Adsorption and Possible Luminescence Detection of Nonylphenol by Eu^{3+}–Smectites

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4-Nonylphenol was effectively adsorbed on Eu^{3+}–smectites, which were prepared by cation exchange reactions of a natural montmorillonite and a synthetic saponite with Eu^{3+} chloride, from aqueous solutions. The appearance of luminescence bands of Eu^{3+} by the excitation of the adsorbed 4-nonylphenol was also observed.

4-Nonylphenol is a biodegradation product of alkylphenol polyethoxylate resin and has been found to be a major estrogenic contaminant to induce feminising effects.[1] The concentration of 4-nonylphenol by the adsorption on solids is a possible solution for the remediation. The removal of 4-nonylphenol by the adsorption onto various porous solids including activated carbons[2] and organically modified nanoporous silicas[3] has been reported. However, adsorbents with better performance (higher adsorption capability, selective adsorption, and stability) are still required. Here, we report the effective adsorption of 4-nonylphenol on Eu^{3+}–smectites from aqueous solution. Smectite group of layered clay minerals has been investigated as a building block of adsorbents of various organic species both from solution and vapor, since the structure is composed of ultrathin (1 nm) silicate layer and the tunable adsorptive properties by the replacement of the interlayer exchangeable cations with appropriate cationic species.[4–6] There is only a report on the adsorption of 4-nonylphenol on a smectite clay (montmorillonite).[7] In this case, only a trace amount of 4-nonylphenol was adsorbed on montmorillonite from water. In the present study, we have introduced Eu^{3+} in the interlayer space of smectites with the expectation that the interactions between Eu^{3+} and 4-nonylphenol are a driving force for the adsorption.

In addition to the concentration of 4-nonylphenol, the detection of its presence is also a topic of interest. In the present system, 4-nonylphenol was detected by the appearance of the luminescence bands of Eu^{3+} by the UV excitation of 4-nonylphenol probably through the energy transfer from 4-nonylphenol to Eu^{3+}.

Eu^{3+}–smectites were prepared from Na^{+}–montmorillonite (Kunipia F, obtained from Kunimine Ind., Co., reference clay sample of the Clay Science Society of Japan) and synthetic Na^{+}–saponite (Sumecton SA, supplied from Kunimine Ind. Co., synthesized by hydrothermal reactions, reference clay sample of the Clay Science Society of Japan) by the ion exchange reactions with EuCl$_3$ solution (water/ethanol (10/90; v/v)) for 1 day at room temperature. The gallery heights of the Eu^{3+}–smectites were determined by subtracting the thickness of the silicate layer (0.96 nm) from the observed basal spacings of 1.53 and 1.50 nm to be 0.57 and 0.54 nm for montmorillonite and saponite, respectively, indicating bilayer of water molecules in the interlayer spaces. The adsorbed amounts of Eu^{3+} on montmorillonite and saponite were determined by ICP analysis to be 102 and 71 mequiv. (100 g clay)$^{-1}$, respectively, which were close to the cation exchange capacities of montmorillonite (119 mequiv. (100 g clay)$^{-1}$) and saponite (71 mequiv. (100 g clay)$^{-1}$),[8] showing quantitative ion exchanges.

The adsorption of 4-nonylphenol on Eu^{3+}–smectites from aqueous solution was conducted by mixing of Eu^{3+}–smectites (10 mg) with 200 mL of aqueous solution of 4-nonylphenol (0.45–2.2 μM; 0.1–5 ppm) for 3 days at room temperature under dark. The adsorbents were separated by centrifugation and the concentration of 4-nonylphenol in the supernatant was determined by photoluminescence spectroscopy (excitation $\lambda_{\max}$ at 276 nm and emission $\lambda_{\max}$ at 304 nm) to determine the adsorbed amount of 4-nonylphenol. According to the Giles classification,[9] the adsorption isotherm of 4-nonylphenol for Eu^{3+}–montmorillonite (Figure 1) was conformed to type-L, showing strong adsorbate–adsorbent interactions. The maximum adsorbed amount was determined from Langmuir plot of the isotherm to be 0.29 mmol g^{-1} (correlation coefficient is 0.997). The basal spacing of Eu^{3+}–montmorillonite (1.53 nm) increased upon the adsorption of 4-nonylphenol to be 1.61 nm. The slope of the isotherm (1.4×10^2 L g^{-1}) for Eu^{3+}–montmorillonite system was quite larger than that for the reported raw montmorillonite (Na^{+}-form of Kunipia F) system[7] (1.5 L g^{-1}). It is thought that the interactions between Eu^{3+} and 4-nonylphenol play a role in the effective adsorption of 4-nonylphenol.

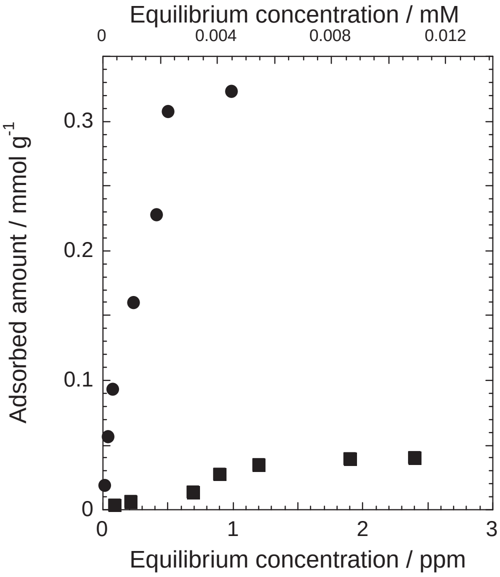

Figure 1. Adsorption isotherms of 4-nonylphenol on Eu^{3+}–smectites from aqueous solutions. Circle and square symbols designate Eu^{3+}–montmorillonite and Eu^{3+}–saponite, respectively.

