mont) interlayers. The HpC compound incorporated with CTA^+ molecules and equal to the cation-exchangeable capacity (CEC) of Mont were found to adsorb almost completely the Np molecules from the aqueous solution by the hydrophobic interaction between the alkyl chains of the CTA^+ and Np molecules. The CuPC molecules were incorporated with the HpC compound in order to add the photodecomposition properties of CuPC to the HpC compound. This HpC/CuPC hybrid efficiently adsorbed the Np molecules from the polluted water, too. Visible-light irradiation of the Np aqueous HpC/CuPC hybrid suspension under O_2 atmosphere at 620 nm decomposed the Np molecules having been adsorbed at the hydrophobic spaces of the HpC/CuPC hybrid materials, forming quinonmethane molecules by the singlet oxygen produced by the photosensitization reaction of the cointercalated CuPC molecules.

Keywords: Photodecomposition; *n*-Nonylphenol; Hydrophobic clay; Phthalocyanine; Purification of polluted water; Organic/inorganic hybrid materials

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1. Introduction

n-Nonylphenol (Np), an endocrine disruption chemical, is also known as a compound which behaves like estrogen in vivo [1,2]. There have been alarming reports regarding Np molecules possessing estrogenicity with the discovery of reproduction abnormalities in fish, amphibians, birds, and mammals [1,2]. Np molecules are widely used for the manufacture of surfactants and also as antioxidants in the plastics industry [2]. Moreover, Np molecules are known as the predominant products in the decomposition of nonylphenol polyethoxylates in environmental water (cf. Scheme 1) [2]. In fact, the Ministry of the Environmental of Japan has reported that Np molecules have caused reproduction abnormalities in medaka even in very dilute concentrations, ca. 10 μg/l, and has verified its strong toxicity. While the establishment of environmental and effluent standards has progressed, the removal and decomposition of Np molecules already dispersed in the environment and the containment of industrial effluents are urgently required. However, Np molecules exist under very dilute conditions in environmental water and effluents and they also have poor solubility. In order to efficiently decompose and detoxify the Np molecules, it is first necessary to concentrate the molecules in some way, although Np molecules dilutely dispersed in water are presently adsorbed and removed by various adsorbents such as activated carbon.

Montmorillonite (Mont), known as a cationic exchangeable clay mineral, can intercalate various cationic molecules including dyes and cationic surfactants into its interlayers by a cation-exchangeable reaction [3–13]. Especially, surfactant intercalating Mont, or so-called hydrophobic clay (HpC), exhibits efficient hydrophobic properties. It has been reported that HpC materials are also able to adsorb organic molecules with high hydrophobicity into its interlayers [14–20]. Such hydrophobic spaces have the ability to adsorb and concentrate organic contaminants with poor polarity from polluted

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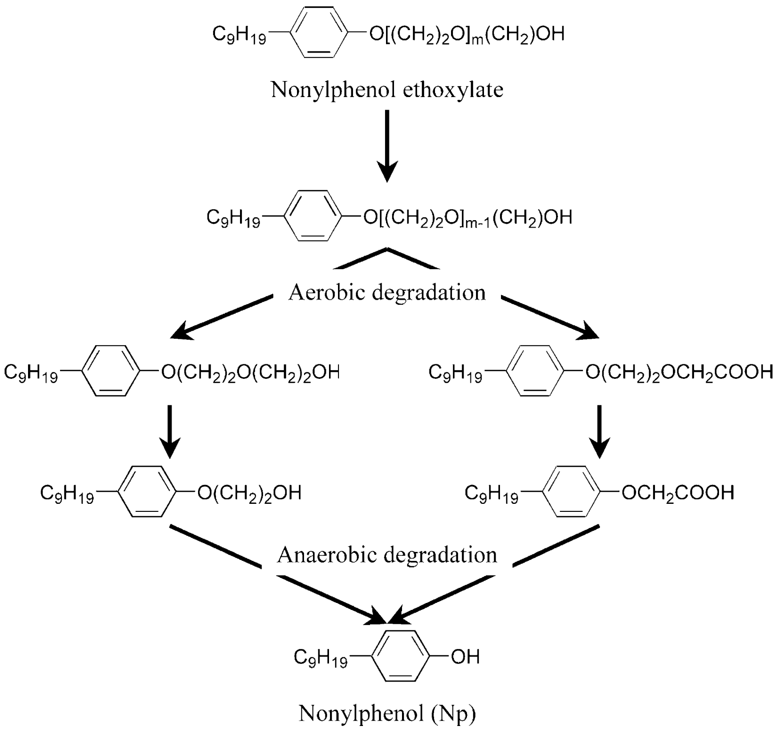


