Institute for Sanitary Engineering,
Water Quality and Solid Waste
Management

Research project:

´´Determination of the process variables for adsorption and desorption of phosphate from wastewater by selective ion exchangers on magnetic particles´´

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Abstract

In this study different process variables were evaluated for the adsorption and desorption of phosphate from wastewater by using selective ion exchangers with magnetic particles modified with layered double hydroxides (LDH). Adsorption and desorption kinetics for pure CaZnFeZr-LDH was performed. The best phosphate adsorption efficiency was achieved with CaZnFeZr-LDH, above 90 % after 1 and 24 h, whereas for the composite particle material with 7,6 wt% CaZnFeZr –LDH the adsorption efficiencies were 85,4 % and 92,1 % after 1 and 24 h, respectively. Ten adsorption/desorption cycles were performed by using three different desorption solutions (1 M $NaHCO_3$, 1 M NaOH+1M Na_2CO_3 and 3 M NaOH) where the last one showed the best performance. The pH effect was studied by using CaZnFeZr-LDH and ZnFerZr-LDH, where the first one achieved higher phosphate uptake. The effect of adsorbent dosage was investigated on filtered and unfiltered wastewater (WW), with 10 mg/L PO_4-P each, wherein the filtered had the best phosphate uptake with 99,2 % after 24 h using a ZnFrZr-LDH dosage of 259 mg/L. The adsorbent dosage was studied on unfiltered WW spiked at three different concentrations of PO_4-P: 10, 100 and 300 mg/L. The phosphate adsorption was also studied at different temperatures: 15, 22, 35 and 50 °C, wherein as the temperature increases the amount of adsorbed phosphate onto the LDH increases as well. Moreover, an adsorption kinetic experiment was performed by using filtered and unfiltered WW spiked with PO_4-P. The first one reached equilibrium at about 4 h with a phosphate uptake of 99 %. Desorption kinetics was developed for the filtered WW and the best performance was in the case of regeneration with a solution of 1 M NaOH in distilled water. The best adsorbent dosage for the maximal removal of 431 mg/L PO_4-P in the Offenburg WW (99,9 % adsorption efficiency) was 3000 mg/L ZnFeZr-LDH. After performing five adsorption/desorption cycles with the Offenburg WW, a conclusion was drawn that it is necessary to maintain pH~7 during the adsorption cycles. The total adsorption efficiency was 94,2 % and from this, 73 % was desorbed.

Keywords: Layered double hydroxides, phosphate recovery, adsorption/desorption cycles, magnetic particles, wastewater.

Acknowledgments

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I would like to say thank you to Dipl.-Ing. Asya Drenkova-Tuhtan for giving me the opportunity to perform this study under her supervision and for her guidance during the same. I clearly state that all the experiments, data calculations and writing of this project were done by me and are reliable.

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List of Symbols and Abbreviations

WWTP	Wastewater Treatment Plant
WW	Wastewater
SST	Secondary Settling Tank
P	Phosphorus
N	Nitrogen
C	Carbon
DNA	Deoxyribonucleic acid
RNA	Ribonucleic acid
ADP	Adenosine diphosphate
ATP	Adenosine triphosphate
C	Carbon
N	Nitrogen
IFDC	International Fertilizer Development Center
IFA	International Fertilizer Industry Association
EBRP	Enhanced Biological Removal of Phosphorus
PAOs	Polyphosphate Accumulating Organisms
LDH	Layered Double Hydroxides
IE	Ion Exchange
CLDH	Calcined Layered Double Hydroxides
SS	Suspended solids
DW	Distilled water
TW	Tap water

Chapter 1: Introduction

1.1 Motivation

There is a significant concern nowadays related to how much phosphorus reserves are globally available, motivating scientists and engineers to find alternatives to obtain phosphorus from secondary sources and to reduce the dependency on the natural mineral reserves.

Phosphorus (P) was discovered by the German alchemist Henning Brandt in the late 1600´s, when he distilled urine and observed that the product shined in darkness and that it was also flammable. Nevertheless, it was no until 1840 that the German chemist Liebig discovered that the soil used in agriculture had a deficiency of P as a nutrient; therefore, it was used for the production of fertilizers (Cordell & White, 2011).

Phosphorus is a non-metal and a very reactive element that exits as two main allotropes, white and red phosphorus, with the first one being the most common. However, it cannot be found as a free element in nature but it is found in many minerals in the form of phosphates on rocks and exists in two forms, as sedimentary rocks and as igneous rocks. The first form also called apatites, where its chemical formula is $Ca_5(PO_4)_3(F,Cl,OH,Br)$ and exists as four types of calcium phosphate apatite: Hydroxyapatite, fluorapatite, chlorapatite, and bromapatite, where the second is the most common. Furthermore, these apatites contain impurities such as humic substances and heavy metals like cadmium, uranium and zinc. The P is present in the phosphate rocks between 30-40 % but as a P_2O_5, this mean that P is present between 5-13 % (Desmidt *et al*, 2015 and Cordell & White, 2011).

