DESORPTION OF RARE EARTH IONS FROM ETHYLENEDIAMINETETRAACETATE-INTERCALATED Cu-Al LAYERED DOUBLE HYDROXIDE USING Fe^{3+}

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Abstract

It is found that rare earth ions combined with ethylenediaminetetraacetate (edta) ions in the interlayers of loaded edta • Cu-Al LDHs (Cu-Al layered double hydroxides intercalated with edta ions) can be exchanged with Fe^{3+} in aqueous solution. The level of recovery decreases in the order of $La^{3+} > Y^{3+} > Sc^{3+}$ for all time durations. The difference between the recovery levels can be attributed to the difference between the stabilities of the corresponding chelate complexes. The chelate formation constant for $Fe(edta)^-$ is much larger than those for $Y(edta)^-$ and $La(edta)^-$, indicating that Fe^{3+} is

effective for the recovery of La^{3+} and Y^{3+}. Thermodynamically, it is difficult for the Fe^{3+} to exchange with the Sc^{3+} combined with edta ions in the interlayers of Sc^{3+}-loaded edta • Cu-Al LDHs, because the chelate formation constant for $Fe(edta)^-$ is close to that for $Sc(edta)^-$.

1. Introduction

Layered double hydroxides (LDHs) are represented by the chemical formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} could be Mg^{2+}, Ni^{2+}, Zn^{2+}, etc.; M^{3+} could be Al^{3+}, Fe^{3+}, etc.; A^{n-} could be CO_3^{2-}, Cl^-, etc.; and x is the $M^{3+}/(M^{2+} + M^{3+})$ molar ratio $(0.20 \leq x \leq 0.33)$ [1]. LDHs have anion-exchange capabilities and can take up inorganic and organic anions in aqueous solution. However, organic-modified LDHs have recently been examined as new adsorbents that can take up metal cations and nonionic organic materials from aqueous solutions [2]. LDHs intercalated with ethylenediaminetetraacetate (edta) are one example of these modified LDHs that can take up heavy metal cations from aqueous solutions [3-10]. We have also examined the uptake of rare earth ions from an aqueous solution using Cu-Al LDH intercalated with edta (edta • Cu-Al LDH) [11]. It is anticipated that the rare earth cations in wastewater that are taken up by edta • Cu-Al LDH can later be reused as electrolytic metals after an electrorefining process. In order to realize the latter process, the rare earth ions absorbed by the edta • Cu-Al LDH must be desorbed in an aqueous solution. To facilitate this process, the edta ion can form chelate complexes with various kinds of metal cations. Depending on the stability of the chelate complex, one metal cation combined with edta ion can be exchanged with another metal cation. Based on this theory, we examine here the desorption of rare earth ions from edta • Cu-Al LDH by using Fe^{3+}. We expect that rare earth ions combined with edta ions in the interlayers of edta • Cu-Al LDHs can be

exchanged with Fe^{3+} in aqueous solution. The Fe^{3+} will form the chelate complexes with edta ions in the interlayers of edta • Cu-Al LDHs, and the rare earth ions will be eluted in aqueous solutions.

2. Experimental

All reagents were of chemical reagent grade (Kanto Chemical Ltd., Japan) and used without further purification. The edta • Cu-Al LDH loaded with rare earth ions, i.e., M^{3+}-loaded edta • Cu-Al LDH $(M^{3+} = Sc^{3+}, Y^{3+}, La^{3+})$, was prepared as follows. The edta • Cu-Al LDH was prepared by suspending Cu-Al oxide, obtained by calcining CO_3 • Cu-Al LDH, in edta solution [11]. The edta • Cu-Al LDH was added to 500mL of 1.0mmol/L $ScCl_3$, YCl_3, and $LaCl_3$ solution, and the resultant suspension was stirred at 30°C for 120 min. The molar ratio of the edta in the Cu-Al LDH to the Sc^{3+}, Y^{3+}, and La^{3+} in the chloride solution was set to 1. The chemical compositions of the M^{3+}-loaded edta • Cu-Al LDH $(M^{3+} = Sc^{3+}, Y^{3+}, La^{3+})$ samples are shown in Table 1. Next, 10mL of $FeCl_3$ solution and 0.2 or 0.5g of the M^{3+}-loaded edta • Cu-Al LDH were placed in 50mL screw-top tubes and shaken at 30°C for 0.5-24h. The molar ratio of Fe^{3+} in the chloride solution to edta ions in the M^{3+}-loaded edta • Cu-Al LDH was set to 1. Samples of the suspension were filtered through a 0.45μm membrane filter. The filtrates were then submitted for inductively coupled plasma-atomic emission spectrometry (ICP-AES) analyses to determine the target metal ion contents.

