New Treatment Methods for Waste Water Containing Chloride Ion Using Magnesium–Aluminum Oxide

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The removal of hydrochloric acid utilizing magnesium-aluminum oxide (Mg–Al oxide), as prepared by the thermal decomposition of hydrotalcite (HT), was investigated. Cl^- in hydrochloric acid can be removed almost 100% by adding 1.75 times the stoichiometric quantity of $Mg_{0.70}Al_{0.20}O$ at 60 °C for 1 h. Mg^{2+} and Al^{3+} in solution after the reaction were not recognized, because the solution was weakly alkaline.

Waste water containing chloride ion which is discharged from such places as landfill is high concentrated saline solution, and it has caused the corrosion of waste pipe, the scale block, or the agricultural wreck of crops by damage from salt.[1,2] The desalting treatment of this waste water with electric dialysis installation is carried out recently, but there are some problems as the existence of K^+ in produced drying salt and absence of receiver of it.[3] New treatment methods for waste water containing chloride ion are desired.
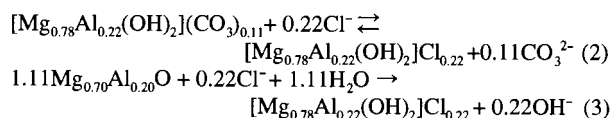
HT ($[Mg^{2+}_{1-x}Al^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O : 0.2 \leq x \leq 0.33$) is a layered double hydroxide with anion exchange properties. HT transforms into Mg–Al oxide when heated to 500–800 °C. The Mg–Al oxide can intercalate anions in solution, and then the original HT structure can be reconstructed as expressed by

$$(1+x/2)Mg_{2(1-x)/(2+x)}Al_{2x/(2+x)}O + x/z\ Y^{z-} + (1+x/2)H_2O \rightarrow$$
$$[Mg_{1-x}Al_x(OH)_2]Y_{x/z} + xOH^- \quad (1)$$
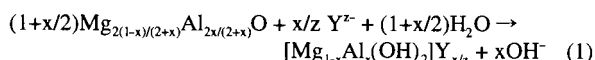
It is expected that the Mg–Al oxide is applied to waste water treatment as remover.[4–6]

In this study, the hydrochloric acid in waste water was targeted as waste water containing chloride ion, and the optimum condition of Mg–Al oxide quantity and time was examined for the removal of Cl^- at various HCl concentration. The differences between HT and Mg–Al oxide were also examined.

CO_3–HT ($[Mg_{0.78}Al_{0.22}(OH)_2](CO_3)_{0.11} \cdot mH_2O$), with an Mg/Al molar ratio of 3.5, was synthesized by "LDH Synthesis by the Variable-pH Method" of S.K.Yun and T.J.Pinnavaia.[7] $Mg_{0.70}Al_{0.20}O$ was prepared by the calcination of CO_3–HT at 500 °C for 1 h. A 0.01–0.5 M HCl solution (10 mL) and $[Mg_{0.78}Al_{0.22}(OH)_2](CO_3)_{0.11} \cdot mH_2O$ or $Mg_{0.70}Al_{0.20}O$ of 0.5–2 times the stoichiometric quantity, according to eqs (2) and (3), were placed in a 50-mL screw tube and shaken at 60 °C for 1–3 h.

$$[Mg_{0.78}Al_{0.22}(OH)_2](CO_3)_{0.11} + 0.22Cl^- \rightleftarrows$$
$$[Mg_{0.78}Al_{0.22}(OH)_2]Cl_{0.22} + 0.11CO_3^{2-} \quad (2)$$
$$1.11Mg_{0.70}Al_{0.20}O + 0.22Cl^- + 1.11H_2O \rightarrow$$
$$[Mg_{0.78}Al_{0.22}(OH)_2]Cl_{0.22} + 0.22OH^- \quad (3)$$

The pH of the solution was measured after the reaction, and Cl^- concentration was determined by ion chromatography. The degree of Mg^{2+} and Al^{3+} leaching were determined by ICP–AES. The precipitates were identified by X-ray diffraction (XRD).

