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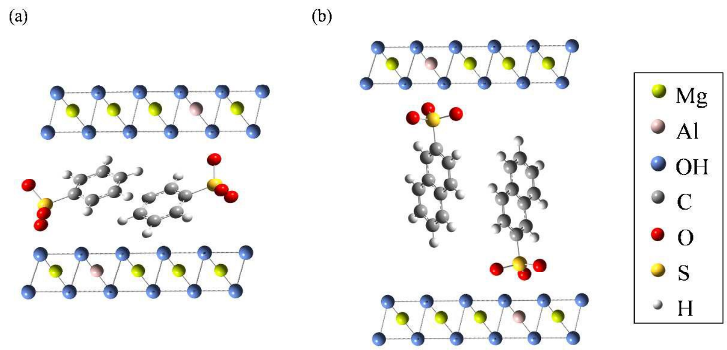

Both (a) benzenesulfonate and (b) 2-naphthalenesulfonate intercalated in the Mg−Al LDH tend to orient perpendicularly as concentration increases.

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Kinetics and equilibrium studies on the removal of aromatic sulfonates from aqueous solution by Mg–Al oxide

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Abstract

Mg–Al oxide, which was obtained via the thermal decomposition of Mg–Al layered double hydroxides (LDHs) intercalated with CO_3^{2-} ($CO_3 \cdot$Mg–Al LDH), was confirmed to take up benzenesulfonate (BS^-) and 2-naphthalenesulfonate (NS^-) in aqueous solution. The removal of BS^- or NS^-, which can be described by pseudo-first-order reaction kinetics, proceeded under chemical reaction control. This process followed a Langmuir-type adsorption; the maximum and equilibrium adsorption constants for NS^- were larger than those for BS^-. Our results suggests that the Mg-Al oxide reacts more favorably with aromatic sulfonates with lower charge density and that the effect of hydrophobic interactions is larger than that of electrostatic interactions. In the initial reaction stage, Mg-Al oxide rehydrates and combines with an aromatic sulfonate to reconstruct the LDH structure; then, the aromatic sulfonates interact in aqueous solution through hydrophobic interactions, facilitating their removal by the Mg-Al oxide. Because the attraction of NS^- molecules is stronger than that of BS^- molecules, the removal of NS^- by the Mg-Al oxide was found to be more efficient than that of BS^-.

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Introduction

Mg–Al layered double hydroxides (Mg–Al LDHs) are typically represented by the formula $[Mg^{2+}_{1-x}Al^{3+}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$, where x is the $Al^{3+}/(Mg^{2+} + Al^{3+})$ molar ratio ($0.20 \leq x \leq 0.33$), and A^{n-} is an anion such as CO_3^{2-} or Cl^-.[1-4] They consist of a stack of Al^{3+}-bearing brucite-like octahedral layers in which the charge of the positive layer is neutralized by the interlayer anions. The interlayer space is also occupied by water molecules present in the hydration shells of these intercalated anions. Mg–Al LDHs intercalated with CO_3^{2-} ($CO_3\cdot$Mg–Al LDH) can be converted into Mg–Al oxides by calcination at 450–800 °C, as expressed by Equation 1:

$$Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \rightarrow Mg_{1-x}Al_xO_{1+x/2} + x/2CO_2 + H_2O \qquad (1)$$

The Mg–Al oxide can then rehydrate and combine with anions to reconstruct the LDH structure:

$$Mg_{1-x}Al_xO_{1+x/2} + x/n\ A^{n-} + (1+x/2)H_2O \rightarrow Mg_{1-x}Al_x(OH)_2A_{x/n} + xOH^- \qquad (2)$$

Recently, Mg–Al oxides have been used to remove organic anions such as Acid Orange 10, Acid Blue, and methyl orange from aqueous solution.[5-7] The adsorption process in the removal of Acid Orange 10 follows a Langmuir model and can be represented by pseudo-second-order reaction kinetics.[5] Mg-Al oxide was found to be superior to activated carbon for the removal of Acid Orange 10 .[5,8] In the removal of inorganic anions

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by Mg-Al LDH and Mg-Al oxide, an anion with a high charge density is more easily intercalated in the interlayer of Mg-Al LDH than an anion with a low charge density.[9,10] However, the principles involved in the removal of organic anions by Mg-Al LDH and Mg-Al oxide are unknown. It is unclear whether an organic anion with a high charge density is more easily intercalated in the interlayer of Mg-Al LDH than an organic anion with a low charge density, as well as than an inorganic anion. Different factors may affect the intercalation of organic anions in the interlayer of Mg-Al LDH. On the other hand, Mg–Al LDHs intercalated with dodecylsulfate (DS^-), 2-naphthalenesulfonate (NS^-), and 2,6-naphthalene disulfonate (2,6-NDS^{2-}) were found to show an uptake capacity for bisphenol A in an aqueous solution, probably because of the hydrophobic interactions between the benzene rings of bisphenol A and the aromatic anion intercalated in the interlayer.[11,12] The uptake of bisphenol A was not based on the anion-uptake property of Mg-Al LDH and Mg-Al oxide, because bisphenol A is nonionic. We have clarified that Mg-Al LDH modified with an organic anion could take up nonionic organic substances owing to hydrophobic interactions.[11,12] Such hydrophobic interactions are predicted to affect the removal of organic anions by Mg-Al LDH and Mg-Al oxide. In this study, this hypothesis was examined for the reconstruction of Mg-Al LDH from Mg-Al oxide. In particular, the removal of aromatic sulfonates such as benzenesulfonate (BS^-) and NS^- by

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the Mg-Al oxide from aqueous solution was investigated for studying the equilibrium and kinetics involved in the removal process. Figure 1 shows the molecular structures of BS^- and NS^-; the molecular geometry of the isolated BS^- and NS^- in the ground state was calculated at the Hartree-Fock/STO-3G level of theory with Gaussian 03.[13] The molecular lengths increase in the order of $BS^- < NS^-$, but the charge density decreases in the order of $BS^- > NS^-$. The effects of the hydrophobic interactions and charge density of the anion on the removal of BS^- and NS^- by the Mg-Al oxide were also investigated.

Experimental

All chemicals were reagent grade and used without further purification. The Mg-Al oxide was obtained by the thermal decomposition of Mg–Al LDH intercalated with CO_3^{2-} (CO_3·Mg–Al LDH), which was prepared using the method described in our previous paper.[14] The Mg-Al oxide contained 39.3 wt% Mg and 10.7 wt% Al, with the Mg/Al molar ratio being 4.1. We prepared BS^- and NS^- solutions by dissolving $C_6H_5NaO_3S$ and $C_{10}H_7NaO_3S$ in deionized water, respectively. The Mg–Al oxide was added to 2 mmol/L BS^- or NS^- solutions (500 mL), and the resultant suspensions were stirred at 10–60 °C for 1440 min. N_2 was bubbled through the solutions throughout the

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procedure, and pH was continuously measured during the reaction. Samples of the suspensions were withdrawn at different time intervals and immediately filtered through a 0.45-μm membrane filter. The filtrates were analyzed for residual BS^- or NS^-. The Mg–Al oxide was used in stoichiometric quantity for BS^- or NS^- removal, as shown in Equations (3) and (4):

$$Mg_{0.8}Al_{0.2}O_{1.1} + 0.2C_6H_5O_3S^- + 1.1H_2O \rightarrow Mg_{0.8}Al_{0.2}(OH)_2(C_6H_5O_3S)_{0.2} + 0.2OH^- \quad (3)$$

$$Mg_{0.8}Al_{0.2}O_{1.1} + 0.2C_{10}H_7O_3S^- + 1.1H_2O \rightarrow Mg_{0.8}Al_{0.2}(OH)_2(C_{10}H_7O_3S)_{0.2} + 0.2OH^- \quad (4)$$

To determine the adsorption isotherm of BS^- or NS^- adsorbed by the Mg–Al oxide, BS^- or NS^- solution (50 mL, 1–15 mM) and Mg–Al oxide (0.1 g) were placed in 100-mL screw-top tubes and shaken at 10–60 °C for 1440 min.

The materials were analyzed using XRD with Cu Kα radiation. For the adsorption experiments, the residual concentrations of BS^- or NS^- in the filtrates were determined using HPLC.

