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Discussion

Comment on “Factors influencing the removal of fluoride from aqueous solution by calcined Mg–Al–CO_3 layered double hydroxides”

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Abstract

Lv et al. [L. Lv, J. He, M. Wei, D.G. Evans, X. Duan, Factors influencing the removal of fluoride from aqueous solution by calcined Mg–Al–CO_3 layered double hydroxides, J. Hazard. Mater. B 133 (2006) 119–128] previously investigated the fluoride removal using calcined Mg–Al–CO_3 layered double hydroxides (CLDH) as the sorbents. The present comment further discusses the mechanism of fluoride adsorption onto CLDH.

Keywords: Calcined Mg–Al–CO_3 layered double hydroxides; Mixed oxides; Memory effect; Fluoride adsorption

1. Introduction

Recently Lv et al. [1] investigated in the above-mentioned paper the removal of aqueous fluoride using calcined Mg–Al–CO_3 layered double hydroxides (CLDH) as the sorbents. This valuable study systematically analyzed the factors influencing the adsorption efficiency of the calcined LDH (CLDH) for fluoride removal. The authors attributed the effective fluoride removal to the structure restoration of CLDH based on XRD results. In fact, there is general consensus that the effective adsorption of some anions over CLDH is mainly ascribed to “memory effect” of CLDH [2–5].

In Lv’s paper the adsorption capacity of fluoride onto CLDH with Mg/Al molar ratio of 1.68 was found to be approximately 200 mg/g at fluoride equilibrium concentration of 275 mg/L (see Fig. 9) [1]. It was noteworthy that if CLDH structure is completely restored and fluoride is considered to be the only compensating anion, the theoretical maximum adsorption capacity of CLDH with Mg/Al molar ratio of 1.68 is estimated to be 163 mg/g, which is markedly lower compared to the observed uptake of CLDH. This suggests that the mechanism of fluoride adsorption is possibly not only dominated by “memory effect” of CLDH. In this comment we further discussed the mechanism of fluoride adsorption onto CLDH.

2. Mechanism of removal of fluoride ions

2.1. Material characterization

Mg–Al–CO_3 LDH with Mg/Al molar ratio of 2.0 was synthesized according to the process described by Ulibarri et al. [2]. CLDH sample was obtained by calcining Mg–Al–CO_3 LDH at 450 °C for 4 h. In order to clarify the structural change of CLDH after fluoride uptake, fluoride loaded CLDH (F-CLDH) samples were also prepared. Typically, 0.70 g CLDH was charged into 200 mL of 500 mg/L fluoride solution and the adsorption was allowed to last 10 h under stirring and N_2 atmosphere. Solid was recovered by fast centrifugation. Part of the solid was dried at 60 °C for 6 h in an oven and the resultant sample is denoted as F-CLDH1. Part of the solid was charged into freeze-drying under vacuum for 12 h and the resulting sample is referred to as F-CLDH2.

XRD patterns of Mg–Al–CO_3 LDH, CLDH and fluoride loaded CLDH are complied in Fig. 1. For F-CLDH2, (0 0 3), (0 0 6) and (0 0 9) reflections, characteristic of LDH structure [1], were markedly weaker compared to F-CLDH1 and LDH indicating that the structure of fluoride loaded CLDH is influenced by the post-treatment conditions. Under atmospheric conditions,

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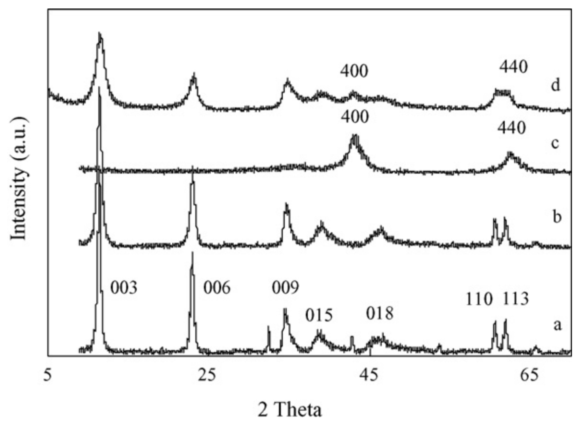

Fig. 1. XRD patterns of: (a) LDH; (b) F-CLDH1; (c) CLDH; (d) F-CLDH2.

