Removal of Phenols by an Organically Modified Layered Niobate $K_4Nb_6O_{17}$ through an Adsorption–photocatalytic Degradation Process

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An organically modified layered niobate was applied to remove phenol and 2,4-dichlorophenol from aqueous solution through an adsorption–photocatalytic degradation process. It showed different performances and structural responses on removal of these two phenols due to their difference in hydrophobicity.

Adsorption and photocatalysis are two of the most usually applied techniques for removal of organic pollutants from water. However, adsorbent regeneration has always been an issue on applying the process of adsorption, whereas low efficiency is often observed in photocatalysis process owing to low concentration of the pollutants in water. The combination of adsorption and photocatalytic degradation appears to be a promising way to overcome these problems. Adsorption of the pollutants on a catalyst can not only remove the pollutants from aqueous solution but also enhance the efficiency of photocatalysis through enrichment of the pollutant molecules on the surface of catalyst. In the mean time, photocatalysis reaction on the catalyst may decompose the adsorbed pollutants and thus restore its adsorption capability.

Organic-modified layered materials like clay minerals have been widely studied as adsorbents for uptake of organic pollutants.[1–3] Among which, we have reported that surfactant-modified hexaniobate $K_4Nb_6O_{17}$ adsorbed substantially organic pollutants like phenols,[2] and furthermore, they showed high adsorption selectivity for more hydrophobic species.[3] Since $K_4Nb_6O_{17}$ is also known as a photocatalyst capable of splitting water into H_2 and O_2,[4] the organically modified niobate may thus be applied to remove organic pollutants through an adsorption–photocatalytic degradation process, where organic pollutants are adsorbed in the hydrophobized interlayer and decomposed by the photoactive niobate layers. However, photocatalytic degradation behavior after adsorption of the pollutants on the modified niobate has yet been studied. Furthermore, since such process may possibly cause the intercalated surfactant loss or to be photocatalytically decomposed, structural stability of the modified niobate becomes a special concern.

We report here the photocatalytic degradation of phenols (as model organic pollutants) after pre-adsorption on a surfactant-modified niobate. Its structural responses on removal of phenols through this process were investigated and their relations with photocatalytic activity were discussed. Although the adsorption–photocatalytic degradation strategy has been followed in other studies to prepare composite catalysts like carbon-coated TiO_2,[5,6] zeolite-supported TiO_2,[7] or TiO_2-pillared clay,[8,9] the use of surfactant-modified layered niobate for photoelimination of organic pollutants has yet been reported. Our data show that the efficiency and structural response of the modified niobate are greatly altered with the hydrophobicity of the phenols.

$K_4Nb_6O_{17}$ synthesized according to the literature[10] was allowed to react with chloride salt of dodecylammonium to give the organically modified niobate (designated as $C_{12}N–Nb_6O_{17}$ hereafter). The catalyst (80 mg) was first subjected to pre-adsorption of phenol or 2,4-dichlorophenol (2,4-DCP) from aqueous solution (70 mL, initial concentration 1 mmol·L^{-1}) for 24 h in dark to reach adsorption equilibrium. Subsequent photocatalytic degradation was conducted in an aerated Pyrex reactor with quartz windows at 298 K. A 250-W high-pressure Hg lamp was used as a light source. The concentration of phenols was measured by a high-performance liquid chromatography analyzer equipped with a UV detector. The original $K_4Nb_6O_{17}$ and a reference catalyst JRC-TiO-4 (P 25 TiO_2) were applied under the same conditions for comparison.

Time evolutions of direct photolysis and photocatalytic degradation of phenol and 2,4-DCP on the catalysts are shown in Figure 1. The steep decreases in the concentrations of phenols after pre-adsorption indicate that $C_{12}N–Nb_6O_{17}$ can effectively adsorb phenols, whereas no obvious adsorption of phenols can be observed on P 25 TiO_2 and $K_4Nb_6O_{17}$.

The photocatalytic reactions follow approximately the

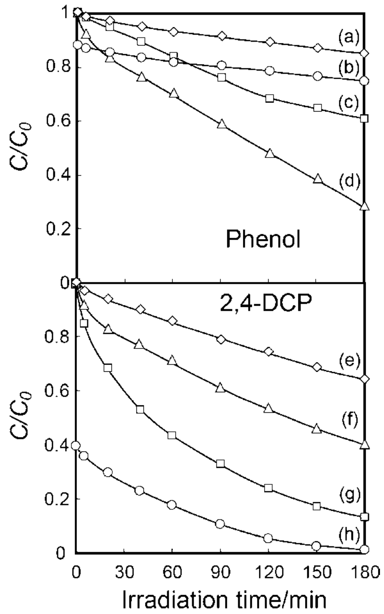

Figure 1. Photodegradation of phenol in blank (a), $C_{12}N–Nb_6O_{17}$ (b), $K_4Nb_6O_{17}$ (c), P 25 TiO_2 (d), and 2,4-DCP in blank (e), P 25 TiO_2 (f), $K_4Nb_6O_{17}$ (g), and $C_{12}N–Nb_6O_{17}$ (h) solutions or suspensions.