Results and Discussion

Kinetics and equilibrium studies of the removal of aromatic sulfonates

Figures 2 and 3 show the effect of temperature on the degree of BS^- and NS^- removal by

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the suspension of Mg−Al oxide in the BS^- and NS^- solutions. In both the adsorbates, the removal increased with time at all temperatures. The Mg-Al oxide was confirmed to take up BS^- and NS^- in aqueous solution according to Equations (3) and (4). For BS^-, the removal rate increased with the temperature at any given time. For NS^-, the removal rate increased with the temperature within 120 min of beginning the process. Figures 4 and 5 show the effect of temperature on pH variation during BS^- or NS^- removal by the suspension of the Mg−Al oxide in the BS^- or NS^- solution. At all temperatures, the pH increased rapidly with time, until it attained the pH of 10–12 and remained constant. This increase in the pH values is attributed to the release of OH^-, as shown in Equations (3) and (4). The accelerated rate of BS^- or NS^- removal at higher temperatures in the initial reaction stage implies that the reaction proceeds under chemical reaction control. Therefore, the kinetics of BS^- or NS^- removal by the Mg–Al oxide was examined until 60 min in order to check the initial reaction rate. First-order kinetics, which depends on the concentration of BS^- or NS^-, can be expressed as follows:

$$-\ln(1 - x) = kt, \tag{5}$$

where x is the degree of BS^- or NS^- removal, t (min) is the reaction time, and k (min^{-1}) is the rate constant for BS^- or NS^- removal. Figures 6 and 7 show the pseudo-first-order plot of BS^- or NS^- removal by the suspension of Mg−Al oxide in BS^- or NS^- solution. In both

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cases, a good linearity was obtained at all temperatures, indicating that BS^- or NS^- removal can be represented by pseudo-first-order reaction kinetics. For BS^-, the apparent rate constants at 10, 30, and 60 °C were found to be 4.7×10^{-3}, 1.4×10^{-2}, and 1.0×10^{-1} min^{-1}, respectively; for NS^-, the corresponding values were 6.0×10^{-3}, 2.2×10^{-2}, and 8.8×10^{-2} min^{-1}, respectively. Thus, the apparent rate constants clearly increased with temperature. An Arrhenius plot of the rate constants (Figure 8) yields an apparent activation energy of 48 and 42 kJ mol^{-1} for BS^- and NS^- removal, respectively. These values confirm that BS^- or NS^- removal by the Mg–Al oxide proceeded under chemical reaction control. This chemical reaction involves the adsorption of BS^- or NS^- by the Mg-Al oxide according to Equations (3) and (4).

Table 1 shows the equilibrium concentration, pH, and relative distribution ratio (*K*) values after the formation of the Mg−Al oxide suspension in the BS^- or NS^- solution. In particular, *K* for the removal of OH^- and BS^- or NS^- by the Mg−Al oxide is defined as follows:

$$K = K_{d,A}/K_{d,OH}\ [\underline{K}_{d,A} = m_A\ (\text{Solid})/m_A\ (\text{Soln.}),\ K_{d,OH} = m_{OH}\ (\text{Solid})/m_{OH}\ (\text{Soln.})] \quad (6)$$

In this case, m_A (Solid) and m_A (Soln.) indicate the amount of BS^- or NS^- in solid and solution, respectively; and m_{OH} (Solid) and m_{OH} (Soln.) represent the amount of OH^- in solid and solution, respectively. *K* values followed the order: $NS^- > BS^-$. The Mg−Al

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oxide was found to take up NS^- more preferentially than BS^-. However, the *K* values for BS^- and NS^- were lower than 1, suggesting that the Mg–Al oxide took up OH^- more preferentially than BS^- and NS^-. Thus, the *K* values followed the order: $OH^- > NS^- > BS^-$. OH^- is produced by the rehydration of the Mg-Al oxide, according to Equations (3) and (4). This is supported by the fact that the solution pH values increase (Figures 4 and 5). As shown in Figures 2 and 3, the Mg-Al oxide cannot take up large amounts of BS^- and NS^- from aqueous solution at the stoichiometric quantity. This is because of the intercalation of the produced OH^- in the interlayer of Mg-Al LDH according to Equation (7).

$$Mg_{0.8}Al_{0.2}O_{1.1} + 0.2OH^- + 1.1H_2O \rightarrow Mg_{0.8}Al_{0.2}(OH)_2(OH)_{0.2} + 0.2OH^- \quad (7)$$

Figures 9 and 10 show the adsorption isotherms for the adsorption of BS^- or NS^- by the Mg–Al oxide. In both the adsorbates, the equilibrium-adsorption amount increased proportionally with the equilibrium concentration at all temperatures. The adsorption isotherms did not follow adsorption models such as Halsey and Henderson models; instead, they appeared a Langmuir-type behavior, as confirmed by using the experimental data in the Langmuir equation shown below:

$$q_e = C_e q_m K_L/(1 + C_e K_L), \quad (8)$$

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where q_e (mmol g^{-1}) is the equilibrium adsorption, C_e (mM) is the equilibrium concentration, q_m (mmol g^{-1}) is the maximum adsorption, and K_L is the equilibrium adsorption constant. This equation can also be expressed as:

$$C_e/q_e = 1/q_mK_L + C_e/q_m. \quad (9)$$

Figures 11 and 12 show a plot of C_e/q_e versus C_e of the adsorption isotherms for the adsorption of BS^- or NS^- by the Mg–Al oxide. In all cases, a good linearity was obtained, confirming that this process follows a Langmuir-type adsorption. Table 2 lists the values of q_m and K_L of BS^- and NS^- adsorbed by the Mg−Al oxide, as determined from the slope and intercept of the linear fit of the data given in Figures 11 and 12. At all temperatures, the maximum and equilibrium adsorption constants for NS^- were larger than those for BS^-. These results also indicate that the Mg−Al oxide can take up NS^- more easily than BS^-.

The results of the kinetics and equilibrium studies clearly suggest that the Mg−Al oxide can be more easily combined with NS^- than with BS^-, i.e., the Mg-Al oxide reacts more favorably with aromatic sulfonates with lower charge density, unlike in the removal of inorganic anions. The effect of hydrophobic interactions is larger than that of electrostatic interactions in the removal of aromatic sulfonates by the Mg-Al oxide. Usually, inorganic anion removal by the Mg-Al oxide is promoted by electrostatic

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interactions, and the order of the inorganic anion removal is controlled by its charge density. It is known that the aromatic rings of two aromatic sulfonates interact via hydrophobic interactions in aqueous solution. The hydrophobic interactions of NS^- molecules are stronger than those of the BS^- molecules, because NS^- has a naphthalene ring in its structure and BS^- has a benzene ring. In contrast, the electrostatic interactions of NS^- are typically weaker than those of BS^-, because its charge density is lower than that of BS^-. In the initial reaction stage, the Mg-Al oxide rehydrates and combines with aromatic sulfonate to reconstruct the LDH structure. Then, the aromatic sulfonate intercalated in the interlayer of the reconstructed Mg-Al LDH attracts the aromatic sulfonate in aqueous solution via hydrophobic interactions, which may promote the removal of the aromatic sulfonate by the Mg-Al oxide. Because the attraction of NS^- molecules is stronger than that of BS^- molecules, the removal of NS^- by the Mg-Al oxide is more efficient than that of BS^-. Notably, the removal of the aromatic sulfonate by the Mg-Al oxide is controlled by hydrophobic interactions.

Molecular orientation of aromatic sulfonates in the interlayer of Mg−Al LDH

Figures 13 and 14 show the XRD patterns of the products obtained by the suspension of Mg−Al oxide in BS^- and NS^- solutions at 30 ºC. The XRD peaks for all the products can be assigned to hydrotalcite (JCPDS card 22-700), indicating that the LDH

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structure was formed after the removal of BS^- and NS^-. This confirms the reconstruction of Mg–Al LDH from the Mg–Al oxide with the intercalation of BS^- and NS^-, as shown in Equations (3) and (4). Because the XRD peaks of LDH are generally indexed on the basis of a hexagonal unit cell, the basal spacing of LDH is equivalent to $1/n^{th}$ of the c parameter, where n is the number of the layer repeat of the unit cell.[15] The basal spacing consists of an Al-bearing brucite-like octahedral layer, whose thickness and interlayer spacing are affected by the size and orientation of the interlayer anion. Based on the XRD patterns, basal spacing d_{003} in the product (Ce = 0.5 mmol L^{-1}) obtained by the suspension of Mg−Al oxide in BS^- solution was calculated to be 8.1 Å (Figure 13(a)). Assuming a brucite-like layer thickness of approximately 4.8 Å, as reported by Miyata,[16] the interlayer spacing is calculated to be 3.3 Å. In this case, the molecular structures of BS^- and NS^- contain a planar-structured aromatic ring, and the molecular size in the direction perpendicular to the planar structure is determined by the size of the $-SO_3^-$ group. As reported in our previous study, the molecular size in this direction is 3.1 Å.[17] This is very close to the interlayer spacing of 3.3 Å for the product with Ce = 0.5 mmol L^{-1}. Therefore, the benzene ring of BS^- may be oriented parallel to the brucite-like host layers of Mg-Al LDH (Figure 15(a)); basal spacing d_{003} in the product (for Ce = 2.8–9.5 mmol L^{-1}) was found to be around 9 Å (Figures 13(b)–(d)), and the interlayer spacing is calculated to be

