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Ionothermal synthesis of aluminophosphates used for ion exchange: Influence of choline chloride/urea ratio

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ABSTRACT

A wide variety of industrial processes produce aqueous effluents that contain heavy metals. Considering the toxicity of metal polluted wastewaters, ion exchange appears as an easy and inexpensive option to remove metal ions from these effluents. There is currently much investigation on synthetic and natural materials to be used as cation exchangers. Among these materials, using microporous molecular sieves have been proposed due to their high surface area, porous diameter and ion exchange capacity. In this work, aluminophosphates (AlPOs) were prepared by the ionothermal method using the eutectic mixture urea/choline chloride (CCh) as solvent and template. Different CCh ratios in the eutectic mixture used in gel synthesis resulted in different structures with very distinguished ion exchange capacities. The main structures obtained were SIZ-2 and AlPO-CJ2. Varying the percentage of CCh in the gel synthesis mixture, it was observed that the AlPO-CJ2 structure is obtained using CCh percentages greater than 50%, while SIZ-2 is obtained using 25% and 33.3% CCh. The structure-directing the interrupted structure are the ammonium cations coming from the partial decomposition of urea. The SIZ-2 prepared using 25% CCh has a somewhat higher ion exchange capacity than that observed using 33.3% CCh. This result is very interesting since CCh is the most expensive component in the eutectic mixture.

1. Introduction

When untreated industrial wastewater containing heavy metals is released into the environment, it can lead to hazardous problems in aquatic life and human health. Some metal ions are very harmful and cannot be treated by conventional biological treatment plants; thus, it is necessary to remove them in order to comply with the concentration levels imposed by the environmental agencies. This can be carried out using different processes, such as chemical precipitation, reverse osmosis, ion exchange and electrochemical technology. The chemical treatment is widely used, but when the ion concentration is very low it is not very effective [1]. The electrochemical technology is very attractive due to its low cost and its capacity to recover solid metals that can be further reused; however, for concentrations lower than 100 ppm the current efficiency is very low [2]. In these cases, the ion exchange can be used to overcome such limitation of the electrochemical process and the concentrated solution obtained after desorption can be treated in an electrochemical reactor. The capacity of an ion-exchanger to release the cations in desorption process permits its use in several consecutive cycles.

In the last few years, there have been a great number of articles in the literature concerning the synthesis of new materials to be used in ion exchange. Natural and synthetic molecular sieves and polymers have been investigated as cation exchangers in order to improve their sorption capacity and reduce their cost. Zeolites and zeotypes are microporous materials known as molecular sieves with three-dimensional open frameworks of corner-linked TO_4 tetrahedral ($T = Si, Al, P$, etc.). Since their discovery, they have been broadly exploited as shape-selective catalysts, sorbents and ion exchangers in different industries and research fields, mainly due to their properties such as high specific surface area, pore diameter, and ion exchange sites [3]. Among these materials, the aluminophosphates, $AlPO_4$-*n*, are microporous inorganic polymers constituted by a three-dimensional framework of alternated AlO_4^- and PO_4^- tetrahedral [4] with a structural neutral charge. This characteristic makes the AlPOs unsuitable to be used as cation exchangers since there are no counter charges available in the structure to be exchanged [5]. However, few years ago, Cooper et al. developed a new technique to prepare aluminophosphates using ionic liquids (IL) and eutectic mixtures (EU) in which these compounds acted as solvent and template, simultaneously [6]. They found that these materials, called zeotypes, have a cation sorption capacity due to their interrupted structure. This new method has been denominated ionothermal synthesis. This new

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class of compounds has some properties that render them a promising alternative as interesting solvents mainly due to their very low vapor pressure [7,8].

In contrast with the hydrothermal synthesis commonly used to prepare AlPOs, the ionothermal synthesis using ILs and EUs have some advantages since these liquids, defined as fused salts in temperatures below 100 °C, can be used to prepare zeolites or aluminophosphates in low vapor pressure, therefore the synthesis occurs at ambient pressure, eliminating safety concerns associated with high hydrothermal pressures [9–11].

In this work, microporous aluminophosphates were synthesized using the eutectic mixture urea and choline chloride (CCh). Different ratios of urea and CCh were used in order to verify their influence on the structure and ion exchange capacity of the aluminophosphate.

2. Experimental section

2.1. Synthesis of choline chloride/urea eutectic mixture

Choline chloride (Sigma–Aldrich) and urea (Synth) were used in different concentration ratios to prepare the eutectic mixture (EU). The urea and CCh mass of each experimental condition was varied according to the molar percentage of CCh in the eutectic mixture: 0%, 25%, 33.3%, 50% and 100%.

2.2. Synthesis of the aluminophosphates

The typical synthesis procedure was as follows: a Teflon-lined autoclave (50 mL) was filled with choline chloride/urea eutectic mixture, phosphoric acid 85 wt.% (Mallinckrodt) and aluminum isopropoxide (Sigma–Aldrich). The gels were prepared with the following molar composition: Al_2O_3:$3P_2O_5$:40EU:$2.9H_2O$, in which the water comes from the H_3PO_4 solution.

