Influence of cation building blocks of metal hydroxide precipitates on their adsorption and desorption capacity for phosphate in wastewater—A screening study

Asya Drenkova-Tuhtan [a,*], Michael Schneider [b,c], Karl Mandel [b,c], Carsten Meyer [a], Carsten Gellermann [b], Gerhard Sextl [b,c], Heidrun Steinmetz [a]

[a] Institute for Sanitary Engineering, Water Quality and Solid Waste Management (ISWA), University of Stuttgart, Bandtäle 2, 70569 Stuttgart, Germany
[b] Fraunhofer Institute for Silicate Research, ISC, Neunerplatz 2, 97082 Würzburg, Germany
[c] University of Würzburg, Chair of Chemical Technology of Materials Synthesis, Röntgenring 11, 97070 Würzburg, Germany

HIGHLIGHTS

- Unique comparison of numerous metal hydroxide adsorbers for phosphate was performed.
- Cations were systematically varied in a wide range to form LDH and related structures.
- Materials were tested in distilled and waste water reaching high adsorption capacity.
- Treatment with 0.5 M NaOH was sufficient to recover >90% of the adsorbed phosphate.
- ZnFeZr and CaZnFeZr have a high potential for phosphate recovery from wastewater.

GRAPHICAL ABSTRACT
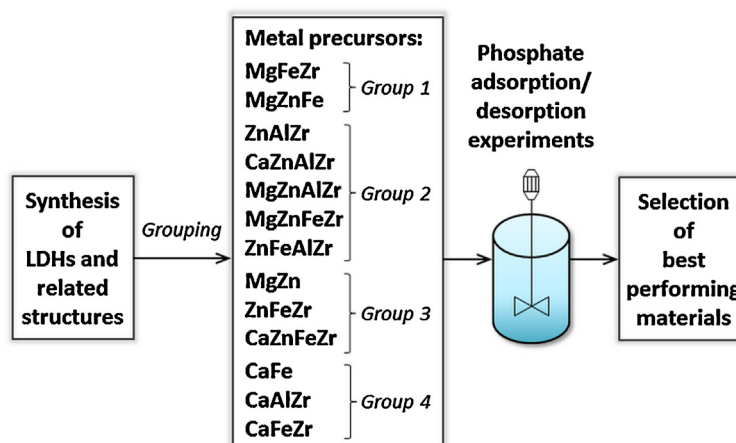
ABSTRACT

Thirteen metal hydroxide adsorbers were synthesized via precipitation by systematically varying different two-, three- and four-valent metal precursors, namely Mg^{2+}, Ca^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+} and Zr^{4+}. The resulting materials were classified in four groups based on their structure, morphology and BET surface area. Two of the groups could be classified as layered double hydroxides (LDH). The rest of the materials could be either only partially related to a LDH-like structure or formed non-layered precipitates. The phosphate removal performance of each adsorber (dose 200 mg/L) was tested in spiked distilled water and municipal wastewater (10 mg P/L) at pH 7–8. The phosphate adsorption capacity of the materials after 1 h varied between 32 mg P/g (for a rod-like-sample, lacking a layered structure) and 51 mg P/g (for a sample appearing as a mixture of particulate matter covered with a web-like structure). Longer contact time (24 h) did not increase significantly the adsorption efficiency. None of the materials was ideally selective for phosphate, especially the ones with a clear LDH structure and highest surface area ($110\,m^2/g$) which adsorbed up to 25 mg/g Cl^- and other competing anions. The adsorbed phosphate could be

* Corresponding author. Fax: +49 711 685 63729.
E-mail addresses: asya.drenkova@iswa.uni-stuttgart.de, drenkova@gmail.com (A. Drenkova-Tuhtan).

desorbed (>90% in most of the cases) by treatment with an alkaline solution (0.5 M NaOH or 1 M NaOH + 1 M NaCl) which turned out to be the best option for regeneration among many other tested combinations.

1. Introduction

Phosphorus is a limiting factor for the growth of organisms and therefore an important nutrient which is excreted by every human being and has to be removed from wastewater due to the risk of causing algae bloom, leading to eutrophication of the receiving water bodies [1]. On the other hand, phosphorus derived from phosphate rock is a valuable, non-renewable and irreplaceable limited resource which the fertilizer industry and modern agriculture heavily depend on. Therefore, developing technologies for its recovery from secondary phosphate rich sources, such as municipal wastewater, is of high importance. The most commonly applied current method for phosphate elimination from sewage is chemical precipitation with metal salts (in some cases also enhanced biological phosphorus removal) and subsequent removal with the sewage sludge. The precipitated metal phosphates alone have no fertilizer value, therefore phosphate has to be recovered from the sludge in a purer form which is a costly process with intensive chemicals consumption [2,3]. Alternatively, phosphorus may also be recovered directly from the wastewater effluent, assuming that no earlier targeted elimination takes place, where it is in a relatively low concentration distributed over a higher hydraulic load. Adsorption is known to be one of the most effective methods for phosphate removal from water in a low concentration range ($\mu g/L$–mg/L). Applying a suitable adsorber may also allow recovery of the phosphate in a pure form through desorption in an appropriate regeneration solution.