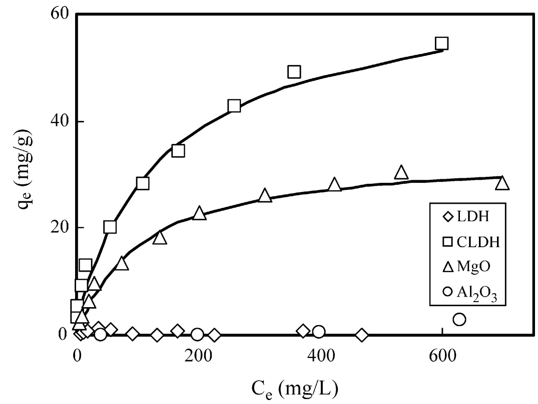

Fig. 2. Adsorption isotherms of fluoride onto LDH, CLDH, MgO and Al_2O_3 at 25 °C and pH 7.0.

further reaction of fluoride loaded CLDH with CO_2 and H_2O in the atmosphere occurred during the drying process [6], which resulted in the loss of valuable information about the structure of fluoride loaded CLDH. This can be effectively overcome using freeze-drying treatment. The weak XRD refraction peaks of F-CLDH2 clearly revealed that the layered structure of CLDH is not completely restored upon fluoride adsorption. In addition, the presence of (4 0 0) and (4 4 0) reflections in F-CLDH2, characteristic of MgO–Al_2O_3 solid solution [7], also proved the conclusion. Similar phenomena were previously observed using a variety of characterization methods, such as EXAFS, in situ X-ray diffraction, ^{27}Al MAS NMR and neutron diffraction [7–9]. Tichit et al. [7] attributed the partially irreversible restoration of CLDH to the concomitant occurrence of dramatic structural modification during calcination process. The coexistence of restored LDH and mixed Mg–Al oxides in F-CLDH2 suggests that fluoride removal may result from fluoride adsorption onto different species.

2.2. Fluoride adsorption

Further investigation on the adsorption behavior of the residual mixed Mg–Al oxides for aqueous fluoride in F-CLDH2 is of crucial importance for clarification of the adsorption mechanism. It should be emphasized that straightforward visualization of fluoride adsorption over the mixed Mg–Al oxides is not feasible due to the difficulty in preparing the particular Mg–Al oxides incapable of structural restoration upon fluoride adsorption. However, study on fluoride adsorption onto MgO or Al_2O_3 can provide valuable information about the adsorption behavior of mixed Mg–Al oxides for fluoride. Therefore, MgO and Al_2O_3 were prepared using precipitation method followed by calcination at 450 °C for 4 h. Fig. 2 shows the adsorption isotherms of fluoride over LDH, CLDH, MgO and Al_2O_3 under atmospheric conditions. LDH and Al_2O_3 showed minor fluoride uptakes and the calcination of LDH led to a markedly increased adsorption capacity of CLDH for fluoride, which is in agreement with Lv's results. Lower fluoride uptake of CLDH was observed compared to Lv's results [1], which is due to the presence of aqueous CO_3^{2-} under atmospheric conditions. It was worthy to note that MgO exhibited marked fluoride adsorption capacity. This clearly points out that besides "memory effect" fluoride adsorption over the mixed oxides also accounts for the removal of fluoride. Among the mixed oxides, MgO acts as a vital component for fluoride removal. This combined adsorption mechanism may explain why a markedly higher fluoride uptake over CLDH can be achieved compared to its theoretical adsorption capacity in Lv's paper [1]. In parallel, the regeneration of fluoride loaded CLDH using Na_2CO_3 aqueous solution deserves reevaluation.

3. Conclusion

Lv et al. studied fluoride removal using CLDH as the sorbents and observed a markedly higher fluoride uptake compared to the theoretical adsorption amount of CLDH for fluoride. XRD results showed that mixed Mg-Al oxides as well as partially restored LDH presented in fluoride loaded CLDH after freeze-drying treatment. In addition, fluoride can be effectively sorbed onto MgO, indicating that fluoride adsorption over mixed oxide along with memory effect accounts for the effective fluoride removal using CLDH as the sorbent.

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