Scheme 1. Production routes of *n*-nonylphenol in an aquatic environment.

water. However, HpC materials, which can adsorb organic toxic contaminants, also create new problems such as the disposal and treatment of the polluted HpC materials. Such concerns can only be solved by the development of completely new HpC materials incorporating organic compounds having photocatalytic characteristics.

The aim of this study is to develop such a new hybrid based on HpC materials, which can effectively adsorb and photodecompose organic toxic contaminants in water and which could operate under visible-light irradiation. In this study, photooxidation using copper-phthalocyanine (CuPC) molecules attributed to the singlet oxygen produced by visible-light irradiation under the presence of O_2 was carried out in an aqueous solution with Np molecules in the presence of HpC/CuPC hybrid materials.

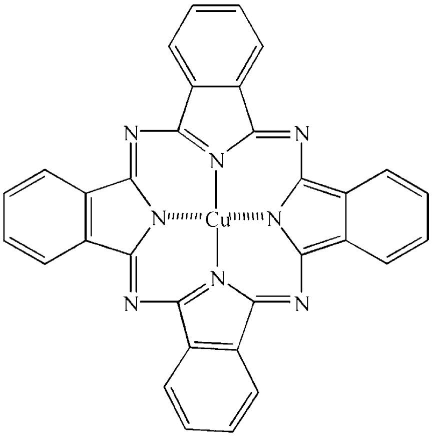
2. Experimental

2.1. Preparation of the hydrophobic clay

Purified standard sodium montmorillonite clay, $Na^{0.33+}[(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2 \cdot nH_2O]^{0.33-}$, with a cation-exchangeable capacity (CEC) of 1.19 meq./g obtained from the Clay Science Society of Japan was used without further purification. Cetyltrimethylammonium bromide (CTAB) was used as the amphiphilic molecules and obtained from Tokyo Chemical Industry Co. Ltd. without further purification. One gram of Mont powder was dispersed in 9 g of distilled and deionized water by stirring and sonication. An aqueous solution with 1.19 mmol of the CTAB molecules was added to the Mont suspension, and was stirred for 24 h at room temperature to intercalate the CTA cations into the Mont interlayers. The obtained HpC white precipitates were separated by filtration, and were dried overnight in vacuo at room temperature after rinsing in distilled and deionized water. The intercalation of the CTA cations into the Mont interlayers could be verified by the increase in the basal spacings, d_{001}, of the Mont layers from 1.23 to 2.12 nm. CHN analysis showed that all of the added CTA cations were included in the obtained HpC hybrid materials.

2.2. Hybridization of copper-phthalocyanine molecules with the HpC materials

Copper-phthalocyanine (cf. Scheme 2) was used as the photosensitizer, donated by Dainihon Ink and Chemicals Inc., without further purification. After *N*,*N*-dimethylformamide including the appropriate amount of CuPC powder was mixed with 10 wt.% of the HpC aqueous suspension, the resulting suspension was stirred overnight at room temperature, and the amounts of CuPC molecules in final suspension were adjusted to 5, 10, 15, 20, and 25 wt.% against the weight of the HpC powders. A blue precipitated powder was isolated by a membrane filter with a pore size of 0.20 mm and dried overnight in vacuo at room temperature after rinsing in distilled and deionized water.



Scheme 2. Structural formula of copper-phthalocyanine.

2.3. *Adsorption of n-nonylphenol*

After one milligram of each hybrid powder was dispersed in 50 ml saturated Np aqueous solution and stirred for a given amount of time at room temperature and after filtration of the HpC or HpC/CuPC hybrid powder, the amount of Np molecules adsorbed by HpC or HpC/CuPC was estimated from the fluorescence intensities of the filtrate Np solutions at 305 nm.

