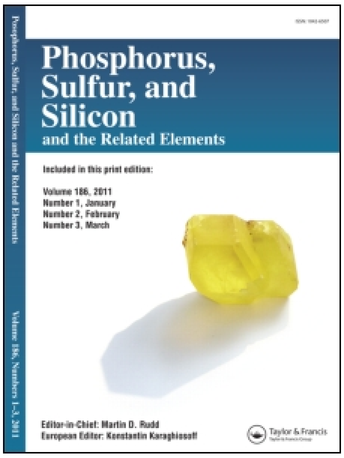

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Phosphate Removal and Recovery with Calcined Layered Double Hydroxides as an Adsorbent

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The adsorption properties of calcined layered double hydroxide (denoted as CLDH) for phosphate and desorption for recovery phosphate were examined. The influences of chemical composition of adsorbents, adsorbent dose, and co-existing anions on the phosphate removal have been investigated. It has been found that the LDHs with Mg/Al molar ratio of 2 represented the highest capacity to remove phosphate from aqueous solution. Phosphate ion removal in presence of other ions decreases in the order $CO_3^{2-} < SO_4^{2-} < F^- < Cl^-$*. Phosphate adsorbed on the CLDH was effectively desorbed at* Na_2CO_3 *solution and the CLDH were reconstruction to LDHs at the same time. Phosphate in the exhausted desorption solution was recovered as calcium phosphate by precipitation with* Ca^{2+}.

Keywords Adsorption; desorption; layered double hydroxides; phosphate; recovery

INTRODUCTION

Eutrophication in rivers, lakes and bays has been increasing, and removal of nutrient salts from the receiving water is an important consideration to control eutrophication. A large amount of used phosphate finally reaches water environment as diluted waste, which often leads to eutrophication of the water environment. Phosphate removal is important to control eutrophication, so phosphorus removal from wastewater has been widely investigated. On the other hand, phosphate is recognized as being one of the resources that will be lost in near future.[1] It is of value to collect the finally disposed phosphates from effluents and drain water before further dispersion and dilution of them in the water

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environment.[2] A phosphate recovery process should be incorporated with a phosphate removal system.

The removal technologies for aqueous phosphate include chemical precipitation,[3,4] crystallization,[5,6] ion exchange, adsorption,[7,8] and biological processes.[9] An adsorption process has been applied widely to treatment containment water because the process has some advantages, such as less production of sludge and easy operation. A variety of adsorbents have been developed for phosphate removal, such as aluminum oxide,[10] iron oxide,[11] zirconium oxide,[12] ion exchange resin,[13] hydrotalcite,[14,15] basic yttrium carbonate,[16] blast furnace slag,[8] and fly ash.[17]

Layered double hydroxides (LDHs), are a class of synthetic anionic clays whose structure can be described as containing brucite-like layers in which some of the divalent cations have been replaced by trivalent ions giving positively-charged sheets. This charge is balanced by intercalation of anions in the hydrated interlayer regions. The general formula is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are metal cations for example Mg^{2+} and Al^{3+}, which occupy octahedral sites in the hydroxide layers, A^{n-} is an exchangeable anion, and x is the ratio $M^{3+}/(M^{2+}+M^{3+})$ and the layer charge will depend on the M^{2+}/M^{3+} ratio. The sorption of anions from aqueous solutions by structural reconstruction of calcined LDHs (CLDH) is based on a very interesting property of these materials, the so-called memory effect. In our previous work, it was also indicated that the CLDH can effectively removal toxic anions (such as fluoride, chloride, bromide, and perchlorate) from water.[18,19]

In this work, the adsorption properties of CLDH for phosphate and the method of regeneration of this material were examined. The influences of CLDH structures, adsorbent dose, initial phosphate concentration, temperature, and co-existing anions on the removal of phosphate have been investigated. It has been found that the LDHs with Mg/Al molar ratio of 2 represented the highest capacity to remove phosphate ion from aqueous solution. Phosphate adsorbed on the CLDH was effectively desorbed at Na_2CO_3 solution and the CLDH were reconstruction to LDHs at the same time. Phosphate in the exhausted desorption solution was recovered as calcium phosphate by precipitation with Ca^{2+}. The results suggest the possibility of an effective system for phosphate removal and recovery, which includes the following processes: adsorption, desorption, recovery of phosphate.