It is important to underline that the sedimentary rocks have varieties of carbonate-fluorapatite, namely francolite, and it is composed mainly of CO with > 1 % of fluorine and also contains Ca, Na and Mg. The igneous rock contains carbonatites and alkali incrustations (Van Kauwenbergh, 2010).

Phosphorus is a very import nutrient for all flora, fauna and human beings because it is present in DNA and RNA molecules, it is the second compound in the animal skeleton, it has an important role in biochemical reactions, it is part of the phosphorus cycle and moreover, contributes to the cellular energy transport as ADP and ATP (Cheng *et al* 2009 and Martin, 2010). In addition, phosphate products are predominantly used in the agricultural and nonagricultural industries. In the former, it is used for the production of fertilizers as pesticides and food additive in the animal feed, where up to 90 % of all mined phosphates rocks are used for this purpose. For the second sector, it is used in the human food industries, in the pharmaceutical industries, for the production of detergents and in chemical industries (Desmidt *et al*, 2015 and Panasiuk, 2010).

The phosphorus, along with the nitrogen (N) and the carbon (C) are elements that regulate the biological activity, where the C and the N can be obtain from the atmospheric air, but this is not the case for P, because it cannot be circulated in the atmosphere easily. Therefore, it is a limiting nutrient in the crop soil and needs to be added as a fertilizer. Due to the steady increase in the world population, there is more demand for the production and use of fertilizers, leading to a lack of P in the world since phosphate rock is not a renewable resource (Cordell *et al*, 2009).

Currently, there are two opinions regarding the supply of phosphate rock; some studies suggest that the reserves will be exhausted over the next 50 to 100 years but other studies say that they are sufficient for the next 400-1000 years. Moreover, the IFA (International Fertilizer Industry Association) recently disproved the phosphate peak of 2009. However, they emphasized that the phosphate rocks is a nonrenewable resource. On the other hand, it is estimated that around the world, 180-190 million tons of phosphate rock is mined every year. (Desmidt *et al*, 2015, Kalmykova *et al*, 2015 and Cooper *et al*, 2011).

As it can be observed in figure 1-1, the three main producing countries of phosphate rocks are China, the United States, Morocco and Western Sahara (De Ridder *et al*, 2012).

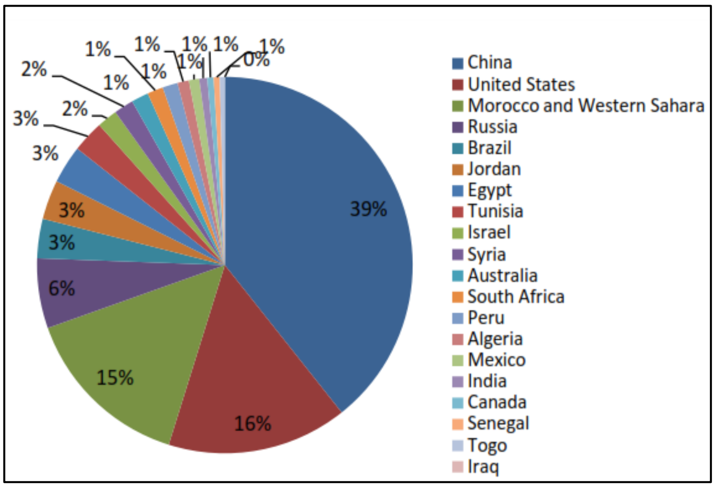

Figure1.1. Main global producers of phosphate rock in 2011 (De Ridder *et al*, 2012).

Regarding the worldwide phosphate rock reserves, it can be observed in figure 1-2 that Morocco, China, the US, South Africa and Jordan are the countries with the most reserves of phosphate rock, meaning around 95 % of it are present in those places, where Morocco has 85 % of that total share. This aspect leads to a geopolitical concern because there is no policy related to the security of the phosphorus between the countries. Furthermore, Finland is the only country in the European Union that has deposits (Cordell and White, 2011 and Cooper *et al*, 2011).