2.4. *Photodecomposition of the Np molecules*

One milligram of the HpC/CuPC powder fully adsorbed (ca. 100 mg/g) with the Np molecules in its hydrophobic interlayers was suspended into 100 ml of saturated Np aqueous solution (ca. 2 mg/l). After the resulting suspended mixture was stirred for 24 h at room temperature with bubbling by O_2 gas for 30 min, the monochromatic light of 620 ± 10 nm was irradiated for the appropriate duration time (∼6 h). The amount of Np was then evaluated by means of fluorescence spectroscopy. Identification of the photolysis products was performed by high-performance liquid chromatography (HPLC) and gas chromatography/mass spectroscopy (GC/MS).

2.5. *Characterization*

X-ray diffraction analysis was carried out with a RINT 2000 diffractometer (RIGAKU) using a Cu Kα radiation source operating at 40 kV and 40 mA. Fluorescence spectra were measured on a FP-750 spectrofluorometer (JASCO). CHN elemental analysis was conducted using a Perkin-Elmer 2400 II CHN elemental analyzer. HPLC was carried out with a Shimadzu HPLC instrument with a UV-Vis detector (Shimadzu SPD-10A) monitored at 275 nm using a ODS column (SHISEIDO) with ethanol/H_2O (30/70 vol.%) as the eluent. GC/MS was carried out with a Shimadzu QP-5000 mass spectrometer with a 0.2 mm × 25 m CBP1-M50-025 capillary column (Shimadzu).

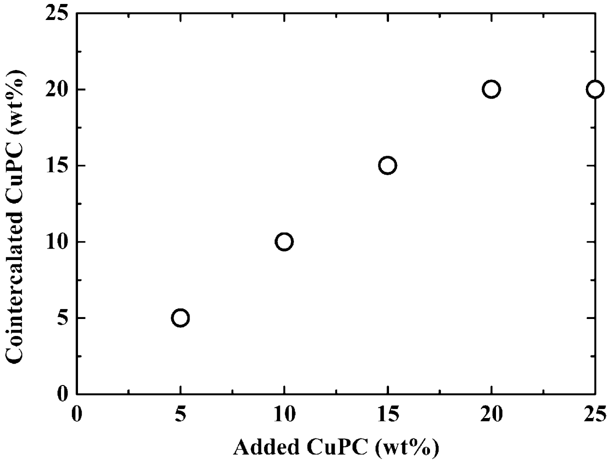


Fig. 1. The dependence of the amount of CuPC added to the HpC suspension on the cointercalated CuPC.

3. Results and discussion

3.1. *Hybridization of CuPC with the HpC hybrid materials*

The amounts of the cointercalated CuPC molecules were plotted against the weight percentages of the added CuPC molecules, as shown in Fig. 1. The cointercalated amount of CuPC linearly increased with an increase in the [CuPC] added, showing a saturation at more than 20 wt.% of the amount of added CuPC. No change of XRD signals of the HpC/CuPC hybrid powders could be observed before and after cointercalation of 20 wt.% CuPC. It can be assumed that the CuPC molecules are accommodated within the vacant spaces of the HpC hybrid, as shown in Fig. 2.

3.2. *Adsorption of the Np molecules by HpC and the HpC/CuPC hybrid materials*

Fig. 3 shows the immersed-time dependence in the adsorption efficiency of the Np molecules, *R*, by the HpC and HpC/20 wt.% CuPC hybrid materials, respectively. The *R* value is defined by the following equation:

$$R\ (\%) = \frac{[\mathrm{Np}]_0 - [\mathrm{Np}]}{[\mathrm{Np}]_0} \times 100 \qquad (1)$$

where $[\mathrm{Np}]_0$ and [Np] are the initial concentration of the aqueous Np solution and the concentration of the remaining Np molecules in bulk solution at a given time, respectively. One milligram of the HpC hybrid material adsorbed ca. 0.1 mg of the Np molecules from an aqueous solution within 10 min. The adsorption phenomenon of the Np molecules may occur by the hydrophobic interactions between the alkyl chains of the CTA cation and the Np molecule, since Mont could adsorb no Np molecules and most of the CTA cations were intercalated in the Mont interlayer spaces in the case of the HpC hybrid material. The present HpC hybrid