Syntheses with excess deionized water and using fluoridric acid 48 wt.% (Mallinckrodt) as mineralizing agents were carried out according to the following molar compositions:

(i) Al_2O_3:$3P_2O_5$:40EU:$64.9H_2O$
(ii) Al_2O_3:$3P_2O_5$:40EU:0.7HF:$2.9H_2O$

Although ionothermal synthesis can be carried out in open vessels under ambient conditions, in this work the synthesis using autoclaves were preferred in order to avoid water loss, whose importance is discussed hereinafter. Stainless steel autoclaves were heated in a stove at 180 °C for 72 h. After the crystallization, the solid product was separated by centrifugation, washed with deionized water and then dried at 110 °C.

2.3. Characterization of the aluminophosphates

The samples were analyzed by powder X-ray diffraction (XRD) with CuKα radiation using a Siemens X-ray diffractometer, model D5005 (40 kV, 40 mA, CuKα radiation with the Ni filter) at a rate of 2° min^{-1} 2θ. Thermogravimetric analysis (TGA) was performed using a TA Instruments, model SDT Simultaneous DSC-TGA. A sample of 20 mg of aluminophosphate was heated at a constant rate of 10 °C min^{-1} under 100 mL min^{-1} oxygen flows. Scanning electron microscopy (SEM) was performed using gold sputtered samples observed in a Scanning Electronic Microscope (Philips, model XL 30 FEG).

2.4. Ion-exchange experiments

Ion exchange experiments were carried out in order to evaluate the ion exchange capacity of new aluminophosphates obtained under the different synthesis conditions.

The aluminophosphates obtained immediately after the syntheses were in their ammoniacal form due to urea decomposition, *i.e.*, the cation compensating the charge in the interrupted framework was NH_4^+. Before using the aluminophosphate in the cation exchange experiments, it was converted to its sodium form by mixing it in a 3.5 mol L^{-1} NaCl (Synth) solution for 24 h. For the ion exchange experiments, $CuSO_4{\cdot}5H_2O$ (Synth) was used as a source of copper ions. Deionized water was used to prepare all solutions.

The batch experiments to measure the ion-exchange capacity (Γ) were carried out in Erlenmeyers, with each one containing a known mass of aluminophosphate (∼0.2 g) and 50 mL of Cu^{2+} solution. They were left under agitation in a shaker for 72 h in order to ensure that the equilibrium condition had been reached. After that, the liquid phase was separated from the solids by vacuum filtration and then the copper concentration in the liquid phase was determined.

The copper concentration was determined using an atomic absorption spectrophotometer Varian, model SpectrAA200. Using a mass balance, the ion exchange capacity (Γ) in the solid phase was determined using Eq. (1), in which t is the time, V the volume, m_s the mass of aluminophosphate, C and C_0 the copper concentration at $t = 0$ and at the instant t, respectively. In the cases in which the time was very long, the equilibrium concentration was reached, with Γ_{eq} corresponding to the ion exchange capacity at the equilibrium conditions [12].

$$\Gamma(t) = (\frac{V}{m_s})(C_0 - C(t)) \tag{1}$$

2.5. Desorption experiments

In order to verify the copper desorption capacity of SIZ-2 previously used in the ion exchange experiments, approximately 0.1 g of Cu/SIZ-2 (SIZ-2 obtained using 33.3% CCh) was added to a 200 mL Erlenmeyer containing 100 mL of NaCl or HCl solution in different concentrations. The mixture was left in a shaker at 30 °C for 72 h. After this time, the solid was separated by filtration and dried at 110 °C. In order to measure the copper concentration in the solid phase, the AlPO was dissolved using hot concentrated HNO_3. The final solution was diluted and the Cu^{2+} was measured using the same previously described atomic absorption spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction (XRD)

Fig. 1 shows the XRD pattern of the sample prepared using a 33.3% of choline chloride (2:1 M). Using this synthesis condition the same aluminophosphate was obtained as that obtained by Cooper et al. the structure denominated SIZ-2 [6]. According to these authors this is an interrupted structure with ion exchange ability. The XRD data of SIZ-2 show a structure by good organization without impurities formation. In this XRD data, the characteristic peaks of the aluminophosphate SIZ-2 are denoted by an asterisk and a strong reflection can be observed at a low value of 2θ.

The effect of adding excess water (A) and HF (B) to the gel synthesis can be also observed in the XRD patterns in Fig. 2. The use of excess water or HF as mineralizing agent resulted in a different structure, the aluminophosphate AlPO-CJ2 [13]. Comparing the XRD patterns it can be observed that AlPO-CJ2 and SIZ-2 had practically the same diffraction peaks, except for the peak in the 2θ, which was about 10.3° for SIZ-2 (denoted by $*$). This characteristic is typical of silicate layers that show greater basal spacing, consequently showing low peak values at 2θ [14]. Thus, the