Table 1. Chemical compositions of M^{3+}-loaded edta • Cu-Al LDH $(M^{3+} = Sc^{3+}, Y^{3+}, La^{3+})$ (wt%)

Sample	Cu	Al	edta	M^{3+}
Sc^{3+}-loaded edta • Cu-Al LDH	45.3	8.2	4.5	0.7
Y^{3+}-loaded edta • Cu-Al LDH	43.0	7.2	4.8	0.5
La^{3+}-loaded edta • Cu-Al LDH	42.9	7.1	4.7	0.5

3. Results and Discussion

The M^{3+} combined with the edta ions in the interlayers of the M^{3+}-loaded edta • Cu-Al LDHs can be exchanged with Fe^{3+} in an aqueous solution according to Equation (1):
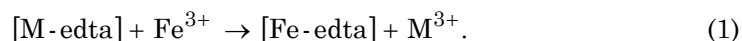
$$[M\text{-}edta] + Fe^{3+} \rightarrow [Fe\text{-}edta] + M^{3+}. \tag{1}$$

Table 2 shows the degree of recovery of La^{3+} from La^{3+}-loaded edta • Cu-Al LDH. In both cases, the degree of La^{3+} recovery was around 80%; therefore, La^{3+} was successfully recovered in an aqueous solution. This suggests that the La^{3+} combined with the edta ions in the interlayers of La^{3+}-loaded edta • Cu-Al LDH was exchanged with Fe^{3+} in an aqueous solution according to Equation (1). The degree of La^{3+} recovery (75.5%) for 0.5g of the loaded LDH was lower than that (81.4%) for 0.2g, suggesting that higher amounts of La^{3+}-loaded edta • Cu-Al LDH make it difficult for the La^{3+} to come into contact with Fe^{3+}.

Table 2. Degree of recovery of La^{3+} from La^{3+}-loaded edta • Cu-Al LDH

Weight/g	La^{3+} recovery /%
0.2	81.4
0.5	75.5

Figure 1 shows the variation in the degree of M^{3+} recovery with the time for which M^{3+}-loaded edta • Cu-Al LDH was suspended in $FeCl_3$ solution ($M^{3+} = Sc^{3+}$, Y^{3+}, La^{3+}). For Y^{3+} and La^{3+}, the degree of recovery initially increased rapidly with time and then remained almost constant. For Sc^{3+}, the degree of recovery initially increased rapidly with time and then decreased gradually. In all cases, the rare earth ions were recovered in aqueous solution, confirming that M^{3+} combined with edta ions in the interlayers of M^{3+}-loaded edta • Cu-Al LDHs can be exchanged with Fe^{3+} in aqueous solutions according to Equation (1). The degree of recovery decreased in the following order for all time durations: $La^{3+} > Y^{3+} > Sc^{3+}$. The levels of recovery of La^{3+}, Y^{3+}, and Sc^{3+} after 24h were 81%, 62%, and 1%, respectively. This difference in the degrees of recovery can be attributed to the difference in the stabilities of the corresponding chelate complexes. The chelate formation constants for $Fe(edta)^-$, $Sc(edta)^-$, $Y(edta)^-$, and $La(edta)^-$ have been reported to be 25.1, 23.1, 18.1, and 15.5, respectively [12, 13]. In other words, the stabilities of the chelate complexes decrease in the following order: $Fe(edta)^- > Sc(edta)^- > Y(edta)^- > La(edta)^-$. Thermodynamically, the ease with which the Fe^{3+} exchanges with the M^{3+} combined with edta ions in the interlayers of M^{3+}-loaded edta • Cu-Al LDHs decreases in the following order: $La^{3+} > Y^{3+} > Sc^{3+}$. The chelate formation constant