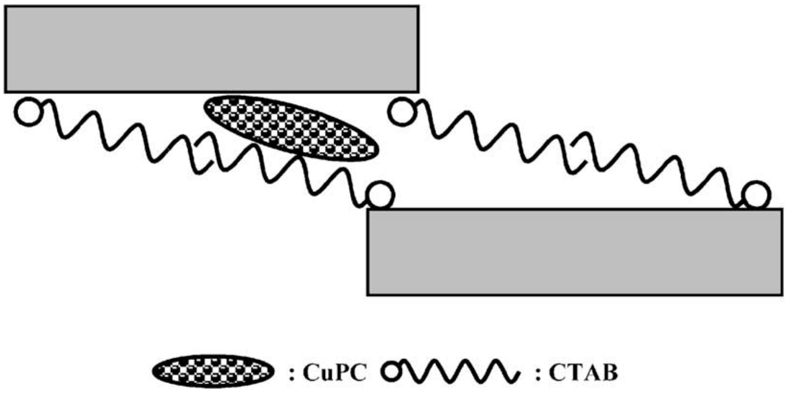


Fig. 2. Presumed intercalation model of CuPC and CTA cations in the Mont interlayer spaces.

material possesses CTA cations equivalent to the CEC, i.e. there is a CTA cation for each cation-exchangeable site. This fact indicates that the HpC hybrid materials have enough vacant space to adsorb the Np molecules within its interlayers, since the occupied area of the cation-exchangeable site (ca. 1.25 nm^2) is five times larger than that of a CTA cation (ca. 0.25 nm^2) within the hexagonal close packing structure.

The HpC/20 wt.% CuPC hybrid materials also exhibited the same adsorption efficiency of the Np molecules as the HpC hybrid materials (ca. 0.38 molecules per site). The adsorption of Np by the HpC hybrid with CuPC was not affected by the amount of cointercalated CuPC molecules, although the vacant spaces in the HpC interlayers decreased by the additional intercalation of CuPC. These results indicate that there may be independent adsorption sites in the HpC hybrid interlayer spaces for Np and CuPC. However, Np adsorption by the HpC/20 wt.% CuPC hybrid materials required a longer intercalation period than that for the HpC hybrid materials. A complete adsorption of Np by the HpC hybrid materials from the Np saturated solution could be attained within 10 min, while the HpC/20 wt.% CuPC hybrid materials required at least 30 min in order to adsorb the Np molecules completely. This intercalation behavior is assumed to occur by way of the following processes: (1) the migration of the adsorbed Np molecule to the equilibrium adsorption site is interrupted by the cointercalated CuPC molecules, or (2) the rearrangement of the intercalated CTA cations and CuPC molecules to adsorb more Np molecules is suppressed by the cointercalated CuPC molecules in the Mont interlayers.

3.3. Photodecomposition of Np molecules by CuPC molecules

Fig. 4 shows the dependence of the photodecomposition of Np molecules on the visible-light irradiation time with CuPC dispersed in aqueous solution. Visible-light irradiation of the Np solution with CuPC molecules at 620 nm under N_2 atmosphere did not initiate any photodecomposition, however, the Np molecules in the bulk gradually disappeared by irradiation at 620 nm under aerated conditions. This indicates that dissolved O_2 molecules are indispensable

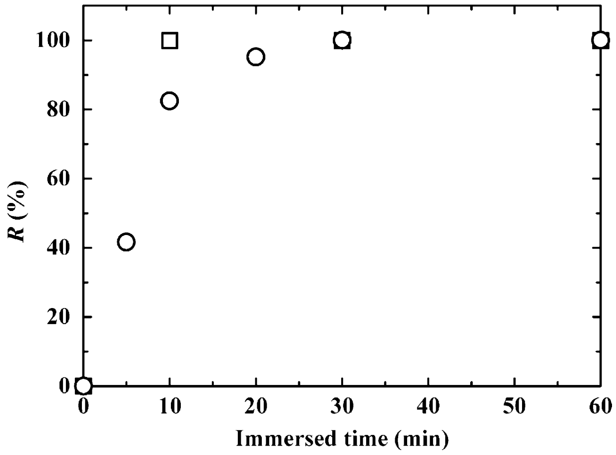


Fig. 3. Immersed-time dependence of the removal rate of the Np molecules from an aqueous solution. Symbols show the HpC (□) and the HpC/20 wt.% CuPC hybrid (○) materials.