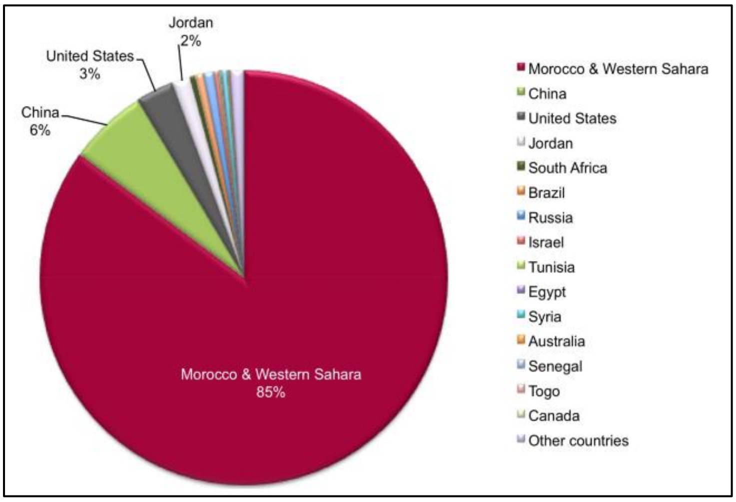

Figure1.2.Global phosphate rock reserves reported in 2010 by IFDC (Cordell and White, 2011).

Germany, which does not have any deposits of phosphate rocks, has to import unmilled P from other countries, such as Syria, Algeria and Egypt. In 2010, Germany imported approximately 118000 Mg and, from this amount, around 60 % was used for the production of fertilizers, 20 % for the development of feedstuffs and 6 % were used for the food industry (LAGA, 2010).

Another very significant issue is the losses present in every use of phosphorus/phosphate which can be seen in figure 1-3.

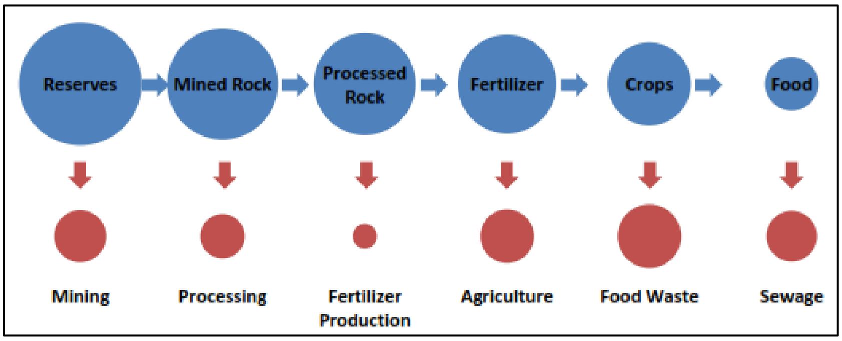

Figure1.3. Major uses and sinks of phosphate (De Ridder *et al*, 2012).

Concerning the figure 1-3, it can be stated that the main sinks of phosphate are in food waste, agriculture, mining and sewage sludge. Therefore, the implementation of new technologies for the recycling of phosphate is of particular interest (De Ridder *et al*, 2012).

In addition to the limited supply, unmanaged loss of P into the water bodies has a negative effect due to microorganisms starting uncontrolled and rapid growth leading to eutrophication. The eutrophication causes a reduction of the biodiversity in the environment and in the water quality, an increase of undesirable organisms that can bring toxic substances, depletion of oxygen and other consequences (Panasiuk, 2010 and Das *et al*, 2006).

1.2 Present solutions for the removal and recovery of phosphorus

Due to the concerns already presented above, there are technologies that have been developed in order to remove and recover P from wastewater. Those associated with this research project will be explained, whereas others are not subject of interest in this work.

The P that enters a WWTP comes predominantly from domestic, but also from agricultural/industrial sources. Once the P goes into the WWTP, it can be particle bound or dissolved in different forms: Around 50 % of it is in the form of orthophosphate (PO_4^{-3}), which is a soluble inorganic compound, then 35 % as polyphosphate that comes principally from detergents and finally 15 % as organic phosphate. Municipal WW contains between 6-8 mg/L of total P and this leads to the necessity to remove it from WWTP (Parsons and Smith, 2008 and Nieminen, 2010).