Table 1. Apparent rate constants for direct hydrolysis and photodegradation of phenol and 2,4-DCP on the catalysts

Photocatalyst	$k_{\mathrm{phenol}}/\mathrm{min}^{-1}$	$k_{2,4\text{-DCP}}/\mathrm{min}^{-1}$
Blank	0.0004	0.0026
$C_{12}N–Nb_6O_{17}$	0.0009	0.0196
$K_4Nb_6O_{17}$	0.0029	0.0120
P 25 TiO_2	0.0065	0.0052

Langmuir–Hinshelwood (L–H) kinetics. Their apparent rate constants obtained from fitting of the L–H equation provided as Figure S1 in Supporting Information[13] are listed in Table 1. Under UV irradiation, since both phenols disappear faster in the suspensions of the catalysts than in the blank solutions, all the catalysts show certain activities for photodegradation of phenol and 2,4-DCP. Hence, the approach of using the surfactant-modified niobate for removal of phenols by combining adsorption and photocatalytic degradation effects is proved feasible. For phenol, although $C_{12}N–Nb_6O_{17}$ shows a certain adsorption capability ($0.105\,\mathrm{mmol \cdot g^{-1}}$ after pre-adsorption), its photocatalytic activity is apparently lower than those of $K_4Nb_6O_{17}$ and P 25 TiO_2. Comparison of their apparent rate constants k_{phenol} gives the same result. On the other hand, $C_{12}N–Nb_6O_{17}$ adsorbs a substantial amount of 2,4-DCP ($0.534\,\mathrm{mmol \cdot g^{-1}}$ after pre-adsorption). The photocatalytic activity for 2,4-DCP as reflected by the apparent rate constant $k_{2,4\text{-DCP}}$ is in the order of $C_{12}N–Nb_6O_{17} > K_4Nb_6O_{17} >$ P 25 TiO_2. Furthermore, since the photoactive niobate accounts for only 55% of the mass of $C_{12}N–Nb_6O_{17}$ based on TG analysis,[3] the real rate constants of $C_{12}N–Nb_6O_{17}$ for phenol and 2,4-DCP are actually higher, up to 0.0016 and 0.0356 (calculated by k/mass ratio of niobate in $C_{12}N–Nb_6O_{17}$), respectively. Thus, the photocatalytic activity per mass of photoactive niobate in $C_{12}N–Nb_6O_{17}$ is still lower than that of the original $K_4Nb_6O_{17}$ for phenol and much superior to those of $K_4Nb_6O_{17}$ and P 25 TiO_2 for 2,4-DCP. In general, $C_{12}N–Nb_6O_{17}$ shows the best performance in terms of removal of 2,4-DCP by combining adsorption and photocatalytic degradation effects.

Structural information of $C_{12}N–Nb_6O_{17}$ was obtained by X-ray diffraction (XRD) measurement. Figure 2 indicates that after adsorption of phenol, $C_{12}N–Nb_6O_{17}$ retains the layered structure observed before the adsorption (Figure 2b). Since the same result was obtained after adsorption of 2,4-DCP in our previous study,[11] it can then be concluded that the layered structure of $C_{12}N–Nb_6O_{17}$ is stable on adsorption of phenols. However, $C_{12}N–Nb_6O_{17}$ exhibits different structural responses to the subsequent photocatalytic degradation of phenol and 2,4-DCP. XRD pattern changes dramatically for phenol: decreased peak intensity, splitting of the basal reflection (around $2\theta = 2–3°$) and the appearance of a new diffraction peak at $2\theta = 10.5°$ (attributed to proton-exchanged layered niobate, typically $H_2K_2Nb_6O_{17}$)[12] imply that part of the interlayer $C_{12}N^+$ is decomposed and resulted in partial collapse of the layered structure (Figure 2d). In contrast, the structure of $C_{12}N–Nb_6O_{17}$ remains unchanged after photodegradation of 2,4-DCP (Figure 2c). This result soundly indicates that although $C_{12}N–Nb_6O_{17}$ is a composite containing organic phase in the interlayer, in this case, its structure can keep solid even if the photocatalytic degradation process proceeds. The difference in hydrophobicity of the substrates is considered to be one of the reasons for the different structural responses. Since $C_{12}N–Nb_6O_{17}$ has better affinity for more hydrophobic species, it adsorbs more 2,4-DCP than phenol.[3] Large amounts of adsorbed 2,4-DCP in the interlayer not only enhances the photocatalytic activity but also protects the interlayer surfactant from being decomposed by consuming the photogenerated oxidative species (•OH, h^+). On the other hand, since phenol is much less adsorbed in the interlayer, part of the surfactant is then decomposed with phenol, which results in partial collapse of the layered structure and a decreased activity for degradation of phenol.

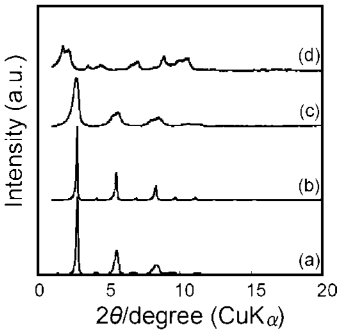

Figure 2. XRD patterns of $C_{12}N–Nb_6O_{17}$ (a), after adsorption of phenol (b), after photodegradation of 2,4-DCP (c), and phenol (d).

In conclusion, the organically modified niobate $C_{12}N–Nb_6O_{17}$ can remove organic pollutants, as exemplified by phenols, from aqueous solution through the adsorption–photocatalytic degradation process. In particular, it shows structural stability and a high efficiency on removal of more hydrophobic species 2,4-DCP by combining the adsorption and photocatalytic degradation effects.

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13 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/.

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