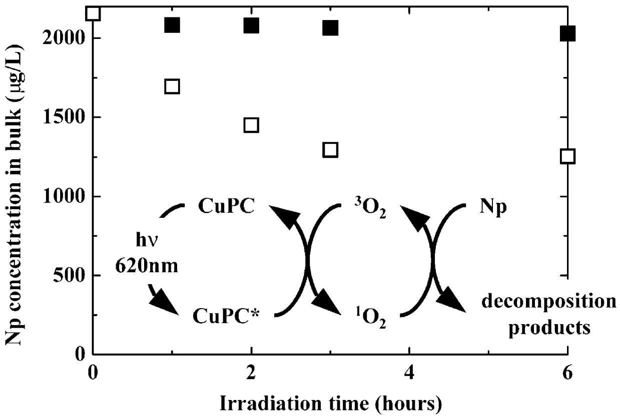


Fig. 4. Irradiation-time dependence of Np concentration in bulk solution. Symbols show the CuPC molecules with (□) and without (■) O_2. Inserted scheme shows the reaction outline of Np photodecomposition.

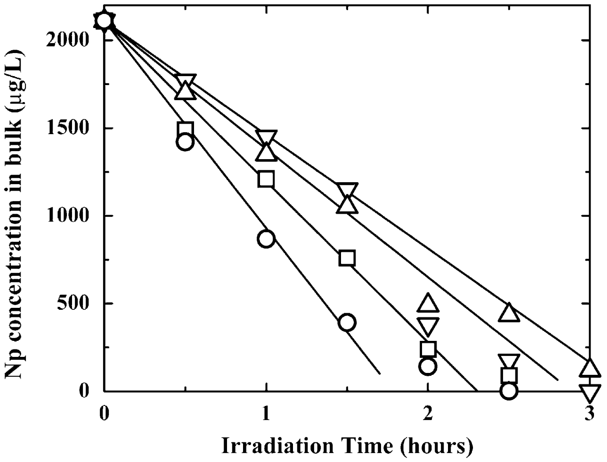


Fig. 5. Irradiation-time dependence of Np concentration in bulk solution. Symbols show the HpC hybrid materials with 5 wt.% (▽), 10 wt.% (△), 15 wt.% (□), and 20 wt.% (○) CuPC under O_2 atmosphere.

for the photodecomposition of the Np molecules to proceed by CuPC. The present photodecomposition reaction can be assumed to be caused by the oxidation attributed to the singlet oxygen produced by the photosensitization of the CuPC molecules as outlined in the inserted Scheme of Fig. 4. However, the CuPC sensitized photooxidation of Np did not proceed completely and was effective for about 40% of the total for 3 h in spite of extensive light irradiation of more than 6 h.