EXPERIMENTAL

Materials

All reagents were analytically pure grade, used as received. The phosphate aqueous solution used in this study was a synthetic wastewater using double distilled water. The standard phosphate solutions used in the experiments were prepared from anhydrous KH_2PO_4. LDHs containing carbonate as the interlayer anion was obtained by using a conventional coprecipitation method. CLDH was obtained by calcining LDHs in a muffle furnace at 500°C for 3 h.

Removal of Phosphate

All sorption studies were carried out in a series of 100 mL conical flasks by subjecting a given dose of CLDH to a period of shaking together with the phosphate synthetic wastewater (50 ml) at 30°C in a thermostatic water shaker. In the experiments, the shaking speed was kept constant at 200 rpm (except for the experiments in which the effect of stirring speed are examined). The adsorbent was separated by filtration, and the filtrate was analyzed for phosphate using spectrophotometric method. Blanks containing no phosphate were used for each series of experiments. The phosphate concentration, the percentage removal of phosphate and the loading capacity of CLDH for phosphate were calculated from the concentrations in solution before and after adsorption, respectively.

Desorption and Recovery of Phosphate

The efficiencies of desorption of phosphate from P-LDHs (CLDH after removal phosphate) were examined with 1.0 g of the CLDH saturated with phosphate under the following conditions: the desorption solutions (50 ml) and shaking at 30°C for 24 h. The desorption ratio is defined as the ratio of the desorbed phosphate amount to the adsorbed one. Since phosphate was enriched through the adsorption—desorption processes, enriched phosphate was recovered as calcium phosphate by addition of $CaCl_2$.

RESULTS AND DISCUSSION

Effect of Chemical Composition of Adsorbents

The effect of varying Mg/Al molar ratio on the phosphate removal was investigated. Table I shows that the retention of phosphate by the CLDH with Mg/Al molar ratio 2 is the best of all, for which the adsorption content reached 0.994 mmol/g. The adsorption content of phosphate by the CLDH with Mg/Al ratios of 3 and 4, are lower than the CLDH with Mg/Al ratio of 2, due to the higher charge density in the layers of CLDH with an Mg/Al ratio of 2 than with 3 and 4. On the other hand, the specific surface areas of CLDH are decrease with increasing Mg/Al

TABLE I The Effect of Chemical Composition of Adsorbents on the Phosphate Removal

Sample	Dosage of CLDH (g/L)	$[PO_4^{3-}]_0$ (mmol/L)	$[PO_4^{3-}]_e$ (mmol/L)	Percentage removal (%)	Loading capacity (mmol/L)
Mg/Al 2—CLDH	1.0	1.0	0.0065	99.35	0.994
Mg/Al 3—CLDH	1.0	1.0	0.0092	99.08	0.991
Mg/Al 4—CLDH	1.0	1.0	0.0637	93.63	0.936
Zn/Al 2—CLDH	1.0	1.0	0.4139	58.61	0.586
Zn/Al 3—CLDH	1.0	1.0	0.4466	55.34	0.553
Zn/Al 4—CLDH	1.0	1.0	0.5083	49.17	0.492

ratio[20] suggests that the retention of phosphate is also related to the surface area of CLDH.

The influence of metal cations in the adsorbents has also been studied. Table I indicates that the retention of phosphate by the MgAl-CLDH is higher than that of ZnAl-CLDH. This is partly due to the lower anion exchange capacity of ZnAl-CLDH, because of the higher atomic weight of Zn compared to Mg.

Effect of Dosage of CLDH

The effect of the dosage of CLDH on the uptake of phosphate with initial concentration of 1.0 mmol/L was studied and the results were shown in Figure 1. It can be seen that the dosage of CLDH significantly influenced the removal of phosphate. The percentage removal of phosphate was 39.1% for 0.2 g/L of CLDH, while it was greatly increased to 97.7% for 1.5 g/L of adsorbent. However, there was only a slight change in the extent of phosphate adsorption when the dosage of adsorbent was over 1.5 g/L. For example, the percentage removal was 99.1% for 3.0 g/L of adsorbent.