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4.2 Å, which expands from that of the product (for *Ce* = 0.5 mmol L^{-1}). As shown in Figure 9 and 13, the equilibrium adsorption amounts and the XRD patterns for *Ce* = 2.8–9.5 mmol L^{-1} were almost similar. This suggests the benzene rings of BS^{-} have a similar orientation in the interlayer of Mg-Al LDH. The interlayer spacing is larger than the molecular size in the direction perpendicular to the planar structure, as determined by the size of the $-SO_3^-$ group. Therefore, the two benzene rings of BS^- may overlap in the brucite-like host layers of Mg-Al LDH (Figure 15(b)). Because the XRD peak at a 2θ value of 22° was observed for the products for *Ce* = 2.8–9.5 mmol L^{-1} as well as for *Ce* = 0.5 mmol L^{-1} (Figure 13), the orientation of the benzene ring of BS^{-} (Figure 15(a)) is considered to be also remained for the products for *Ce* = 2.8–9.5 mmol L^{-1}. Because of their weaker hydrophobic attractions, the BS^- molecules cannot be fully accommodated in the interlayer of Mg-Al LDH (such as in the case of perpendicular orientation). However, data in Figures 13(b)–(d) support the presence of hydrophobic interactions between the benzene rings of BS^{-} in the interlayer of Mg-Al LDH.

In addition, basal spacing d_{003} in the product (Ce = 0.03 mmol L^{-1}), which was obtained by the suspension of Mg−Al oxide in the NS^- solution, was found to be 8.3 Å (Figure 14(a)), and the interlayer spacing was calculated to be 3.5 Å. This is very close to the molecular size in the direction perpendicular to the planar-structured naphthalene ring

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as determined by the size of the $-SO_3^-$ group. This indicates that the naphthalene ring of NS^- may be oriented along an arrangement that is parallel to the brucite-like host layers of Mg-Al LDH (Figure 16(a)). Figure 14(b) displays the expansion of basal spacing d_{003} from 8.3 to 9.0 Å. As shown in Figure 10, the equilibrium adsorption amount increased as *Ce* increased from 0.03 to 1.1 mmol L^{-1}. Because the XRD shoulder peak is also observed at a 2θ value of 5º (Figure 14(b)), the orientation of the naphthalene ring of NS^- is probably different from that shown in Figure 16(a). Figures 14(c) and (d) show spacings d_{003} and d_{006} of around 19 and 9 Å, respectively, which indicate an interlayer spacing of around 14 Å. This value is larger than the molecular size (9.16 Å) of NS^- (Figure 1(b)). Therefore, the naphthalene ring of NS^- may be oriented along an arrangement that is perpendicular to the brucite-like host layers of Mg-Al LDH (Figure 16(b)). This phenomenon has also been reported in our previous paper.[17-19] In particular, the XRD patterns for the NS^--intercalated Mg–Al LDH prepared by co-precipitation[18] are similar to those for the products obtained by the suspension of the Mg-Al oxide in NS^- solution. Data in Figure 14(b) also suggest the presence of the perpendicular orientation. Because of their stronger hydrophobic attraction, NS^- molecules can be effectively accommodated in the interlayer of Mg-Al LDH in a perpendicular orientation. Figures 14(b)–(d) confirm the presence of hydrophobic interactions between the benzene rings of NS^- in the

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interlayer of Mg-Al LDH.

Effect of temperature at longer time durations

Table 2 shows that the maximum and equilibrium adsorption constants decrease when the temperature is increased from 30 to 60 ºC for both BS^- and NS^-. Table 3 shows the amount of BS^- and NS^- removed by the Mg−Al oxide at 1440 min. At 60 ºC, the BS^- removal was determined to be 44.5% at 180 min (Figure 2), decreasing to 12.9% at 1440 min. At the same temperature, the NS^- removal was found to be 38.8% at 240 min (Figure 3), decreasing to 23.3% at 1440 min. At 1440 min, while the amounts of BS^- and NS^- removed decreased at 60 ºC, they were almost constant at 10 and 30 ºC. Table 4 shows the change in the pH value on BS^- and NS^- removal by the Mg−Al oxide at 1440 min. For both adsorbates, the pH values at 10 and 30 ºC were almost constant from the last points shown in Figures 4 and 5 to 1440 min. However, at 60 ºC, the pH value on BS^- removal was determined to be 10.7 at 180 min (Figure 4), decreasing to 10.4 at 1440 min. At the same temperature, the pH value on NS^- removal was found to be 10.4 at 240 min (Figure 5), decreasing to 10.2 at 1440 min. These results suggest that OH^- was anion-exchanged with BS^- and NS^- intercalated in the Mg-Al LDH interlayer at 60 ºC, as shown in Equations. (10) and (11).

$$Mg_{0.8}Al_{0.2}(OH)_2(C_6H_5O_3S)_{0.2} + 0.2OH^- \rightleftarrows Mg_{0.8}Al_{0.2}(OH)_2(OH)_{0.2} + 0.2C_6H_5O_3S^- \quad (10)$$

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$$Mg_{0.8}Al_{0.2}(OH)_2(C_{10}H_7O_3S)_{0.2} + 0.2OH^- \rightleftarrows Mg_{0.8}Al_{0.2}(OH)_2(OH)_{0.2} + 0.2C_{10}H_7O_3S^- \quad (11)$$

Although the removal of BS^- and NS^- by Mg−Al oxide was promoted in the initial reaction stage at 60 ºC, the intercalation of OH^- was probably promoted in the second reaction stage owing to the increased activity of OH^- at 60 ºC. This is in agreement with the findings discussed above that K follows the order $OH^- > NS^- > BS^-$. In the case of the lower OH^- activity at 10 and 30 ºC, the anion exchange of the intercalated BS^- and NS^- with OH^- is not promoted in the second reaction stage.

Conclusions

Data presented in this work confirmed that Mg-Al oxide can take up benzenesulfonate (BS^-) and 2-naphthalenesulfonate (NS^-) from aqueous solution, and that the removal can be described by pseudo-first-order reaction kinetics. BS^- or NS^- removal by Mg–Al oxide proceeds under chemical reaction control. Interestingly, our data showed that the Mg−Al oxide preferentially takes up OH^- over BS^- and NS^-, with relative distribution ratio (K) following the order: $OH^- > NS^- > BS^-$. This process follows a Langmuir-type adsorption, and the maximum and equilibrium adsorption constant for NS^- were larger than those for BS^-, confirming that the Mg-Al oxide reacts more

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favorably with NS^- than with BS^-. The fact that Mg-Al oxide preferentially reacts with aromatic sulfonates with lower charge density is in contrast to the trend observed for the removal of inorganic anions. For the removal of aromatic sulfonates, the effect of the hydrophobic interactions is larger than that of electrostatic interactions. Although the order of the inorganic anion removal is controlled by the charge density, the removal of aromatic sulfonates by the Mg-Al oxide was found to be controlled by hydrophobic interactions. In the initial reaction stage, the Mg-Al oxide rehydrates and combines with the aromatic sulfonate to reconstruct the layered double hydroxide (LDH) structure. Then, the aromatic sulfonate, intercalated in the interlayer of the reconstructed Mg-Al LDH, interacts with the aromatic sulfonates via hydrophobic interactions, which facilitates their removal. Because the attraction of NS^- molecules is stronger than that of BS^- molecules, the removal of NS^- by the Mg-Al oxide was found to be more efficient. For BS^-, the benzene ring is possibly oriented along an arrangement that is parallel to the brucite-like host layers of Mg-Al LDH in the case of a low equilibrium concentration (Ce). With increasing *Ce*, the two benzene rings may overlap. For NS^-, the naphthalene ring may be oriented along an arrangement that is parallel to the brucite-like host layers of Mg-Al LDH in the case of a low *Ce*. With increasing *Ce*, the naphthalene ring of NS^- is possibly oriented along an arrangement that is perpendicular to the brucite-like host

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layers of Mg-Al LDH.

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Figure legends

Fig. 1. Molecular structure of (a) BS^- and (b) NS^-.

Fig. 2. Effect of temperature on the degree of BS^- removal by the suspension of the Mg−Al oxide in BS^- solution.

Fig. 3. Effect of temperature on the degree of NS^- removal by the suspension of the Mg−Al oxide in NS^- solution.

Fig. 4. Effect of temperature on pH variation during BS^- removal by the suspension of the Mg−Al oxide in BS^- solution.

Fig. 5. Effect of temperature on pH variation during NS^- removal by the suspension of the Mg−Al oxide in NS^- solution.