In order to completely decompose the Np molecules by visible-light irradiation, the photodecomposition of the Np molecules was investigated in HpC/CuPC hybrid powders. The irradiation-time dependence of Np concentration was shown in Fig. 5. The Np concentration in the bulk decreased with an increase in the irradiation time for all the HpC/CuPC hybrid materials, and visible-light irradiation for 2 h almost completely photodecomposed the Np molecules. This is explicable by the increase in the collisional probability of Np with the singlet oxygen caused by the existence of both CuPC and Np molecules in the HpC interlayer spaces. Although the lowering of the irradiation efficiency due to incident-light scattering and/or reflection by clay layers was prospective, photodecomposition reaction adequately proceeded. Thus, this result indicates that the present photodecomposition reaction has higher reaction efficiency. A linear relationship in the irradiation time versus the Np concentration for all the HpC/CuPC hybrid materials was observed, suggesting the photodecomposition of Np molecules to be in zero order, as depicted in Fig. 6. Here, the hydrophobic interlayer spaces of the HpC/CuPC hybrid materials were already filled with the Np molecules before irradiation at 620 nm. Therefore, it is concluded that photodecomposition of Np molecules could take place within the hydrophobic interlayer spaces in the present system. The resulting decomposition products could be exchanged with Np in the bulk by desorption from the HpC/CuPC hybrid interlayers. Such a catalytic cycle is repetitive, giving rise to the complete disappearance of the Np molecules in the bulk solution. Since the amount of Np molecules adsorbed in the HpC/CuPC hybrid interlayer is believed to remain constant during this catalytic reaction, the decrease in the concentration of Np in

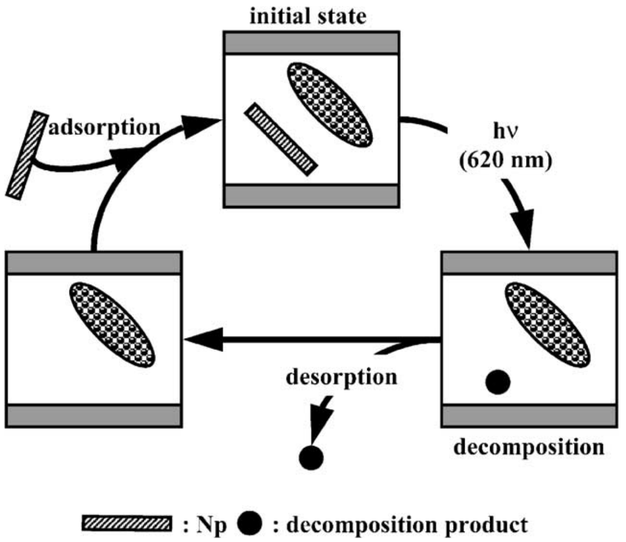


Fig. 6. Reaction mechanism of Np photodecomposition by the HpC/CuPC hybrid materials. In this figure, the CTA cations have been omitted.

Table 1
Reaction constants, *k*, for Np photodetoxification with HpC/CuPC hybrid materials

	CuPC content (wt.%)	k ($\times 10^2$ mol/(dm^3 s))
HpC/CuPC/5	5	1.06
HpC/CuPC/10	10	1.19
HpC/CuPC/15	15	1.50
HpC/CuPC/20	20	1.93

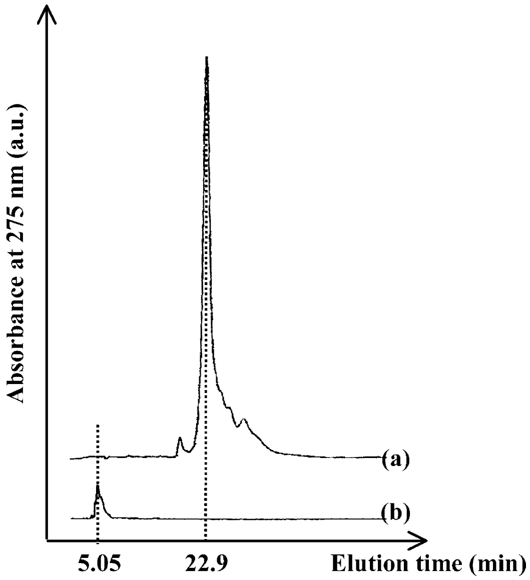


Fig. 7. Chromatograph of the saturated Np aqueous solution (a), and the bulk solution after photodecomposition due to the HpC/CuPC hybrid materials under O_2 atmosphere (b).