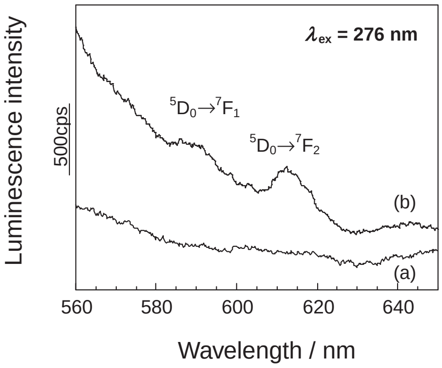

Figure 2. Photoluminescence spectra of (a) Eu^{3+}–montmorillonite and (b) Eu^{3+}–montmorillonite–4-nonylphenol.

In addition to the effect of the interlayer cations, the nature of silicate layer also affected the 4-nonylphenol adsorption. When Eu^{3+}–saponite was used as adsorbent, L-type isotherm was obtained (Figure 1). The maximum adsorbed amount was 0.04 mmol g^{-1}, which is smaller than that (0.29 mmol g^{-1}) for Eu^{3+}–montmorillonite system. It has been pointed out that the π-interactions between phenyl rings and oxygen plane on the silicate layer of smectites are a possible driving force for the adsorption of nonionic aromatic compounds.[5,10,11] The basicity of the oxygen plane depends on whether the smectite is di- or tri-octahedral subgroup.[12] The larger surface basicity for montmorillonite (di-octahedral subgroup) compared with saponite (tri-octahedral subgroup)[13] is a origin of the observed effective adsorption of 4-nonylphenol on Eu^{3+}–montmorillonite.

The maximum adsorbed amount of 4-nonylphenol on Eu^{3+}–montmorillonite (0.29 mmol g^{-1}) is in the same range of the amount of 4-nonylphenol adsorbed on the reported organically modified nanoporous silica (0.8 mmol g^{-1}),[3] while that is almost still smaller if compared with activated carbons (a few mmol g^{-1}),[2] partly due to the density of carbon and silicate based materials. Besides the adsorbent characteristic, the present Eu^{3+}–montmorillonite shows a unique photoluminescence characteristic for possible detection.

The photoluminescence spectrum[14] of the product obtained after the adsorption of 4-nonylphenol on Eu^{3+}–montmorillonite is shown in Figure 2, together with that of Eu^{3+}–montmorillonite. The photoluminescence of Eu^{3+} ($^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ transitions) for Eu^{3+}–montmorillonite–4-nonylphenol was observed at 592 and 614 nm, respectively (Figure 2b) at the excitation wavelength of 276 nm (π–π^* transition of 4-nonylphenol). On the contrary, luminescence was not observed by the excitation of Eu^{3+} (394 nm) before and after the adsorption of 4-nonylphenol. 4-Nonylphenol was thought to act as a quencher of the excited Eu^{3+}. We assumed that the possibility of the energy transfer from 4-nonylphenol to Eu^{3+} was larger than that of thermally competitive back energy transfer from the excited state of Eu^{3+} to triplet-excited state of 4-nonylphenol. Quenching of Eu^{3+} luminescence by iron in the structure of montmorillonite is expected to be a reason of the phenomenon as reported for Eu^{3+} exchanged montmorillonite.[15] The luminescence intensities ($^5D_0$–$^7F_1$) observed for the Eu^{3+}–saponite–4-nonylphenol system (5×10^1–1×10^2 cps) are in the same range of those (5×10^1–3×10^2 cps) for the Eu^{3+}–montmorillonite–4-nonylphenol system. Therefore, the adsorbed water molecules are also thought to deactivate the excited state of Eu^{3+}. The photoluminescence was not observed for the aqueous suspension of the Eu^{3+}–montmorillonite containing 4-nonylphenol, while that for the powder after the removal of water was observed as shown in Figure 2b. Thus, the present results on the appearance of luminescence are accounted for the replacement of the adsorbed water molecules located close to Eu^{3+} with 4-nonylphenol.

This work demonstrates that Eu^{3+}–montmorillonite adsorbed 4-nonylphenol effectively from aqueous solution as a result of interactions between Eu^{3+} and 4-nonylphenol as well as those between silicate layer and 4-nonylphenol. We also reported the appearance of photoluminescence of Eu^{3+} by the excitation of 4-nonylphenol, which can be applied for the detection of 4-nonylphenol. Since montmorillonite is an abundant natural resource and chemically and thermally stable, the application to adsorbents (for example, selective adsorption for 4-nonylphenol) is worth further investigating.

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14 Steady-state luminescence spectra were recorded on a HITACHI F-4500 fluorospectrophotometer. The spectra were recorded as powder, which composed MgO (50 mg) and Eu^{3+}–montmorillonite–4-nonylphenol (10 mg). Scanning speed of the spectrometer was 60 nm min^{-1}.

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