for $Fe(edta)^-$ is much larger than those for $Y(edta)^-$ and $La(edta)^-$. Therefore, Fe^{3+} is effective for recovering La^{3+} and Y^{3+} from loaded edta • Cu-Al LDHs but is not effective for the recovery of Sc^{3+}. This is because the chelate formation constant for $Fe(edta)^-$ is close to that for $Sc(edta)^-$, meaning that it is thermodynamically difficult for the Fe^{3+} to exchange with the Sc^{3+} combined with edta ions in the interlayers of Sc^{3+}-loaded edta • Cu-Al LDHs. Figure 1 shows that the degree of Sc^{3+} recovery initially increased rapidly and then decreased gradually with time. In the initial stage, some amount of Fe^{3+} could exchange with the Sc^{3+} in the edta • Cu-Al LDH because of the concentration gradient. However, the released Sc^{3+} was probably exchanged with the Fe^{3+} combined with edta ions in the interlayers of edta • Cu-Al LDHs because of the thermodynamic equilibrium of the exchange reaction.
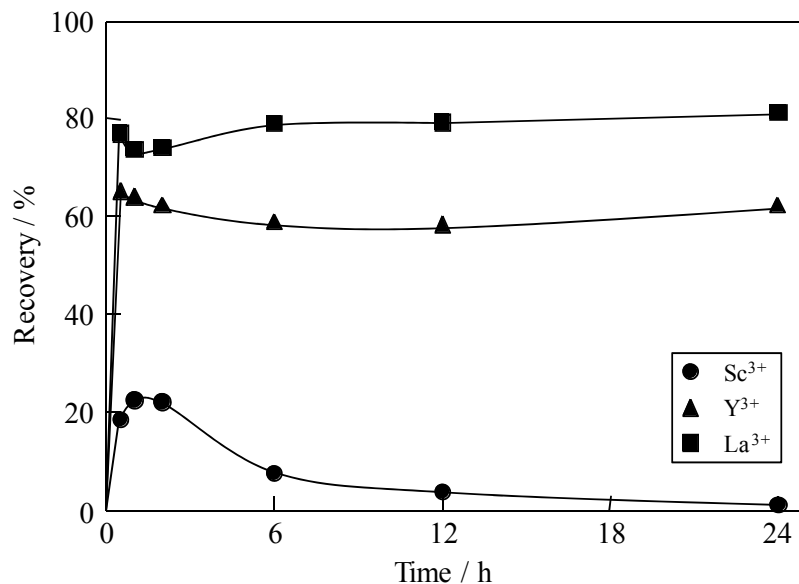
Figure 1. Variation in the degree of M^{3+} recovery with time for which M^{3+}-loaded edta • Cu-Al LDH was suspended in $FeCl_3$ solution (M^{3+} = Sc^{3+}, Y^{3+}, La^{3+}) for 0.2g of M^{3+}-loaded edta • Cu-Al LDH and Fe^{3+}/edta = 1.

In summary, this study has examined the desorption of rare earth ions absorbed by edta • Cu-Al LDHs using Fe^{3+}. The ease of desorption is dependent on the stability of the corresponding chelate complex.

4. Conclusion

M^{3+} ions combined with edta ions in the interlayers of M^{3+}-loaded edta • Cu-Al LDHs could be exchanged with Fe^{3+} in aqueous solution (M^{3+} = Sc^{3+}, Y^{3+}, La^{3+}). For Y^{3+} and La^{3+}, the recovery initially increased rapidly with time and then remained almost constant. For Sc^{3+}, the recovery initially increased rapidly with time and then

decreased gradually. The degree of recovery decreased in the following order for all time durations: $La^{3+} > Y^{3+} > Sc^{3+}$. This difference in the degrees of recovery can be attributed to the difference in the stabilities of the corresponding chelate complexes. The chelate formation constant for $Fe(edta)^-$ is much larger than that for $Y(edta)^-$ and $La(edta)^-$. Therefore, Fe^{3+} is effective for the recovery of La^{3+} and Y^{3+} from loaded edta $\bullet$ Cu-Al LDHs. Thermodynamically, it is difficult for the Fe^{3+} to exchange with the Sc^{3+} combined with edta ions in the interlayers of Sc^{3+}-loaded edta $\bullet$ Cu-Al LDHs, because the chelate formation constant for $Fe(edta)^-$ is close to that for $Sc(edta)^-$.

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