Figure 1 shows the time dependence of Cl^- removal from 0.5

M HCl solution using $Mg_{0.70}Al_{0.20}O$ or $[Mg_{0.78}Al_{0.22}(OH)_2](CO_3)_{0.11}$ of 1.75 times the stoichiometric quantity at 60 °C. $[Mg_{0.78}Al_{0.22}(OH)_2](CO_3)_{0.11}$ showed only negligible hydrochloric acid removal. $Mg_{0.70}Al_{0.20}O$ exhibited a much higher degree of Cl^- removal, almost 100% after 0.5–1 h. It was confirmed by XRD that $Mg_{0.70}Al_{0.20}O$ was restored to Cl–HT after 10 min. In the case of adding CO_3–HT, Cl^- can hardly exchange with CO_3^{2-} that has been intercalated in HT since the charge density of CO_3^{2-} is higher than that of Cl^-. The degree of anion intercalation in HT is ordered $CO_3^{2-} > SO_4^{2-} > OH^- > Cl^-$.[8] It is thought that with Mg–Al oxide, Cl^- was easily intercalated into the reconstructed HT because CO_3^{2-} and OH^- was nonexistent in the initial reaction stage.
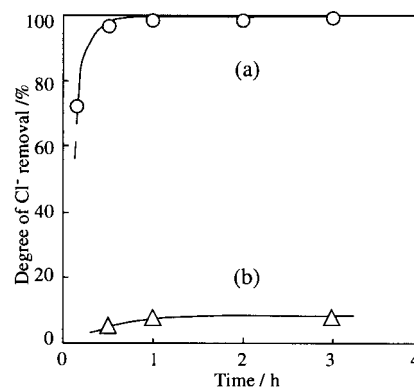

Figure 1. Time dependence of Cl^- removal from 0.5 M HCl solution using (a)$Mg_{0.70}Al_{0.20}O$ or (b)$[Mg_{0.78}Al_{0.22}(OH)_2](CO_3)_{0.11}$ of 1.75 times the stoichiometric quantity at 60 ℃.

The following study was carried out in order to determine the $Mg_{0.70}Al_{0.20}O$ quantity for the removal of Cl^-. The reaction was allowed to proceed for 3 h, and equilibrium was thought to be completely attained within that time.

Figure 2 shows the relationship between Cl^- removal from 0.5 M HCl solution and the $Mg_{0.70}Al_{0.20}O$ quantity at 60 °C for 3 h. Almost 100% Cl^- removal was achieved by adding $Mg_{0.70}Al_{0.20}O$ of 1.75 times the stoichiometric quantity. Excessive amounts of $Mg_{0.70}Al_{0.20}O$ were required to remove Cl^-. This is because OH^- is produced by the reconstruction reaction, as expressed by eq (3), and there is competition between the reactions of OH^- and Cl^-, as expressed by
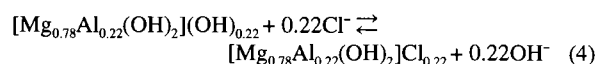
$$[Mg_{0.78}Al_{0.22}(OH)_2](OH)_{0.22} + 0.22Cl^- \rightleftarrows$$
$$[Mg_{0.78}Al_{0.22}(OH)_2]Cl_{0.22} + 0.22OH^- \quad (4)$$

Figure 3 shows the relationship of dissolved Mg^{2+} and pH to the $Mg_{0.70}Al_{0.20}O$ quantity at 60 °C for 3 h. The pH after the reaction increased with increasing the $Mg_{0.70}Al_{0.20}O$ quantity, and reached pH 8.6 at the stoichiometric quantity. The amount
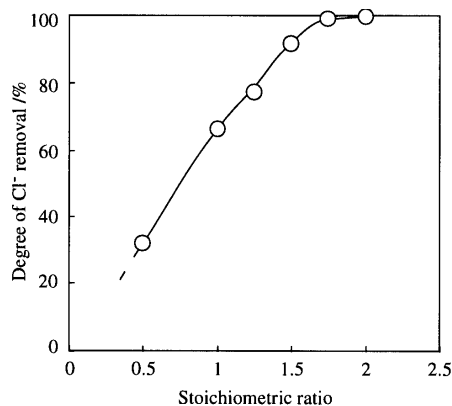
Figure 2. Relationship between Cl⁻ removal from 0.5 M HCl solution and the $Mg_{0.70}Al_{0.20}O$ quantity at 60 ℃ for 3 h.
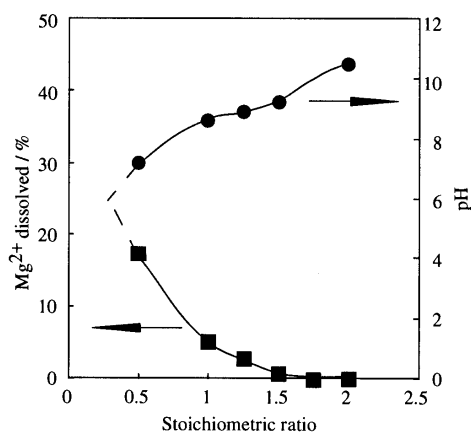

