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Immobilization of ammonium and phosphate in aqueous solution by zeolites synthesized from fly ashes with different compositions

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ABSTRACT

Immobilization of ammonium and phosphate by zeolites synthesized from low-calcium (LC-Z) and high-calcium (HC-Z) fly ashes is studied. LC-Z has higher ammonium immobilization capacity while HC-Z has better performance in phosphate uptake. As part of Ca^{2+} released from HC-Z compete with ammonium the exchangeable sites in LC-Z, LC-Z can affect phosphate immobilization of HC-Z, and HC-Z also lowers ammonium uptake of LC-Z. Separate dosing of LC-Z and HC-Z, i.e., first LC-Z and then HC-Z, is proved better than mixed dosing at simultaneous immobilization of ammonium and phosphate. The effect parameters for phosphate and ammonium immobilization of LTH-Z are investigated.

1. Introduction

Before discharging into the river, a considerable amount of ammonium and phosphorus in the industrial and municipal wastewater is removed after being treated in the sewage treatment plant. However, the remaining ammonium and phosphorus in the discharged effluent still becomes an environmental problem if discharged into a waterway with low water flow, as ammonium and phosphorus can encourage entrophication of the waters receiving the discharge [1]. The development of the efficient technology for ammonium and phosphorus removal thus receives great attention, as the complementary and substitute technique for the conventional sewage treatment technology.

Many materials immobilizing ammonium and phosphate are thus developed in various studies [2–13]. Among the materials, zeolite exhibits a great potential [13]. With high cation exchange and adsorption capacity, zeolites are hydrated aluminum–silicate minerals with three-dimensional honeycomb structure [14,15]. They uptake ammonium through ion-exchange, and immobilize phosphate by adsorption and precipitation of calcium phosphate. The natural zeolites have strong ability to uptake the ammonium. However, these zeolites are usually less effective for phosphate immobilization due to their low calcium and iron content [16,17], and exhibit poor performance in phosphate immobilization.

Fly ash is a waste material generated from electric power plants. As the chemical composition of fly ash is similar to that of volcano which is the predecessor of zeolite, the fly ash can be converted into zeolite through hydrothermal and fusion methods [18–20]. The synthesized zeolites from fly ash have been used widely for pollutants removal in gas, wastewater and polluted soil [21]. The chemical composition of fly ashes is also different from each other, and fly ash used for cement and concrete in China (GB/T 1596-2005) classifies fly ashes into three groups: low-calcium fly ash (CaO < 5%), intermediate-calcium fly ash (CaO ≈ 15%), and high-calcium fly ash (CaO > 15%). The synthesized zeolites from different fly ashes exhibit different properties. Zeolite synthesized from low-calcium fly ash (LC-Z) exhibits much better performance in ammonium uptake [22]. Zeolite synthesized from high-calcium fly ash (HC-Z) had higher phosphate immobilization capacity than that from low-calcium fly ash [23]. This indicates that HC-Z and LC-Z can be used together to immobilize simultaneously the ammonium and phosphate. However, how to operate the process receives little attention.

In the present study, the LC-Z and the HC-Z were synthesized, respectively. Their effectiveness in the simultaneous immobilization of phosphate and ammonium was studied with two different operation modes including mixed dosing and separate dosing. By comparing the obtained results, the authors analyzed the different performance of the two operation modes. The influence of pH, adsorbent dosage and initial pollutant concentration on the simultaneous immobilization of phosphate and ammonium by LC-Z and HC-Z with separate dosing was investigated in real wastewater. The main effects and their interaction of the parameters considered were studied by using a 2^3 factorial design.

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2. Materials and methods

2.1. Zeolite synthesis and characterization

Low-calcium fly ash (LC-F) (CaO content = 3.31% < 15%) and high-calcium fly ash (HC-F) (CaO content = 37.55% > 15%) were obtained from a power plant located in China. An alkaline fusion prior to hydrothermal method described previously was adopted for the synthesis of zeolite [24]. The analysis for X-ray diffraction (XRD), special surface area (SSA), cation exchange capacity (CEC), phosphate immobilization capacity (PIC) and chemical compositions were conducted with the methods and equipments described in previous papers [25,26]. The obtained chemical compositions of the fly ashes and synthesized zeolites are shown in Table 1.