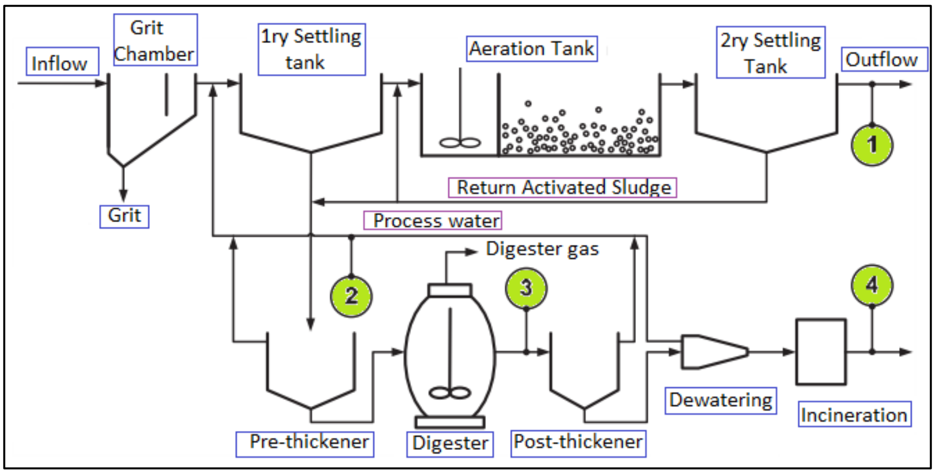

Figure1. 4. Possible points of phosphorus recovery within a WWTP scheme (DWA Working Group CEC 1.1, 2013).

As it can be observed in figure 1-4, the P can be removed from 4 different stages of the wastewater or sludge treatment line within a WWTP. The **first stage** corresponds to the **outflow**, which contains less than 5 mg P/L dissolved, if no earlier targeted elimination takes place, then the **second stage** is the sludge liquor that has 20-100 mg P/L which is also dissolved, the **third stage** belongs to the **digested sludge** containing 30-40 gP/kg which is chemically/biologically bound and finally, the **fourth stage** is the **sludge ashes** that has 60-80 g P/kg which is chemically bound. From each stage, the phosphorus removal potential is 55, 50, 90 and 90 %, respectively (DWA Working Group CEC 1.1, 2013).

Currently, two main processes are applied for phosphorus removal from wastewater: Chemical precipitation and enhanced biological removal of phosphorus (EBRP). The <u>chemical precipitation</u> can remove around 90 % of the P of the total inflow. This procedure consists in the use of chemical salts of Fe^{+2}, Fe^{+3} and Al^{+3} bound to chloride or sulphates ions. Once the salt has been added, the metal phosphate solids precipitate and form chemical sludge which is withdrawn together with the excess activated sludge. The disadvantage of this process is that the sludge contains metals (Parsons and Smith, 2008).

Concerning the <u>enhanced biological removal of phosphorus</u>, the main idea of the process is to reduce the quantity of P in the effluent of a WWTP. For this purpose it is necessary to use specific microorganisms called Polyphosphate Accumulating Organisms (PAOs). Those organisms take up the excess phosphate present in the WW, which can be done under anaerobic conditions.

The EBRP transforms the P that is diluted into more concentrated form which is stored inside of the bacteria and results in sludge with around 60-90 % of PAOs (Yuan *et al*, 2012).

For the recovery of P, there are three main processes that will be explained briefly in this work:

a) Precipitation and struvite crystallization from sludge liquor: Both processes transform the dissolved PO_4-P in the sludge liquors into a solid form. The precipitation involves the use of chemicals in order to obtain calcium phosphate or struvite $[(NH_4)MgPO_4 \cdot 6H_2O]$. The difference between both is time, where the precipitation is faster and the crystallization is slower. Two different techniques can be used for this purpose: Precipitation in stirred reactors or crystallization in fluidized bed reactors. The general idea is first to nucleate small pieces of crystals and then to let the crystals grow which helps for the transportation of the ions from the solution to the crystal surface. It is important to manage the reaction parameters such as pH and temperature for the development of the crystals (Nieminen, 2010; Parsons and Smith, 2008 and Ewert *et al*, 2014).

b) Wet chemical technologies for P-recovery from sludge and sludge ash: Chemically and biologically bound P in sludge or sludge ash can be re-dissolved by utilization of a strong acid or base. Later on phosphate can be recovered via precipitation (e.g. struvite), ion exchange, nanofiltration, etc. (Nieminen, 2010). The ion exchange method will be explained in chapter 2.

c) Thermal-chemical treatment: It is used for the removal of heavy metals that are present in the sewage sludge. Phosphorus is concentrated and the sludge ashes which contain around 17 % of P_2O_5 and the product can be used for fertilizers production (Nieminen, 2010).

1.3 Aim and specific objectives

This research project aims to find another sustainable solution for the removal and the recovery of P from a WWTP. The main task is to determine the influence of the different process variables on the adsorption and desorption of phosphate from WW by using a selective ion exchangers on magnetic particles. The following specific objectives were formulated:

- ✓ To evaluate the efficiency of adsorption and desorption of phosphate (PO_4-P) on a pure LDH material, as well as the kinetics of the reactions.