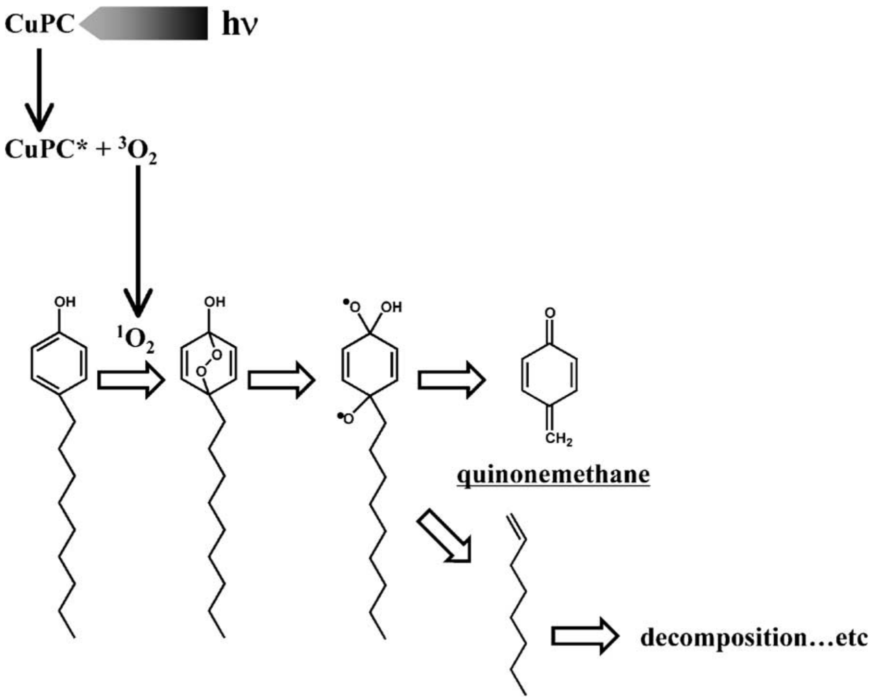


Fig. 8. Photodecomposition mechanism of the Np molecules by the CuPC molecules cointercalated in the HpC hydrophobic interlayer spaces under O_2 atmosphere.

the bulk is observed to be in zero order. Thus, the concentration of Np in the bulk during this catalytic reaction can be expressed by the following equation:

$$[\mathrm{Np}]_t = [\mathrm{Np}]_0 - kt \qquad (2)$$

where $[\mathrm{Np}]_t$ is the concentration of the Np molecules at a given irradiation time and k is the reaction rate constant of the Np photodecomposition. Table 1 summarizes the reaction rate constants of Np photodecomposition for the HpC/CuPC hybrid materials. As can be seen, the reaction rate constants increased with an increase in the amount of CuPC molecules cointercalated in the hydrophobic interlayer spaces. These results indicate an increase in the production of $^1O_2$. As a result, it can be concluded that the rate constants of this photooxidation increased due to an increase in the collisional probability of the Np molecules with $^1O_2$ in the hydrophobic interlayer spaces of the HpC/CuPC hybrid.

3.4. Identification of the products of the photodecomposition

Fig. 7 shows the HPLC profiles of the bulk solution before and after photodecomposition. Although the peaks due to the Np molecules were observed around 23 min before irradiation, the photolysis mixture showed a new peak at ca. 5 min with complete disappearance of the originated Np molecule peak (Rt ∼ 23 min). GC/MS analysis also indicated that the newly formed product possesses a molecular peak at $m/z = 106$ and two fragment peaks at $m/z = 91$ and 77, which could tentatively be assigned to be quinonemethane. These results could clarify the reaction mechanism of the present photodecomposition as shown in Fig. 8. It is, thus, assumed that the present HpC/CuPC hybrid materials could efficiently adsorb Np molecules from polluted water, and could also convert the adsorbed Np molecules into quinonemethane by irradiation with visible light of 620 nm.

4. Conclusions

The hydrophobic clay with Cu-phthalocyanine (HpC/CuPC) prepared in this study were found to almost completely remove toxic Np molecules from polluted water (<1 mg/l). The HpC/CuPC hybrid material absorbed and concentrated the Np molecules by the hydrophobic interaction between the alkyl chains of Np and the CTA cations in the interlayer spaces. Then, significantly, these adsorbed Np molecules were decomposed into quinonemethane by the photosensitization of CuPC excited by visible-light irradiation of 620 nm. The present clay/organic hybrid materials are, thus, potential candidates to use as an environmental clean-up catalyst.

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