Fig. 6. Pseudo-first-order plot of BS^- removal by the suspension of the Mg−Al oxide in BS^- solution.

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Fig. 7. Pseudo-first-order plot of NS^- removal by the suspension of the Mg−Al oxide in NS^- solution.

Fig. 8. Arrhenius plot of the apparent rate constant of BS^- and NS^- removal by the suspension of the Mg−Al oxide in BS^- and NS^- solutions.

Fig. 9. Adsorption isotherm of BS^- adsorbed by the Mg−Al oxide for 1440 min.

Fig. 10. Adsorption isotherm of NS^- adsorbed by the Mg−Al oxide for 1440 min.

Fig. 11. C_e versus C_e/q_e plots for the adsorption isotherm of BS^- adsorbed by the Mg−Al oxide.

Fig. 12. C_e versus C_e/q_e plots for the adsorption isotherm of NS^- adsorbed by the Mg−Al oxide.

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Fig. 13. XRD patterns for the products obtained by the suspension of the Mg−Al oxide in BS^- solution at 30 ºC; (a) *Ce* = 0.5 mmol L^{-1}, (b) *Ce* = 2.8 mmol L^{-1}, (c) *Ce* = 5.0 mmol L^{-1}, (d) *Ce* = 9.5 mmol L^{-1}.

Fig. 14. XRD patterns for the products obtained by the suspension of the Mg−Al oxide in NS^- solution at 30 ºC; (a) *Ce* = 0.03 mmol L^{-1}, (b) *Ce* = 1.1 mmol L^{-1}, (c) *Ce* = 2.9 mmol L^{-1}, (d) *Ce* = 7.7 mmol L^{-1}.

Fig. 15. Proposed molecular orientation of BS^- intercalated in the interlayer of Mg−Al LDH; (a) *Ce* = 0.5 mmol L^{-1}, (b) *Ce* = 2.8–9.5 mmol L^{-1}.

Fig. 16. Proposed molecular orientation of NS^- intercalated in the interlayer of Mg−Al LDH. (a) *Ce* = 0.03 mmol L^{-1}, (b) *Ce* = 2.9–7.7 mmol L^{-1}.

Table captions

Table 1. Equilibrium concentration and pH and relative distribution ratio (*K*) after the suspension of the Mg−Al oxide in BS^- or NS^- solution.

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Table 2. Values of q_m and K_L on BS^- and NS^- adsorbed by the Mg−Al oxide.

Table 3. BS^- and NS^- removal by the Mg−Al oxide at 1440 min.

Table 4. pH value on BS^- and NS^- removal by the Mg−Al oxide at 1440 min.

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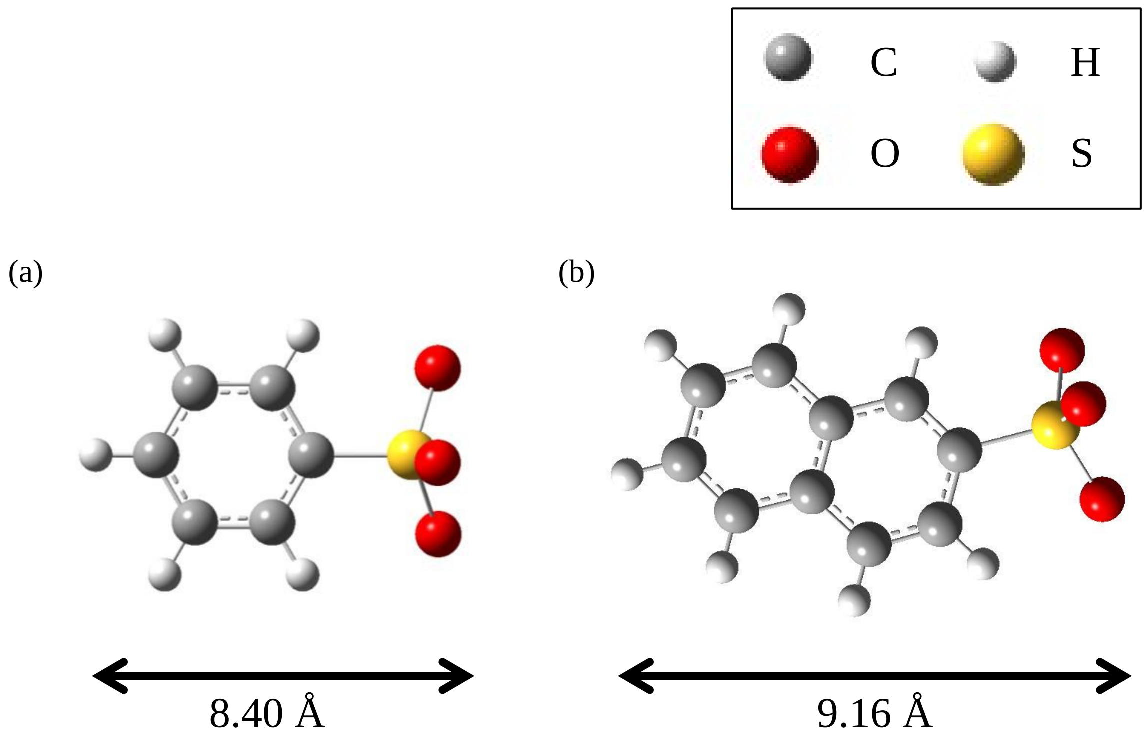

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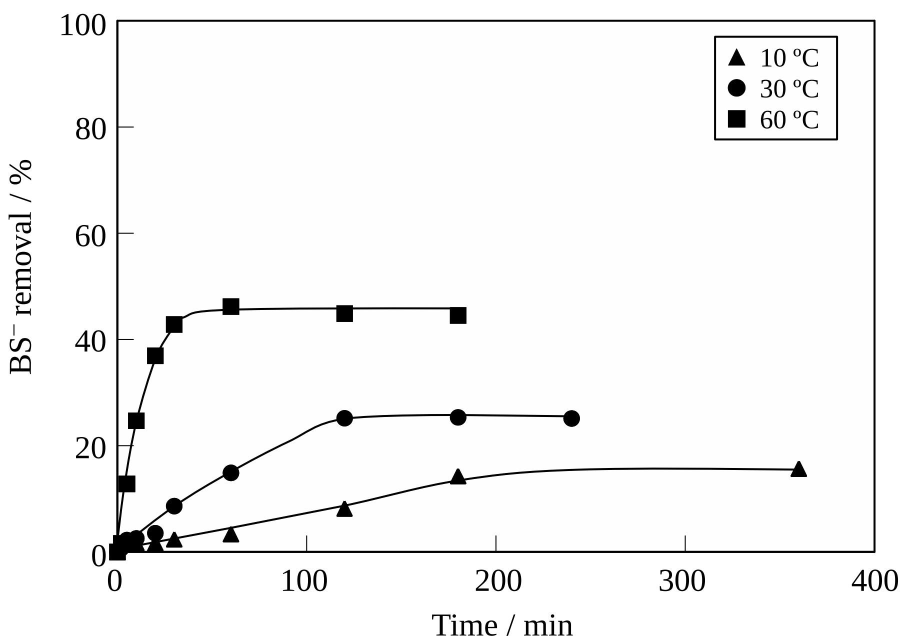

Fig. 2. Effect of temperature on the degree of BS^- removal by the suspension of the Mg−Al oxide in BS^- solution.

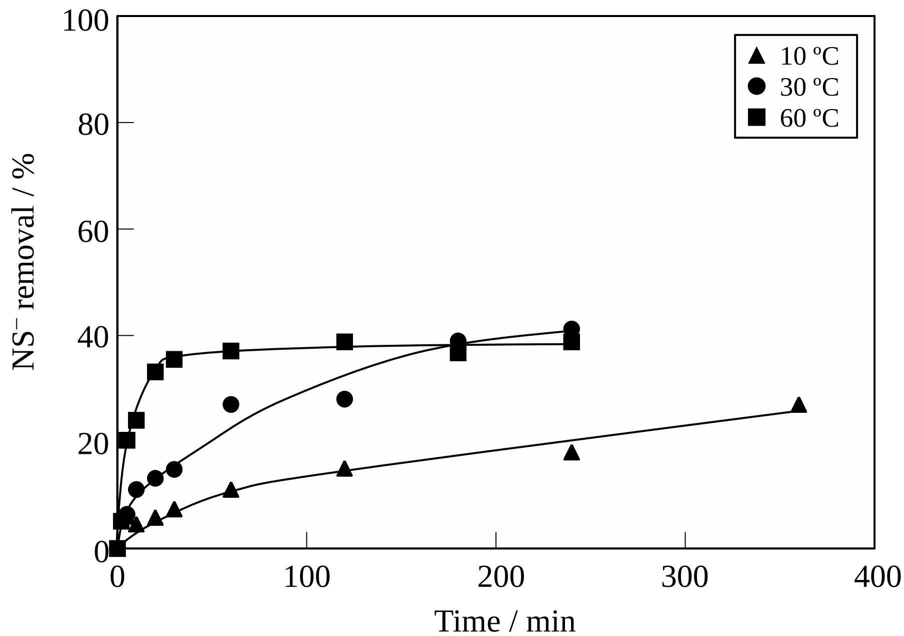

Fig. 3. Effect of temperature on the degree of NS^- removal by the suspension of the Mg−Al oxide in NS^- solution.