- ✓ To compare the influence of different particle synthesis methods on PO_4-P adsorption performance.
- ✓ To find out the best desorption solution after tenth adsorption and desorption cycles of particles reuse and regeneration in three different solutions.
- ✓ To investigate the pH effect on the adsorption of phosphate and to find out which is the optimum pH value for such adsorption by using two types of magnetic LDH-particle materials.
- ✓ To study the effect of adsorbent dosage on the adsorption of phosphate on filtered and unfiltered wastewater, both spiked with H_3PO_4, at 22 °C with two different LDH-particle materials.
- ✓ Develop adsorption isotherms in filtered wastewater spiked with H_3PO_4 under different temperatures: 15, 22, 35 and 50 °C by using water bath and conclude which is the optimum temperature for the reaction.
- ✓ To analyze the adsorption and the desorption kinetics of phosphate on LDH-loaded magnetic particles at room temperature and pH 7,5.
- ✓ To study the effect of adsorbent dosage on the adsorption of phosphate from sludge filtrate after acid dissolution from the WWTP Offenburg and perform fifth adsorption and desorption cycles with the composite particles.

1.4 Research project structure

The first chapter explained the main issues concerning the lack of P around the world as well as the current solutions for the removal and recovery of it. It described the main aim and the specific objectives of this research project.

The second chapter is based on literature review and explains what are layered double hydroxides (LDH) as wells as the principles of ion exchange. This chapter summarizes also some preliminary studies carried out at an earlier stage of the research project which served as a base for the design and performance of the current experiments.

The third chapter describes in details the eight different experiments which were performed with pure LDH and LDH deposited on magnetic particles, in order to determine the different process variables for the adsorption and desorption of phosphate from WW by using selective ion exchange.

The fourth chapter includes the discussion of the results from the different experiments and concludes about the optimum range of the reaction parameters, such as temperature, pH, contact time and different concentrations of H_3PO_4 and LDH-particles for the adsorption and desorption of phosphate from WW.

The fifth chapter contains the main conclusions of this work as well as some recommendations for the development of further research.

Chapter 2: Ion exchange and layered double hydroxides

2.1 Ion Exchange

Ion exchange (IE) is a process in which ions present in a solution are exchanged using a highly polyelectrolyte insoluble solid that is in contact with the solution ions. This ion exchanger contains ions which are to be interchanged with the targeted ions in certain solution. Furthermore, the IE is a reversible and stoichiometric process. This method is used mainly for water softening in the field of drinking water treatment (Meyer, 2014 and Jeffery *et al,* 1989).

It is important to mention, that the exchange of ions has a strong dependency on the charge valence and the weight of the ions that are involved in the process. In the case of phosphate, due to its low concentration in the wastewater 4 to 16 mg/L (Mandel *et al,* 2013 and Rittmann *et al*, 2011), IE is very suitable for the recovery of P, but regular techniques like ion exchange resins cannot be used, even when the phosphate has a high molecular weight and a high charge valence (Martin, 2010).

On the other hand, since the ion exchange depends on the charge valence of the ion, phosphate can be found as different species at different pH values, i.e. as monovalent ($H_2PO_4^-$), as divalent (HPO_4^{2-}) and as trivalent (PO_4^{3-}), equation 1:

$$\begin{aligned} &H_3PO_4 \xrightarrow{pK_{a_1}=2.15} H_2PO_4^- + H^+ \\ &\xrightarrow{pK_{a_2}=7.20} HPO_4^{2-} + 2H^+ \xrightarrow{pK_{a_3}=12.33} PO_4^{3-} + 3H^+ \end{aligned} \qquad (1)$$

This means that it can exist as the divalent anion HPO_4^{2-} and as the intermediate monovalent anion $H_2PO_4^-$ in wastewater streams where pH is close to neutral. Additionally, the divalent anion presents two donor electrons, whereas the monovalent just one, which means that both can act as ligands for the attraction and the formation of complexes with transition metals and, i.e. with the metals contained in the LDH structure, resulting in the removal of phosphate from wastewater streams (Martin, 2010; Chitrakar *et al*, 2007 and Yang *et al*, 2015).

Therefore, some of the ion exchange processes that could be utilized in this work for the removal and the recovery of phosphate are capacitive deionization on oppositely charged electrodes, iron-based layered double hydroxide (LDH) compounds that release cations and/or hydroxides and metal-loaded chelating resin used to selectively remove phosphate (Rittmann *et al*, 2011). The LDH will be explained in detail because of its relevance to this work.