Furthermore, the higher adsorbent dose results in a lower loading capacity of CLDH at a fixed only a slight change concentration (1 mmol/L), as shown in Figure 1, consistent with the argument that the surface sites of the adsorbent are heterogeneous. According to the surface-site heterogeneity model, the surface is composed of sites with a spectrum of binding energies. At low adsorbent dose, all types of sites are entirely exposed and the adsorption on the surface is saturated fast, showing a high loading capacity. However, at high adsorbent dose, the availability of higher energy sites decreases with a larger fraction of lower energy sites occupied, resulting in a low loading capacity.

The distribution coefficient K_D can be employed to describe the binding ability of solid surface for adsorbates. The K_D values of the

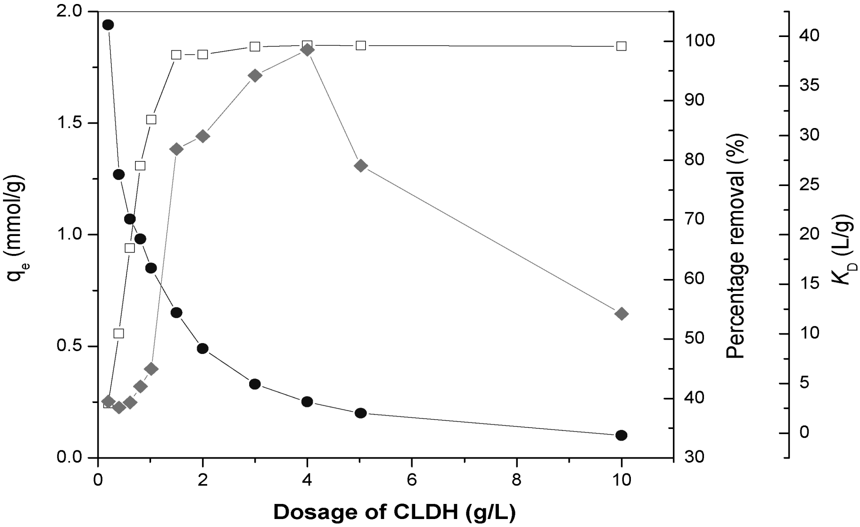

FIGURE 1 Effect of dosage of CLDH on the phosphate removal. (●) loading capacity vs. dosage of CLDH; (□) percentage removal vs. dosage of CLDH; (♦) distribution coefficient (K_D) vs. dosage of CLDH (V = 50 ml, $[PO_4^{3-}]_0 = 1.0$ mmol/L, T = 30°C, t = 24 h).

adsorption were calculated as Equation (1):[19]

$$K_D = C_s/C_w \tag{1}$$

where C_s is the concentration of phosphate in solid particles (mmol/g) and C_w is the concentration of phosphate in water (mol/L). As can be seen from Figure 2, the distribution coefficient K_D increased with increasing adsorbent dose in the range of 0.2–4.0 g/L and decreased with increasing adsorbent dose in the range of 4.0–10.0 g/L. It implies that the surface of CLDH is heterogeneous. If the surface is homogeneous, the K_D values should not change with adsorbent concentration.

Co-Existing Anions in Phosphate Contaminants

Phosphate-containing wastewater usually consists of many ions such as sulfate, chloride, carbonate, fluoride. These anions compete with phosphate ion to be intercalated into CLDH. The effect of co-existing anions on the removal of phosphate ion with initial concentration of 1.5 mmol/L was studied. Figure 2 indicates that the loading capacity of phosphate slightly decreases with increasing concentration of co-existing anions, and reaches nearly 10% when the concentration of co-existing exceeds