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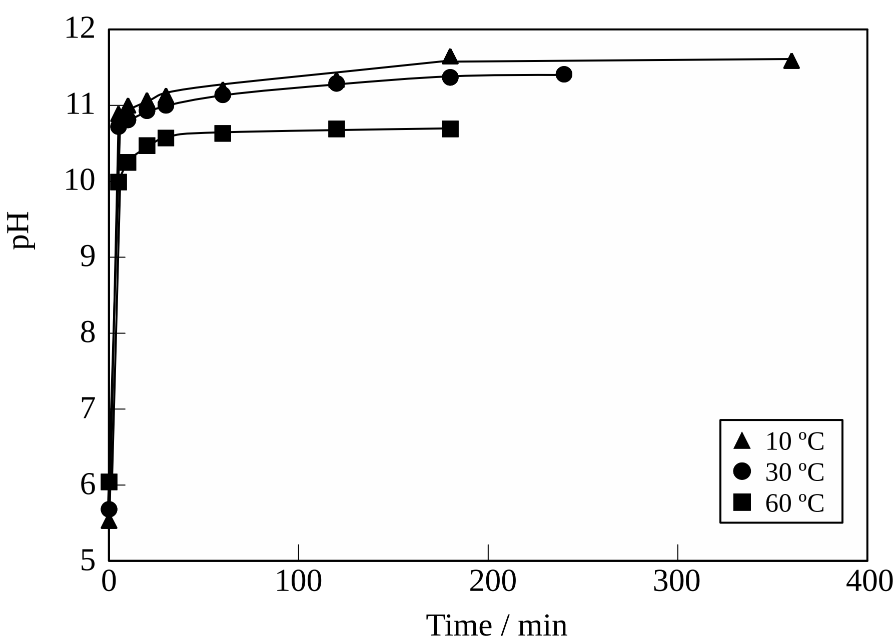

Fig. 4. Effect of temperature on pH variation during BS^- removal by the suspension of the Mg−Al oxide in BS^- solution.

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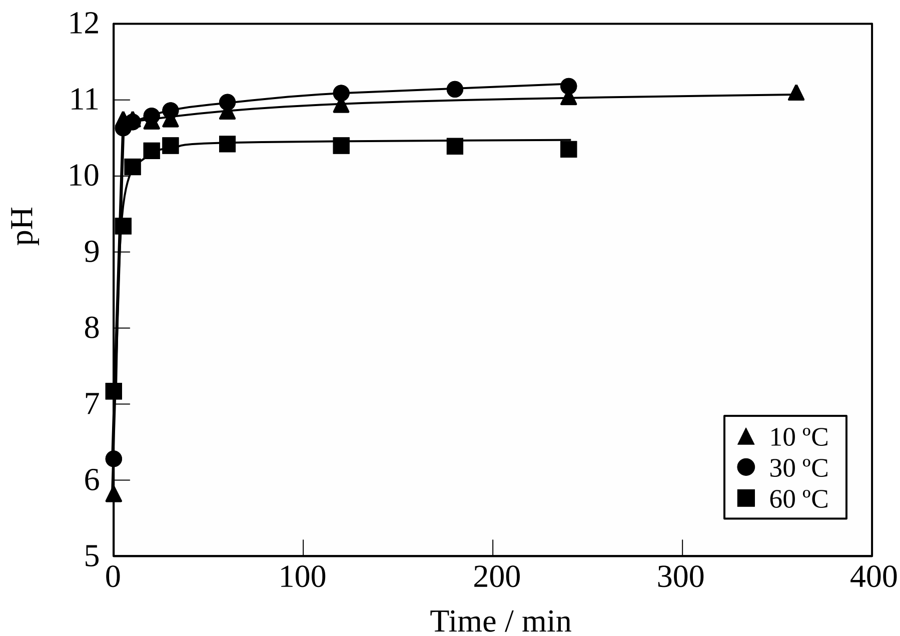

Fig. 5. Effect of temperature on pH variation during NS^- removal by the suspension of the Mg–Al oxide in NS^- solution.

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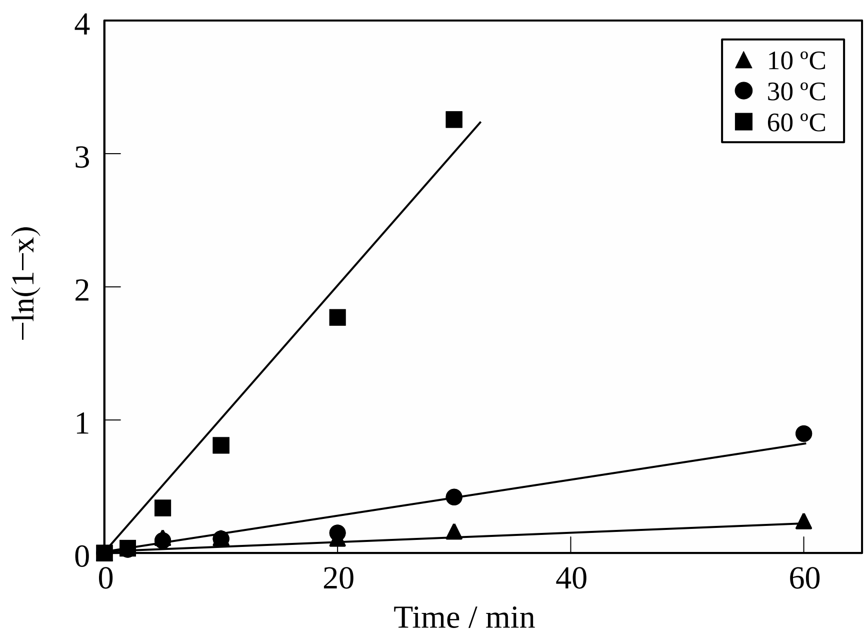

Fig. 6. Pseudo-first-order plot of BS^- removal by the suspension of the Mg−Al oxide in BS^- solution.

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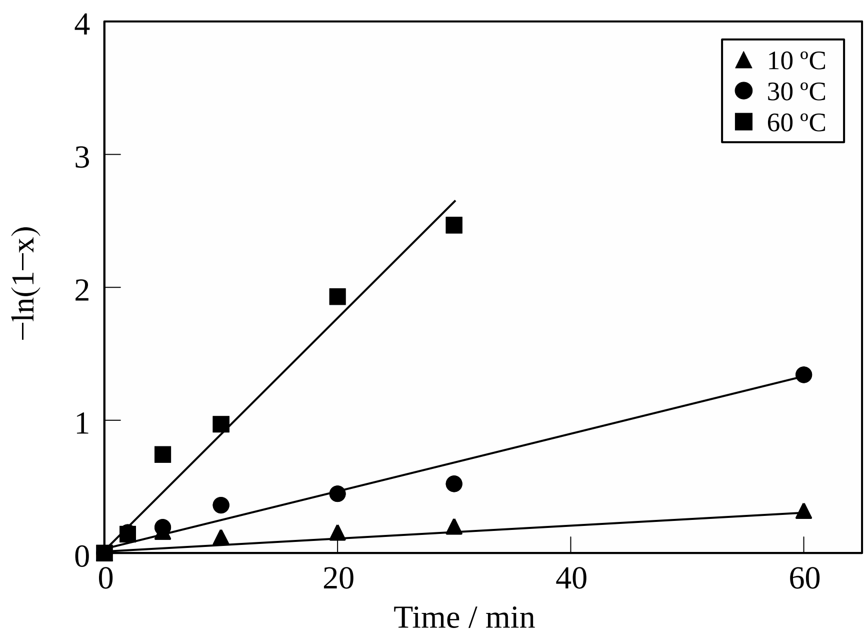

Fig. 7. Pseudo-first-order plot of NS^- removal by the suspension of the Mg−Al oxide in NS^- solution.