2.2 Layered double hydroxides (LDH)

The layered double hydroxides, known also as hydrocalcite-like compounds (HTlc), have been studied widely in the last three decades for their synthesis and applications. LDHs exist as minerals ($Mg_6Al_3(OH)_{16}CO_3 \cdot 4H_2O$) but they can also be economically synthetized in a relatively simple manner. The LDHs are anionic clays with two-dimensional nanostructure, as shown in figure 2-1, where the brucite-like sheets ($Mg(OH)_2$), are positively charged and those charges are balanced by the intercalation of anions in the hydrated interlayered spaces. The layers can have monovalent, divalent, trivalent and, even, tetravalent cations and these results in a highly positive LDH material. Since the LDHs have a weak interlayer bonding, they are perfect for the caption of organic and inorganic anions. On the other hand, those interlayer anions are linked by weak electrostatic forces that permit the ion exchange. However, the ion exchange is not the only mechanism contributing to the removal of phosphate - electrostatic attraction and formation of ligands can occur as well (Goh *et al,* 2008 and Yan *et al,* 2015).

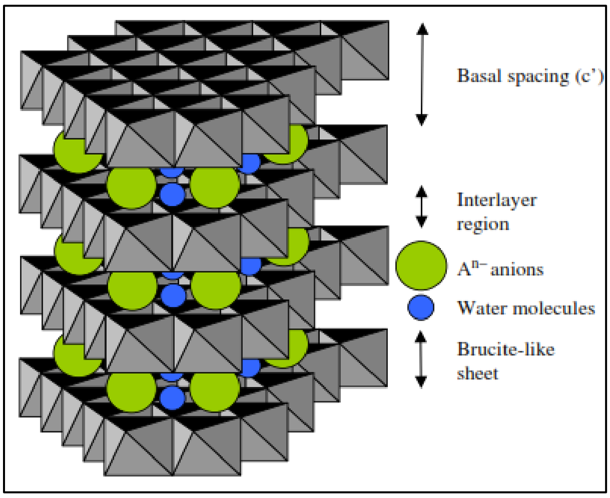

Figure 2. 1. Structural representation of LDH materials (Goh *et al,* 2008).

The general formula of a LHD is given in equation 2, where M^{2+} and M^{3+} are the divalent and trivalent cations, respectively, A^{n-} is the interlayer anion with a valence n that can be organic, inorganic, carboxylate, oxyanion or coordination compounds, and x has values between 0,1 and 0,33 and. When this value is not in this range, impurities can be incorporated (Goh *et al*, 2008 and Koilraj and Kannan, 2010).

$$[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O \qquad (2)$$

The LDH materials are widely used as adsorbents and ion exchangers because they have a high anion exchange capacity (3,0-4,8 meq/g), their surface area is large (20-120 m^2/g), they have a structure that is resistant to water and they have a high positively charged layer. The LDHs have special affinity to inorganic anions with small ionic radii and high valence charges. In the case of monovalent anions, the affinity decreases in the following order: $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$ and, in the case of divalent ions, CO_3^{2-} is preferably adsorbed by LDHs as well as PO_4^{3-}. Several studies have shown their effectiveness as selective adsorbents for the removal of phosphate from sea water, simple electrolytes and drain effluents (Koilraj and Kannan, 2010, Cheng *et al*, 2010 and Cai *et al*, 2012).

2.3 State of the Art

2.3.1 Phosphate uptake behavior of ZnAlZr ternary layered double hydroxides through surface precipitation

Koilraj and Kannan, 2010, introduced the Zr^{+4} on the Zn-Al LDH and varied the atomic ratio of Zn/(Al+Zr) (2-4) and Al/Zr atomic ratio 0,7:0,3 by using as interlayer anion carbonate. The idea was to create a LDH material with a highly positive charge by using Zr^{+4} and hence to increase the uptake of phosphate. It was observed that the uptake of phosphate incremented with the decrease of the atomic ratio in Zn/Al and Zn/(Al+Zr). The contact time, the phosphate initial concentration, adsorbent amount and variation of temperature were studied.

The adsorption experiments were carried out at 30 °C. The samples were prepared from a phosphate stock solution of 1000 mg/L, prepared by using KH_2PO_4, which all had a pH of 5,5 (except the pH effect that was investigated in a range between 2,0 and 12,0). The pH was adjusted by using dilute HCl or NaOH. A concentration of 200 mg P/L solution was used and 1g/L of particles. The contact time was 2 h.

Between $ZnAl_2$-LDH and $ZnAlZr_4$-LDH, the best phosphate uptake was observed in the second case with 91 mg P/g while the first showed an uptake of 9 mg P/g. Regarding the contact time, the uptake of phosphate increased with time, reached its maximum after 2 h and then came to equilibrium. The maximum phosphate uptake was observed on $ZnAlZr_4$-LDH with 91 mg P/g. In addition, various concentrations of adsorbent were tested, from 0,24 to 3 g. An increse in the phosphate uptake was obserevd up to an adsorbent dose of 1 g $ZnAlZr_4$-LDH/L and then a decrease was detected.