In the recent years intensive research focused on developing materials that are potentially promising adsorbers for phosphate [4–14]. In particular, combinations of two, three and even four valent metal cations, precipitated to hydroxides, appear to be promising candidates. Often these elemental combinations form positively charged layered structures, known as layered double hydroxides (LDHs). A wide variety of LDHs and other hydroxide precipitates has been investigated lately with respect to their phosphate adsorption properties [15–25]. However, the results of these studies cannot be compared easily. One of the reasons is the diversity of metal hydroxide synthesis methods carried out in many different ways by the different research groups. For instance, synthesis via coprecipitation which itself varies in the process details provided by each group [18,22,24,26], high temperature hydrolysis using urea [21,27,28], ion exchange [29], hydrothermal synthesis [18,29], or sol–gel methods [29] were reported. Another problem in comparing the phosphate adsorption capacity of the various adsorber materials synthesized by the different groups is that their performance is evaluated under different conditions, e.g. in deionized water [20,30,31], synthetic wastewater [6,18,24,25], municipal wastewater [30,32], sea water [6,17–19] or even sewage sludge filtrate [16]. Moreover, adsorption conditions are also different in terms of contact time, pH, adsorber dose, phosphate concentration, etc.

In this study we systematically varied the metal cations in a broad range, forming metal hydroxides such as LDH and related structures, in order to evaluate the influence of the metal building blocks on the phosphate adsorption and desorption performance within the hydroxide structures. The reaction conditions were kept constant during the synthesis of every material in order to provide a reliable basis of comparison for evaluating the

Table 1
Characteristics of the spiked municipal wastewater effluent used in the experiments.

Parameter	Spiked wastewater effluent
pH	7.2
Conductivity ($\mu S/cm$)	1086
TSS (mg/L)	1.0
COD (mg/L)	18.0
TC (mg/L)	45.4
TOC (mg/L)	6.24
TIC (mg/L)	39.2
P_{total} (mg/L)	9.93
PO_4-P (mg/L)	9.71
N_{total} (mg/L)	10.7
NH_4^+-N (mg/L)	0.043
NO_3^--N (mg/L)	9.22
NO_2^--N (mg/L)	0.08
Cl^- (mg/L)	149
SO_4^{2-} (mg/L)	76
Na^+ (mg/L)	135
Ca^{2+} (mg/L)	84
K^+ (mg/L)	18
Mg^{2+} (mg/L)	13
Si (mg/L)	2.3
Zn^{2+} (mg/L)	0.053
Fe (mg/L)	0.1

performance of the different structures. Furthermore, phosphate adsorption/desorption efficiencies of the samples were also compared under identical conditions.

2. Materials and methods

2.1. Reagents and materials

Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$) and zirconium(IV) oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) were purchased from Sigma–Aldrich (Germany), calcium chloride dehydrate ($CaCl_2 \cdot 2H_2O$) and zinc chloride ($ZnCl_2$) were purchased from Carl Roth (Germany) and used as received. Sodium hydroxide (NaOH) for the particles synthesis was obtained from VWR Chemicals (Germany), hydrochloric acid (HCl, 36%) was purchased from Carl Roth (Germany). Orthophosphoric acid (H_3PO_4, 85%) for spiking the wastewater samples, as well as sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) for pH regulation were purchased from Merck KGaA (Germany).

All wastewater samples were collected from the effluent of the wastewater treatment plant for education and research at the Institute for Sanitary Engineering, Water Quality and Solid Waste Management (ISWA), University of Stuttgart, Germany. The phosphate depleted wastewater was spiked with orthophosphoric acid (H_3PO_4) to reach the desired initial PO_4-P concentration. The composition of the spiked wastewater is summarized in Table 1. Furthermore, a phosphate working solution was prepared in purest form with double distilled water and addition of orthophosphoric acid (H_3PO_4) in order to avoid competition of other anions and determine the maximum capacity of the adsorbers. Phosphate desorption solutions were prepared with sodium hydroxide (NaOH), sodium chloride (NaCl), sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$) from Merck KGaA (Germany) and used also for regeneration of the materials.