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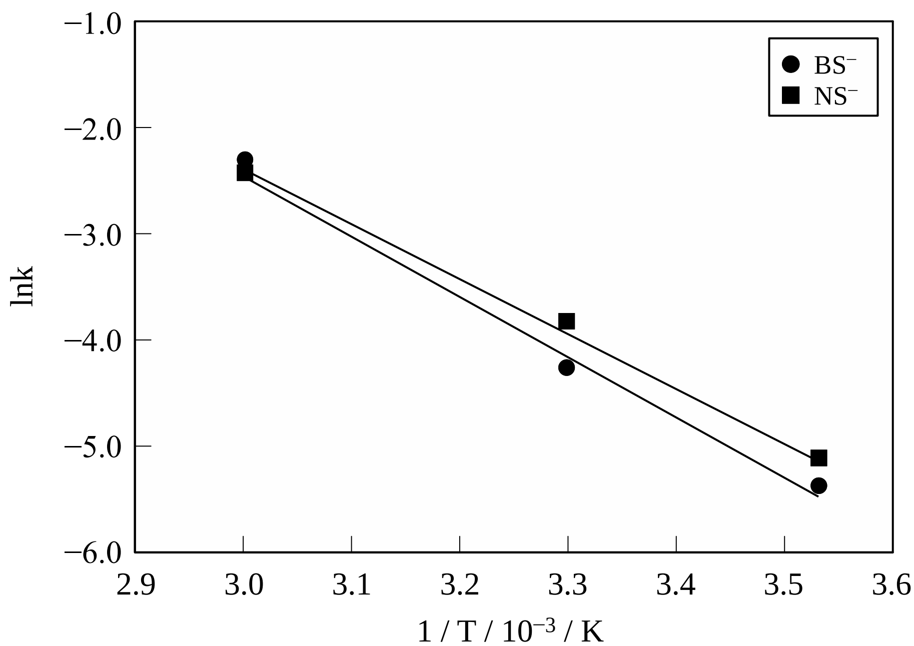

Fig. 8. Arrhenius plot of the apparent rate constant of BS^- and NS^- removal by the suspension of the Mg−Al oxide in BS^- and NS^- solutions.

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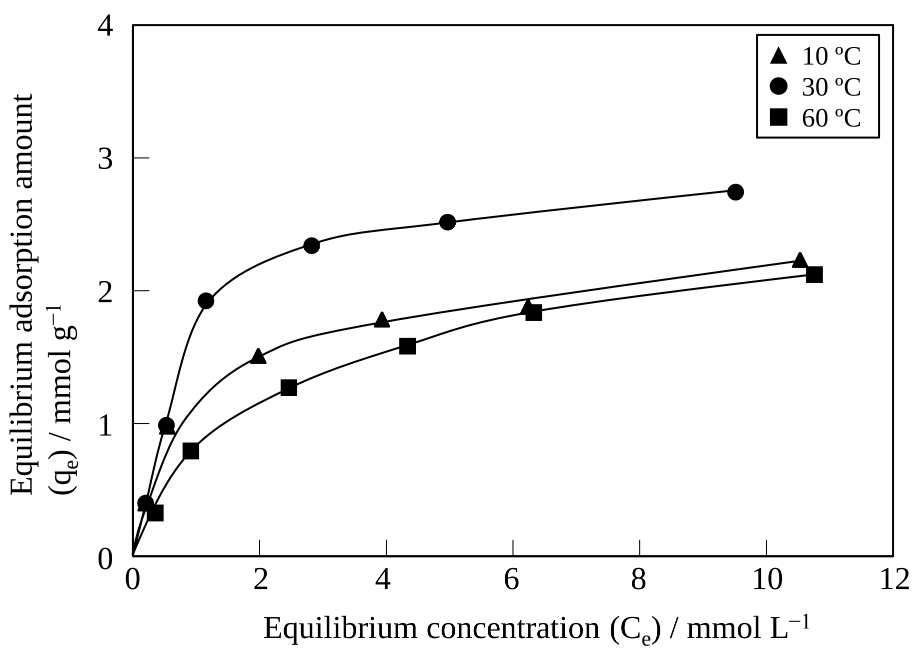

Fig. 9. Adsorption isotherm of BS^- adsorbed by the Mg−Al oxide for 1440 min.

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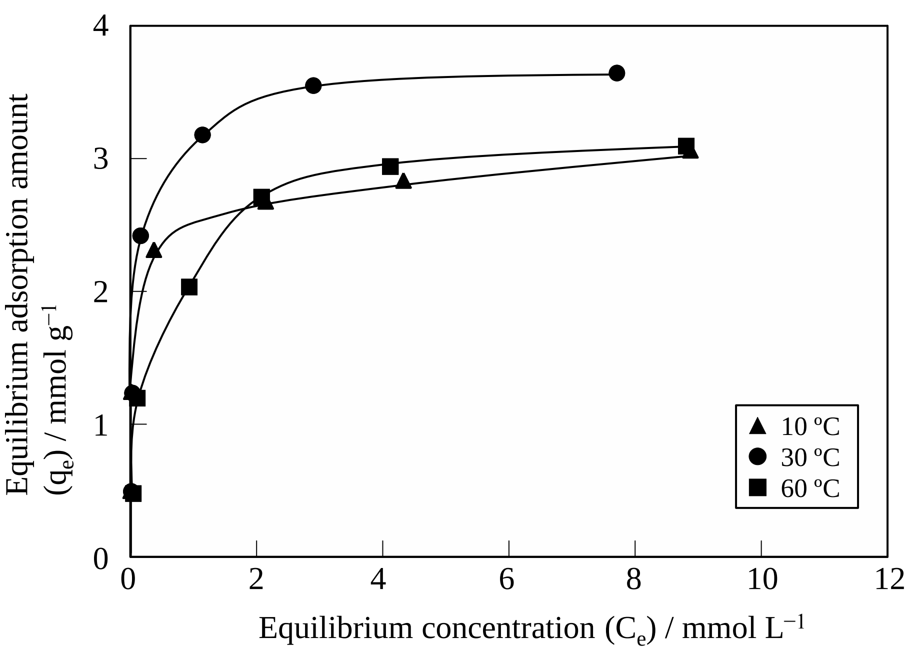

Fig. 10. Adsorption isotherm of NS^- adsorbed by the Mg−Al oxide for 1440 min.

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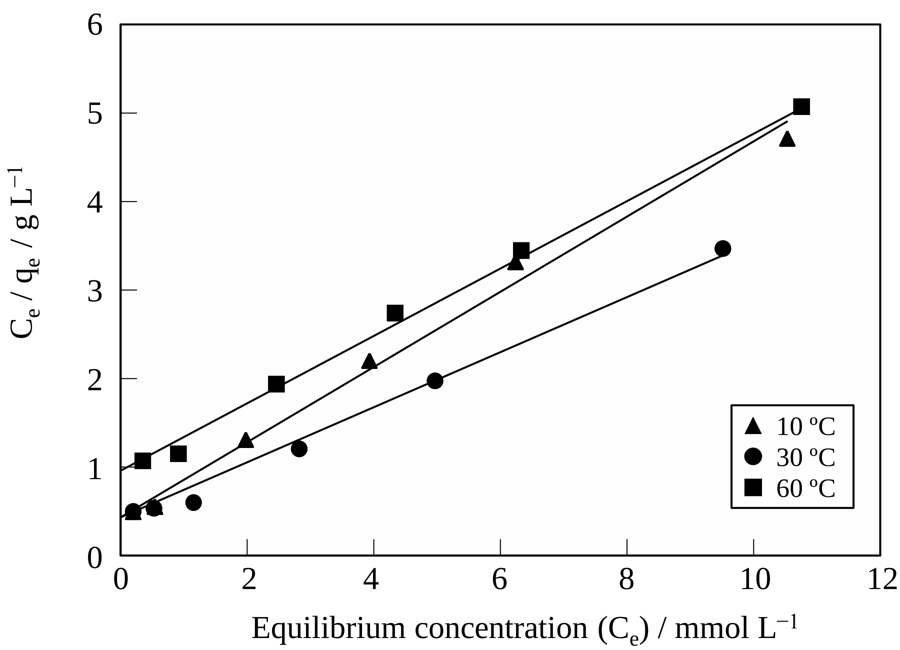

Fig. 11. C_e versus C_e/q_e plots for the adsorption isotherm of BS^- adsorbed by the Mg−Al oxide.