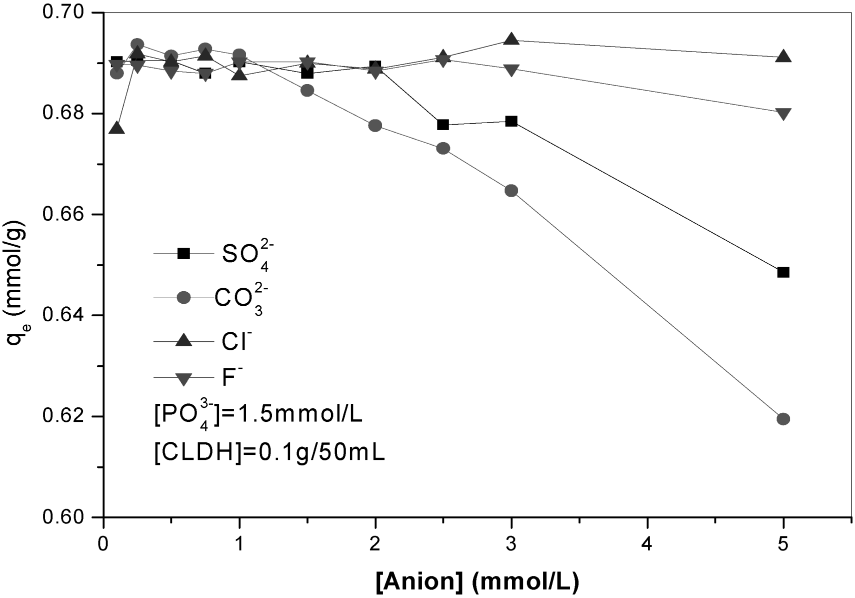

FIGURE 2 Effect of co-existing anions on the phosphate removal. (V = 50 ml, $[PO_4^{3-}]_0$ = 1.5 mmol/L, T = 30°C, [CLDH] = 2.0 g/L).

5 mmol/L. Phosphate ion removal in presence of other ions decreases in the order $CO_3^{2-} < SO_4^{2-} < F^- < Cl^-$. The effect of these anions on phosphate removal may be contributed to their affinity towards CLDH which have greater affinities for anions with higher charge density. The Z/r (charge/radius) values of the anions varies in the order CO_3^{2-} (2/1.85) > SO_4^{2-} (2/2.40) > F^- (1/1.33) > Cl^- (1/1.81), i.e., multivalent anions are adsorbed more readily than monovalent anions.

Phosphate Desorption

Since ion exchange is generally reversible, the phosphate desorption performance was examined. The desorption ratios with several

TABLE II The Composition of the Desorption Solutions and the Desorption Ratios

Desorption solution	Desorption ratio (%)
1 mol/L NaCl	12
1 mol/L NaOH	48
1 mol/L Na_2CO_3	90

desorption solutions are shown in Table II. The desorption efficiencies in a 1 mol/L NaCl solution and in a 1 mol/L NaOH solution were lower than that in a 1 mol/L Na_2CO_3 solution which desorbed effectively is 90%. Phosphate desorption decreases in the order $CO_3^{2-} > OH^- > Cl^-$. The effect of these anions on phosphate desorption may be contributed to their affinity towards LDHs. The Z/r (charge/radius) values of the anions varies in the order CO_3^{2-} (2/1.85) $> PO_4^{3-}$ (3/3.40) $> OH^-$ (1/1.40) $>$ Cl^- (1/1.81).

CONCLUSIONS

CLDH can be used for efficient removal of phosphate pollutant from wastewater. The retention of phosphate by the CLDH with Mg/Al molar ratio 2 is the best of all, for which the adsorption content reached 0.994 mmol/g. The CLDH is reconstructed to P-LDHs after uptake of phosphate as expected, which is called memory effect. Increasing dosage of CLDH, the percentage removal of phosphate is increased, while the loading capacity is decreased. The percentage removal was 99.1% for 3.0 g/L of adsorbent. Phosphate removal in presence of other ions decreases in the order $CO_3^{2-} < SO_4^{2-} < F^- < Cl^-$. But phosphate desorption decreases in the order $CO_3^{2-} > OH^- > Cl^-$, which related the Z/r (charge/radius) values of the anions varies.

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