The temperature effect was analyzed in the range of 30 to 80 °C. Significant variation in the phosphate uptake by ZnAlZr$_4$-LDH was observed at the different temperatures. The effect of the initial concentration of phosphate was investigated in the range of 10 to 250 mg P/L. The uptake of phosphate increased up to 200 mg P/L and then a sauration behavior was revealed. The phosphate uptake increased with decreasing pH and reached its maximum (110 mg P/g) at pH 2,3.

In addition, phosphate desorption experiments with the ZnAlZr$_4$-LDH in different desorption solutions were performed: Water, 1 M NaCl, 1 M NaOH and 1 M Na$_2$CO$_3$. Desorption was higher with the Na$_2$CO$_3$ solution, up to 80 % of phosphate was desorbed from the ZnAlZr$_4$-LDH. Moreover, the reusability of the samples was investigated by performing six cycles. It was found that the capacity of adsorption/desorption decreased with increasing number of cycles.

2.3.2 **Layered double hydroxide ion exchangers on superparamagnetic microparticles for recovery of phosphate from wastewater**

Several studies have been done for the recovery of phosphate from WW by using superparamagnetic microparticles modified with ion exchanger materials. Mandel *et al*, 2013, used MgAl-LDH and MgFe-LDH doped with Zr ions in order to increase the selectivity. Those LDHs were preciptated in a NaOH solution (pH 10,0) and then ultrasonically deposited on multicore Fe$_3$O$_4$ integrated into a matrix of SiO$_2$. They performed this under batch and continuous processes, as observed in figure 2-2. The LDH materials are charged positively while the superparamagnetic particles bear a negative charge, which form a composite material that has a strong attraction between the LDHs and the superparamagnetic particles.

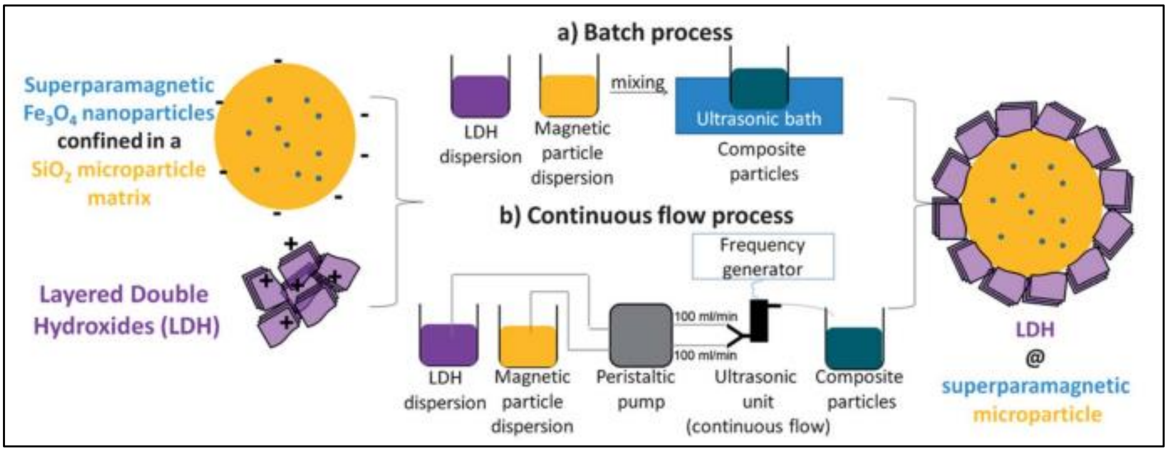

Figure 2 2. Composite formation by ultrasonic treatment in batch and continuous processes (Mandel *et al*, 2013).

Once obtained, the composite materials were used for the recovery of phosphate from distilled water and from WW, where the initial concentration of PO_4^{3-} was adjusted to 10 mg/L PO_4-P with H_3PO_4. Both water and WW had a neutral pH and the corresponding volume of composite particles was added to each of them in order to have a LDH concentration of 200 mg/L in 100 mL of those water solutions. The contact times were 1 h and 24 h, at 20 °C with stirring. At the end, a magnet was used for the separation of the particles and the supernatant liquid was collected for analysis. The concentration of phosphate was measured photometrically. Additionally, the composite materials were regenerated with 100 mL of two desorption solutions: 0,1 M NaOH and 2,0 M NaCl with a contact time of 24 h.