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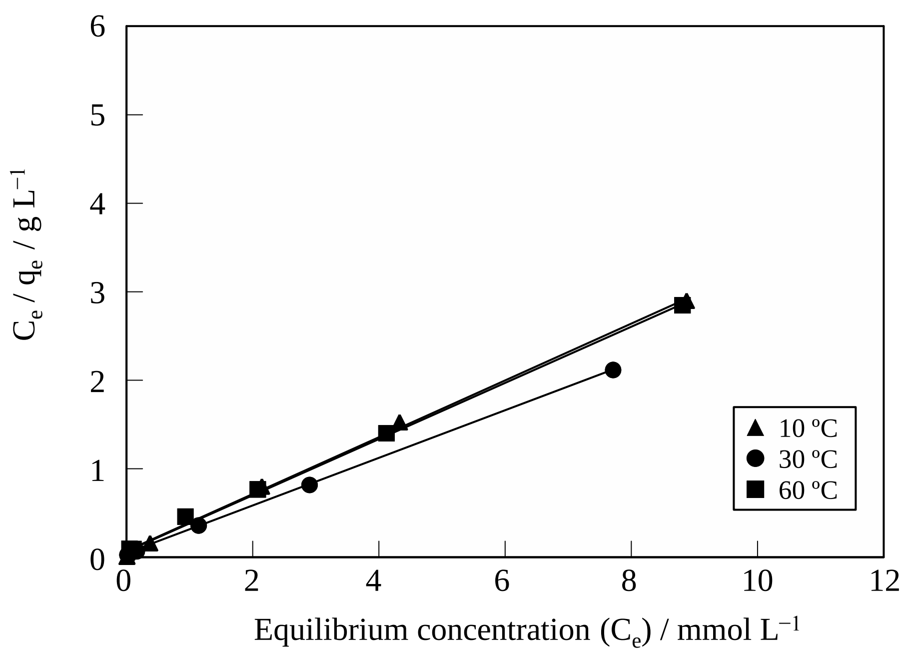

Fig. 12. C_e versus C_e/q_e plots for the adsorption isotherm of NS^- adsorbed by the Mg−Al oxide.

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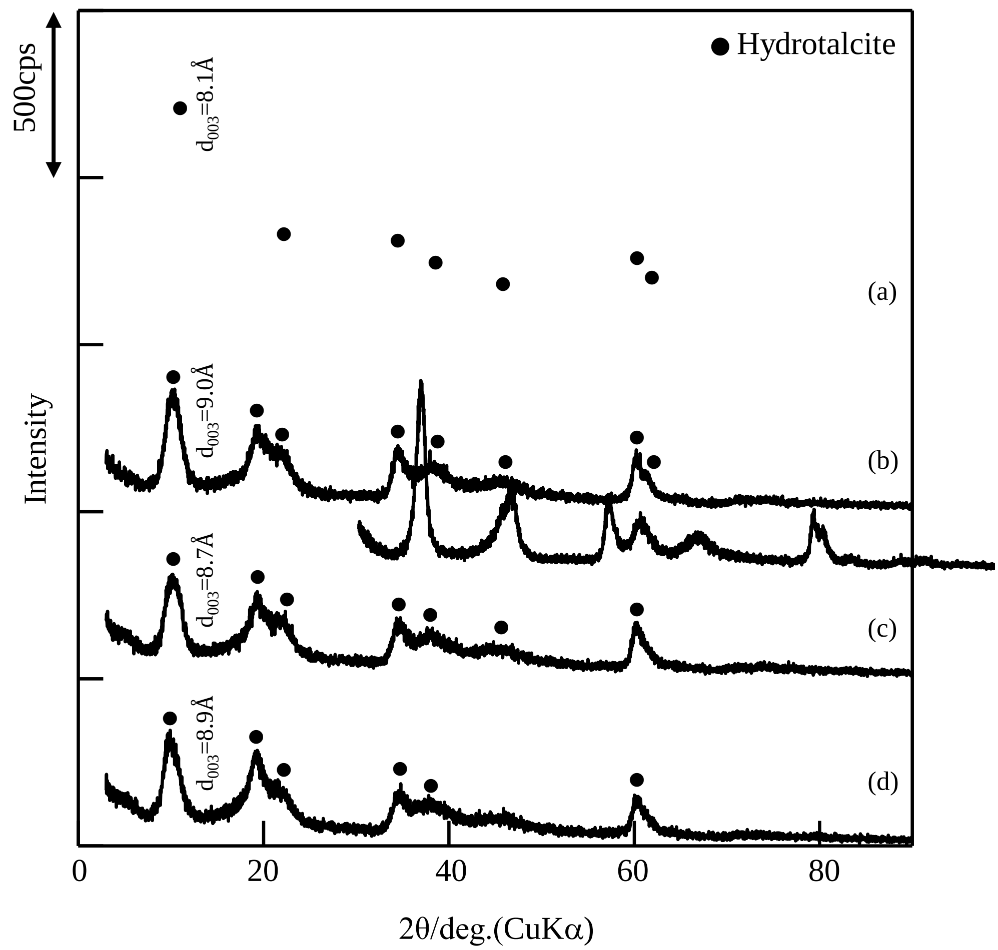

Fig. 13. XRD patterns for the products obtained by the suspension of the Mg−Al oxide in BS^- solution at 30 ºC; (a) Ce = 0.5 mmol L^{-1}, (b) Ce = 2.8 mmol L^{-1}, (c) Ce = 5.0 mmol L^{-1}, (d) Ce = 9.5 mmol L^{-1}.

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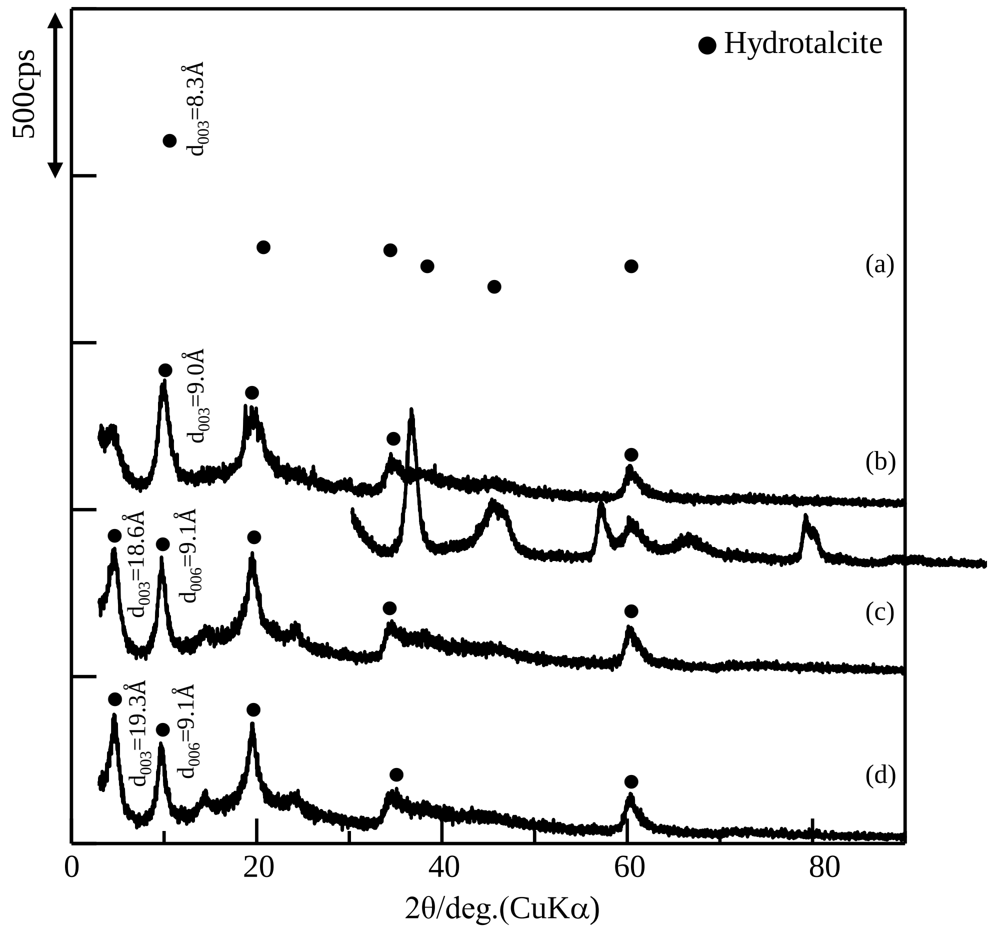

Fig. 14. XRD patterns for the products obtained by the suspension of the Mg−Al oxide in NS^- solution at 30 ºC; (a) Ce = 0.03 mmol L^{-1}, (b) Ce = 1.1 mmol L^{-1}, (c) Ce = 2.9 mmol L^{-1}, (d) Ce = 7.7 mmol L^{-1}.