2.2. Batch experiments

1) Mixed dosing: LC-Z and HC-Z were added simultaneously into the solution and then agitated. LC-Z and HC-Z with mixed dosing were called MLH-Z for short.
2) Separate dosing: LC-Z was added first into the solution. The solution was agitated first with LC-Z and then centrifuged. The sediment obtained by centrifugation was removed. Secondly, HC-Z was added into the resultant supernatant and agitated. LC-Z and HC-Z with separate dosing were called LTH-Z for short.
3) Performance of MLH-Z and LTH-Z in the simultaneous removal of phosphate and ammonium.
   To investigate the immobilization efficiency of MLH-Z for ammonium and phosphate, 25 mL of solution containing phosphate and ammonium simultaneously, prepared with anhydrous NH_4Cl and $(NH_4)2HPO_4$ (analytical grade), was agitated with MLH-Z in 100 mL stoppered conical flasks at 25 °C. The adsorbent dosage was 4 g/L with the LC-Z/HC-Z ratio range of 0:5–5:0, and the magnetic stirrer was 180 rpm. The initial ammonium and phosphate concentrations were 50 mg P/L and 10 mg N/L, respectively. The N/P ratio was chosen as 5 here since the concentrations of ammonium and phosphate present in domestic waste waters in China typically have an N/P ratio of 5 [23]. The pH of the solution was adjusted to 7.5 by adding 1 mol/L of HCl or NaOH, according to the previous studies (the previous studies showed that the optimal pH for ammonium and phosphate removal using the synthesized zeolite was 8.0 and 7.0, respectively) [25,26]. The pH of the solution was monitored by a pH meter (DELTA 320). The previous studies showed that the sufficient time to reach equilibrium for ammonium and phosphate using the synthesized zeolites was 1.25 and 28 h, respectively. To achieve the equilibrium, the solution was agitated with MLH-Z for 28 h.
   To compare the performance of MLH-Z and LTH-Z in the simultaneous immobilization of ammonium and phosphate, the solution containing both phosphate and ammonium was treated by MLH-Z and LTH-Z at 25 °C, respectively. The initial concentration of ammonium and phosphate was 50 mg/L and 10 mg/L, respectively. Based on the above studies, the LC-Z/HC-Z ratio in MLH-Z and LTH-Z was chosen as 4:1 which was optimal for the solution containing 50 mg/L ammonium and 10 mg/L phosphate. The adsorbent dosage was 4 g/L. To achieve the equilibrium, for the solution treated by MLH-Z, the solution was agitated with MLH-Z for 28 h. For the solution treated by LTH-Z, the solution was agitated firstly with LC-Z for 1.25 h, and then centrifuged. The resultant supernatant was then agitated with HC-Z for 28 h. The other working conditions were the same as those mentioned above.
4) Reason for the different performance of MLH-Z and LTH-Z in the simultaneous removal of phosphate and ammonium. To analyze the reason, the effect of ammonium in the phosphate immobilization capacity of HC-Z and the influence of phosphate on the ammonium uptake of LC-Z were investigated. The influence of LC-Z on the phosphate immobilization capacity of HC-Z was studied, and the impact of HC-Z on the ammonium uptake of LC-Z was also analyzed.
   To investigate the effect of ammonium on the phosphate immobilization using HC-Z, the phosphate immobilization using HC-Z was conducted with the ammonium concentration of 0–50 mg/L which was obtained through adding ammonium solution prepared from NH_4Cl (analytical grade). The initial phosphate concentration was 100 mg/L and the HC-Z dosage was 2 g/L.
   To study the effect of phosphate on the ammonium uptake by LC-Z, the ammonium uptake was studied with the LC-Z dosage of 4 and the initial ammonium concentration of 50 mg/L. The phosphate concentration was in the range of 0–50 mg/L, which was obtained through adding phosphate solution prepared from KH_2PO_4 (analytical grade).
   To analyze the effect of LC-Z on the phosphate immobilization of HC-Z, the phosphate immobilization was studied with LC-Z of 0–10 g/L and the phosphate initial concentration of 100 mg/L at 25 °C. The results were compared with those obtained by MLH-Z with HC-Z of 2 g/L and LC-Z of 0–10 g/L.
   To investigate the effect of HC-Z on the ammonium uptake of LC-Z, the ammonium uptake was conducted with HC-Z of 0–10 g/L and the ammonium initial concentration of 50 mg/L. The same experiment was studied by using MLH-Z with LC-Z of 4 g/L and HC-Z of 0–10 g/L. The obtained results were compared with each other.
   To study the interaction between LC-Z and HC-Z, the experiments using distilled water instead of the ammonium and phosphate solution were also conducted following the same procedure. The concentrations of Na^+, K^+, Ca^{2+}, and Mg^{2+} in distilled water treated by MLH-Z with the different dosage and LC-Z/HC-Z ratio were measured by inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 2000, PerkinElmer Co., USA). The dosage and LC-Z/HC-Z ratio of MLH-Z were listed in Table 2.
5) The influence of pH, adsorbent dosage and initial pollutant concentration on the simultaneous immobilization of phosphate and ammonium by using LTH-Z.

To explain the effect of adsorbent dosage, initial pollutant concentration and pH, the ammonium and phosphate immobilization was conducted in real wastewater from Gaobeidian Sewage Treatment Plant in Beijing, China. The Na^+, K^+, Ca^{2+} and Mg^{2+}

Table 1
Chemical compositions of fly ashes (wt%).

Component	Content (%)			
	LC-F	HC-F	LC-Z	HC-Z
SiO_2	75.69	30.76	50.76	23.75
Al_2O_3	6.43	14.31	15.18	9.06
Fe_2O_3	5.45	10.27	5.41	9.37
CaO	3.31	37.55	2.09	32.51
Na_2O	0.51	0.15	16.24	1.02
K_2O	0.07	1.27	0.016	0.037
MgO	0.12	3.03	0.072	2.62