Abstract

The aim of this work is to investigate the orthophosphate adsorption by layered double hydroxides (LDH) in order to optimize the LDH for future implementation for recovery of orthophosphate from wastewater. Phosphate is a vital fertilizer in the agriculture. However, the current phosphate deposits will be depleted within 50-400 years. Hence, recycling of the phosphate such as recovery of phosphate is needed. LDH are a potential orthophosphate adsorbent due to their high affinity for orthophosphate compared to other anions. The LDH material consist of positively charged layered with intercalated anions in between the layers. The anions can be exchanged with other anions which gives LDH unique anion exchange properties. The macroscopic properties of orthophosphate adsorption by LDH such as time, adsorption isotherms, pH etc. have been extensively studied. However, detailed mechanistic insight on the adsorption is still lacking, but necessary for optimizing the LDH for optimal efficiency, and recyclability.

In this work the mechanism for orthophosphate adsorption for CaAl-, MgAl-, ZnAl- and MgFe-LDH is investigated by ^{31}P MAS NMR spectroscopy combined with complementary characterization techniques such as PXTD, FT-IR and SEM. From the ^{31}P MAS NMR spectra the different number of adsorption sites can be identified and quantified. From the combination with PXRD and ^{27}Al MAS NMR spectroscopy, the adsorption sites can be assigned. The mechanism for the orthophosphate adsorption is found to be dependent on the cation composition. The CaAl-LDH completely dissolves and calcium phosphates precipitates, whereas the orthophosphate adsorption for MgAl-LDH occurs through intercalation, surface adsorption and adsorption to amorphous aluminum hydroxide (AOH) present in LDH samples. Surface adsorption was found to be the dominating adsorption site, however adsorption by (AOH) constituted up to 39 % of the orthophosphate adsorbed by the LDH samples. For ZnAl-LDH the adsorption was a combination of surface adsorption, adsorption to AOH and precipitation of aluminum and zinc phosphates. PXRD indicated that the ZnAl-LDH layers might exfoliate during phosphate adsorption. For MgFe-LDH the paramagnetic nature of Fe^{3+} was exploited to determine that orthophosphate binds through outer-sphere complexation. In addition, due to the high adsorption from AOH, it was investigated if pure Al containing LDH could be obtained from urea hydrolysis by variation of temperature, post synthesis treatment and different heating methods. The purity of the obtained LDH product depended on the divalent cation. Almost pure NiAl-, CoAl- and ZnAl-LDH but not MgAl-LDH could be obtained.