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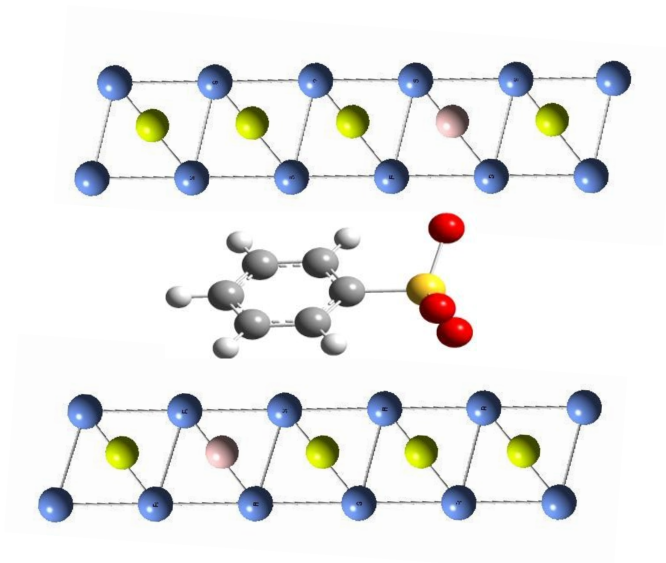
(a)



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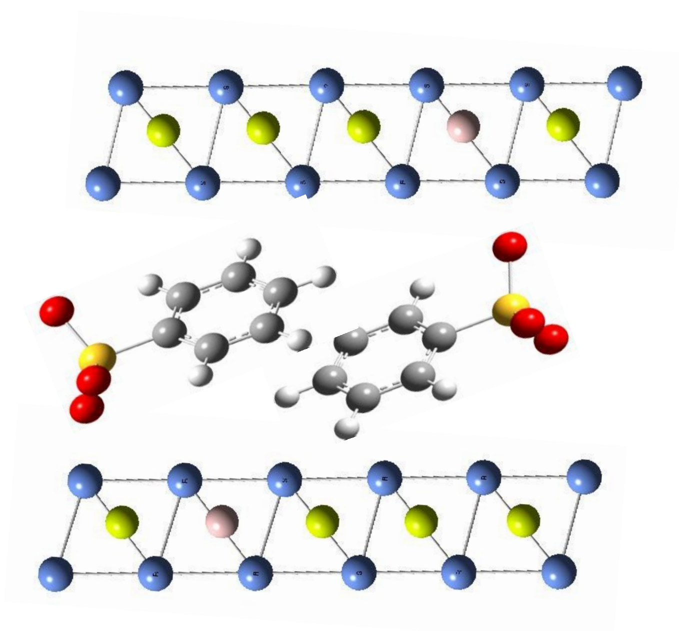

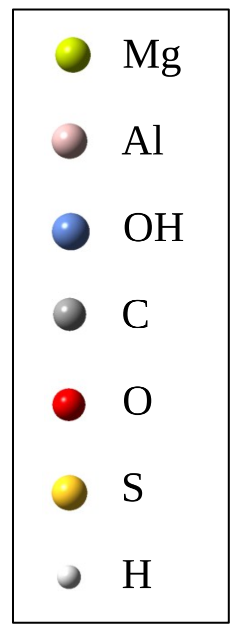

Fig. 15. Proposed molecular orientation of BS^- intercalated in the interlayer of Mg–Al LDH; (a) Ce = 0.5 mmol L^{-1}, (b) Ce = 2.8–9.5 mmol L^{-1}.

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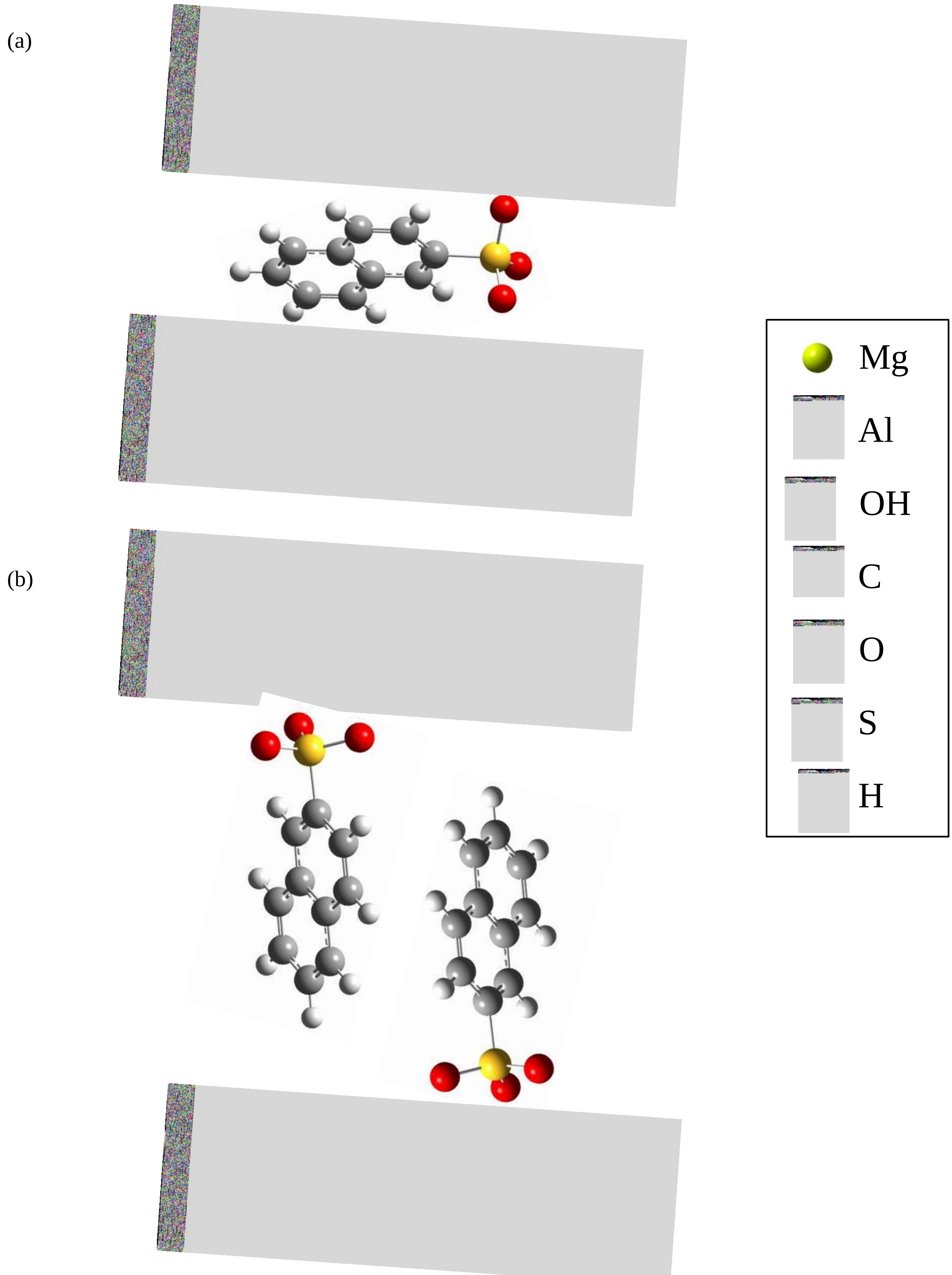

Fig. 16. Proposed molecular orientation of NS^- intercalated in the interlayer of Mg–Al LDH. (a) Ce = 0.03 mmol L^{-1}, (b) Ce = 2.9–7.7 mmol L^{-1}.

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Table 1. Equilibrium concentration and pH and relative distribution ratio (*K*) after the suspension of the Mg−Al oxide in BS^- or NS^- solution.

	Equilibrium concentration/ mmol L^{-1}	Equilibrium pH	*K*
BS^-	1.6	10.9	0.14
NS^-	1.3	11.3	0.85

Initial BS^- or NS^- concentration: 2 mmol L^{-1}, Mg−Al oxide quantity: stoichiometric quantity, Temperature: 30 ºC, Time: 24 h.

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Table 2. Values of q_m and K_L on BS^- and NS^- adsorbed by the Mg−Al oxide.

Adsorbate	BS^-			NS^-		
Temperature / ºC	10	30	60	10	30	60
q_m / mmol g^{-1}	2.4	3.1	2.6	3.1	3.7	3.2
K_L	0.92	0.86	0.42	7.60	9.69	2.98

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Table 3. BS^- and NS^- removal by the Mg−Al oxide at 1440 min.

BS^- / %			NS^- / %		
10 ºC	30 ºC	60 ºC	10 ºC	30 ºC	60 ºC
16.6	21.5	12.9	36.7	36.6	23.3

Initial BS^- or NS^- concentration: 2 mmol L^{-1}, Mg−Al oxide quantity: stoichiometric quantity.

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Table 4. pH value on BS^- and NS^- removal by the Mg−Al oxide at 1440 min.

BS^-			NS^-		
10 ºC	30 ºC	60 ºC	10 ºC	30 ºC	60 ºC
11.5	11.5	10.4	11.4	11.3	10.2

Initial BS^- or NS^- concentration: 2 mmol L^{-1}, Mg−Al oxide quantity: stoichiometric quantity.

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