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Adsorption of Oxoanion onto Layered Double Hydroxides

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Eutrophication in surface waters (i.e. lakes and seas) occur due to the increased discharge of industrial wastewater and sewage in recent years. This has a dire consequence of developing red tide blooms in surface water bodies. A reduction in concentrations of nutrient salts is essential to reduce loadings in surface water bodies. Nutrient salts, especially phosphate, have a greater impact in the proliferation of harmful algal blooms. In this study, the removal of nutrient salts in aqueous solutions was investigated using anionic clays such as layered double hydroxides (LDH), and also the adsorption mechanisms of nutrients salts onto LDH was described.

LDH can be formulated by $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{x/n} \cdot yH_2O]$. M^{2+} and M^{3+} denote divalent and trivalent metals, respectively, and A^{n-} is an anion of which the valence is n . LDH consist of a positively charged brucite-like octahedral layer and a interlayer containing anions and water molecules. The positively charged layer is formed by partial substitution of a trivalent metal for a divalent one. The layer can be stacked, and the balancing interlayer anions can be exchanged for other anions. LDH have received considerable attention in recent years because of their great anion-exchange capacity.

LDH which has Mg^{2+} and Al^{3+} as divalent and trivalent metals is one of the naturally occurring compounds, and it is known as hydrotalcite. In this study, Mg-Al LDH which contains hydroxide ions in interlayer space (hydroxide-LDH) was synthesized and used in the following experiments. And phosphate, nitrate and silicate ions, all of them are oxoanion, were taken up as nutrient salts.

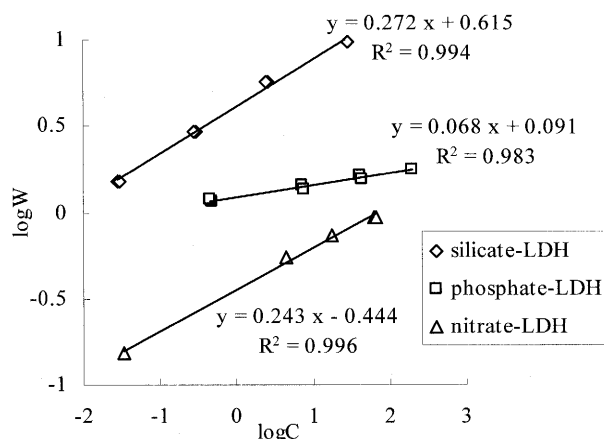


Figure 1 Freundlich isotherm of oxoanion onto Mg-Al LDH.

From the result of adsorption experiments, the adsorption isotherms were drawn. And in all cases, the Freundlich isotherm, $\log W = (1/n)\log C + \log k$, was applicable (Figure 1). W (mmol/g) is the amount of adsorption, C (mmol/l) is the equilibrium concentration of adsorbate, n and k are constants. The n and k values were obtained from the intercept and slope of the isotherm, respectively. The k value implies the affinity and the adsorption capacity of adsorbate for adsorbent. The k values of each oxoanion onto Mg-Al LDH were in the sequence silicate ($k = 1.85$) > phosphate ($k = 1.10$) > nitrate ($k = 0.64$), respectively.

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The XRD patterns (Figure 2) indicated that the solid products still had the LDH structure, and the (003) interplanar spacing of oxoanion adsorbed Mg-Al LDH were slight expanded in comparison with those of hydroxide-LDH. It suggests that each oxoanion intercalated in the interlayer spaces of Mg-Al LDH. The XRD patterns of nitrate-LDH was almost the same profiles with hydroxide-LDH, whereas those of silicate-LDH and phosphate-LDH were broad profiles compared to others.

The FT-IR spectra of oxoanion adsorbed Mg-Al LDH showed the absorption peak of each oxoanion. It indicated that oxoanion certainly adsorbed onto the LDH solid phase.