Figure 3. Relationship of dissolved Mg^{2+} and pH to the $Mg_{0.70}Al_{0.20}O$ quantity at 60 ℃ for 3 h.

of dissolved Mg^{2+} decreased with increasing the $Mg_{0.70}Al_{0.20}O$ quantity. It is thought that the once dissolved Mg^{2+} was reprecipitated as hydroxide with increasing pH, since the solubility product of $Mg(OH)_2$ is small. This was confirmed by XRD analysis of the precipitates. Dissolved Al^{3+} was not recognized. Since Al is amphoteric, it initially dissolves, but it precipitates as a hydroxide as the reaction progresses.

The following study was carried out in order to know the degree of Cl⁻ removal for various concentrations of HCl. The reaction was finished within 1 h in consideration for the industrialization of this waste water treatment.

Figure 4 shows the effect of HCl concentration on the removal of Cl⁻ using $Mg_{0.70}Al_{0.20}O$ of 1.75 times the stoichiometric quantity at 60 °C for 1 h. The degree of Cl⁻ removal decreased with decreasing HCl concentration. The degree of Cl⁻ removal was almost constant at 0.1–0.5 M HCl, but the removal decreased significantly below 0.1 M HCl. It is suspected that the rate of intercalation by Cl⁻ was faster than the rate of acid neutralization with the reconstruction reaction of $Mg_{0.70}Al_{0.20}O$ as increasing HCl concentration, and Cl⁻ was intercalated into the reconstructed HT promptly without the competition reactions as expressed by eq (4). The residual concentrations of Cl⁻ was 0.009 M at 0.5 M HCl. It has satisfied the desirable concentration range, since the concentrations of Cl⁻ should be below 0.014M to prevent the agricultural wreck of crops by damage from salt.[2]
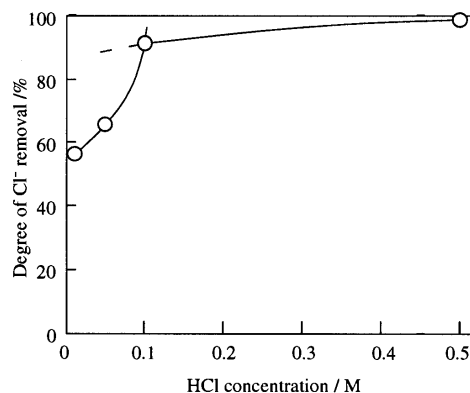

Figure 4. Effect of HCl concentration on the removal of Cl⁻ using $Mg_{0.70}Al_{0.20}O$ of 1.75 times the stoichiometric quantity at 60 ℃ for 1 h.

The intercalation capacity of Cl⁻ in NaCl solution with Mg–Al oxide is investigated.[9,10] The degree of Cl⁻ removal was 50% by adding Mg–Al oxide of 2.5 times the stoichiometric quantity at 80 °C for 1 h, and it was known that the degree of Cl⁻ removal was low because OH⁻ was easily intercalated with increasing pH as expressed by eq (3).[9] However, in this study, it was clear that Cl⁻ was removed above 90% by using Mg–Al oxide of 1.75 times the stoichiometric quantity in the strong hydrochloric acid below initial pH 1.

The advantage of this treatment method is that Mg–Al oxide can be used efficiently as increasing initial HCl concentrations. The treatment method for waste water containing chloride ion $(CaCl_2)$ which is discharged from landfill is thought that HCl and $CaSO_4·2H_2O$ are produced by adding H_2SO_4 to this waste water, and Mg–Al oxide is applied for the removal of the produced HCl. It is also thought that Mg–Al oxide is applied for the removal of HCl which is discharged from garbage incinerator or flon decomposition plants. It is expected that the produced Cl–HT can be used as ion exchanger for removing phosphorus to prevent eutrophication of surface water by algae bloom.[11] Kawamoto et al. have reported that residual concentrations of the phosphate ion from rural sewages treated with Cl–HT were less than 1 mg/L.[12]

References and Notes
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