To consider the adsorption mechanisms of each oxoanion, the measurement of zeta potential was conducted. Figure 3 shows the result of zeta potential change with pH variation. The zeta potential of hydroxide-LDH changed due to dissociation reaction of hydroxyl group on its layer surface. The behavior of hydroxide-LDH and nitrate-LDH on the zeta potential change were almost similar, and their point of zero charge (PZC) were pH 7.9 and 7.5, respectively. It indicates that nitrate ions inspired simply adsorption onto Mg-Al LDH by anion-exchange reaction because that reaction have little influence on zeta potential. On the contrary, silicate-LDH exhibited the similar behavior to and phosphate-LDH, and their PZC were pH 5.5 and <5.5, respectively. This obvious shift of PZC to lower pH is suggesting that silicate and phosphate ions strongly affected the zeta potential on Mg-Al LDH and formed the inner-sphere complex with Mg-Al LDH surfaces by ligand substitution reaction because adsorption on the external surfaces should induce changes in zeta potential.

The adsorption of nitrate onto Mg-Al LDH is caused by exchanging with interlayer hydroxide ions. On the other hand, the adsorption of silicate and phosphate are not only produced by anion-exchange reaction onto Mg-Al LDH, but also by ligand substitution reaction. LDH has two kinds of anion retention sites, and adsorption mechanisms of oxoanion onto LDH vary according to the species of oxoanion.

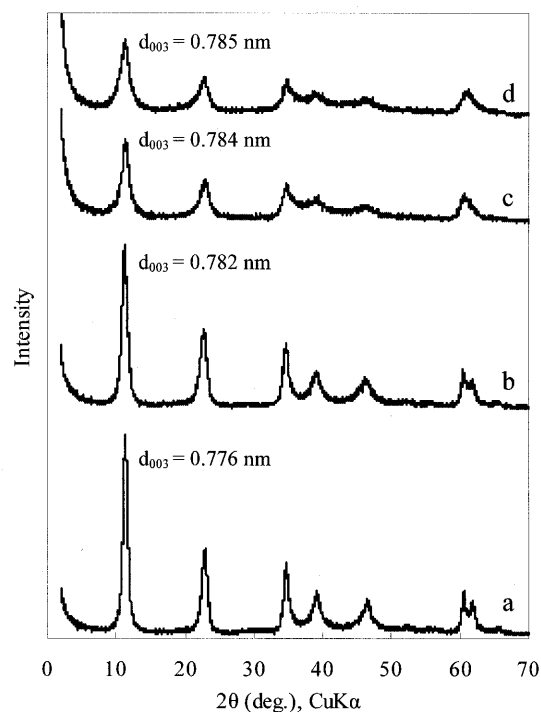


Figure 2 Powder XRD patterns of: (a) hydroxide-LDH, (b) nitrate-LDH, (c) silicate-LDH, (d) phosphate-LDH.

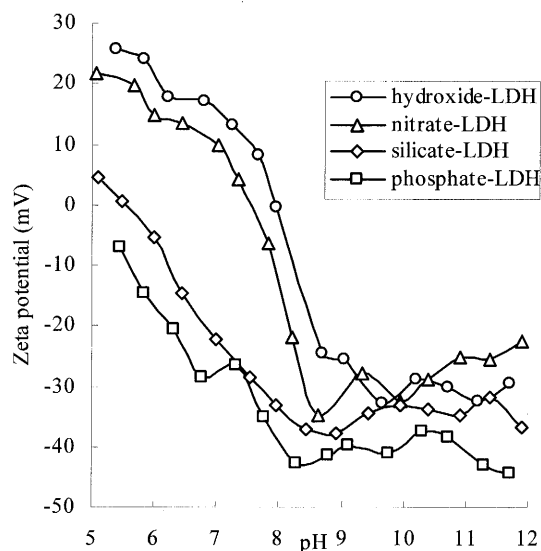


Figure 3 Zeta potential of oxoanion adsorbed Mg-Al LDH.