It was observed that after the first two desorption cycles, the MgFeZr-LDH had the highest efficiency. Regarding the phosphate uptake, the best composite material was MgFeZr-LDH with 30 mgPO_4-P/g LDH.

2.3.3 Phosphate recovery from wastewater using engineered superparamagnetic particles modified with layered double hydroxide ion exchangers

Drenkova-Tuhtan *et al*, 2013, after the sceening of various LDH materials, the MgFeZr-LDH material was chosen for the development of phosphate adsorption kinetic experiments and the dependency parameters that were studied were contact time, pH, concentration of particles and adsorption isotherm. Desorption studies were also performed to understand the recovery of phosphate and regeneration of the particles after 15 cycles. It was observed, that the phosphate adsorption in each cycle was in the range of 75 to 97 % with a contact time of 1 h.

As it was mentioned in Mandel *et al*, 2013, the concentration of LDH used was 200 mg/L LDH. In contrast, in the research of Derenkova-Tuhtan *et al*, 2013, the use of 400 mg/L LDH in 1,0 L of WW-PO_4-P was investigated, where the adsorption kinetics were carried out at three pH ranges: 4,5-5,0; 5,5-6,0 and 7,0-8,0 at 20 °C with a contact time of 24 h, and 10 mL samples were taken at certain times. After that, the phosphate concentration was analyzed photometrically. The results can be seen in figure 2-3. The adsorption isotherm experiment was done at 20 °C at pH 4,5 and a contact time of 24 h. The pH effect in the range from 3,0 to 9,0 with regulation of pH with 1 M HCl and 1 M NaOH was also studied. Afterwards, they investigated the phosphate adsorption under different particles concentration from 40 to 1500 mg/L at pH 4,5.

For the desorption experiments, different desorption solutions of 1,0 L each were used: NaCl, NaOH, $NaHSO_4$, $NaHCO_3$ and NaOH+NaCl at diverse concentrations and pH values and with a contact time of 1 h, except the last desorption solution that was performed for 30 min. Finally, 15 cycles of adsorption/desorption were run.

The best adsorption kinetic was observed at pH 4,5-5,0 having 90 % of the total phosphate adsorbed, which reached after 45 min with a maximum phosphate uptake of 23 mg P/g LDH, as shown in figure 2-3. Due to this, in this research project most of the experiments of phosphate adsorptions were carried out up to 1 h, because the adsorption efficiency is really high within this time. Regarding the adsortion isotherm, the maximum phosphate uptake was 35 mg PO_4-P/g LDH. Concerning the different particle concentrations, at 1000 mg/L almost 100 % of the phosphate was removed. From all the desorption solutions that were tested, the best desorption efficiency (98,2 %) was observed with the 1 M NaOH+4 M NaCl. Finally, within the 15 cycles, the maximum efficiency was observed after 3 cycles, reaching a 99 % adsorption, as can be seen in figure 2-4.

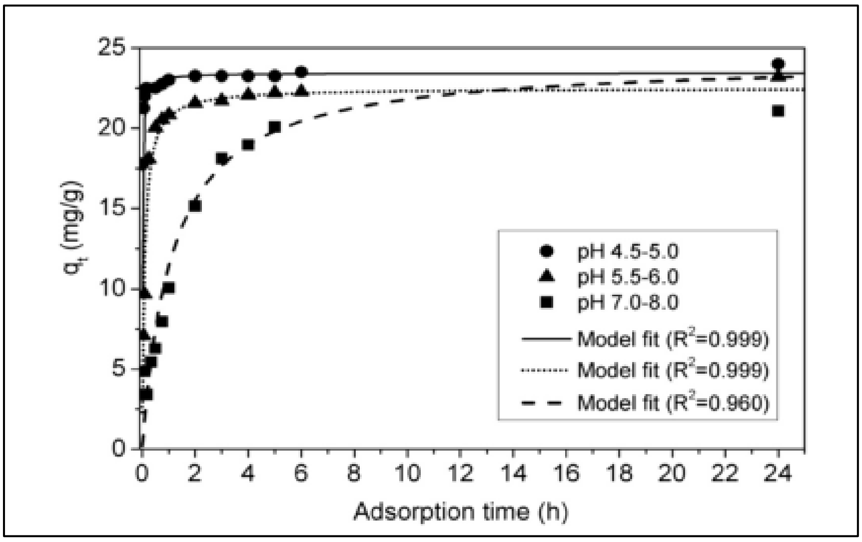

Figure 2 3. Phosphate adsorption kinetic on 400 mg/L of MgFeZr-LDH at three different pH ranges values (Drenkova-Tuhtan *et al*, 2013).

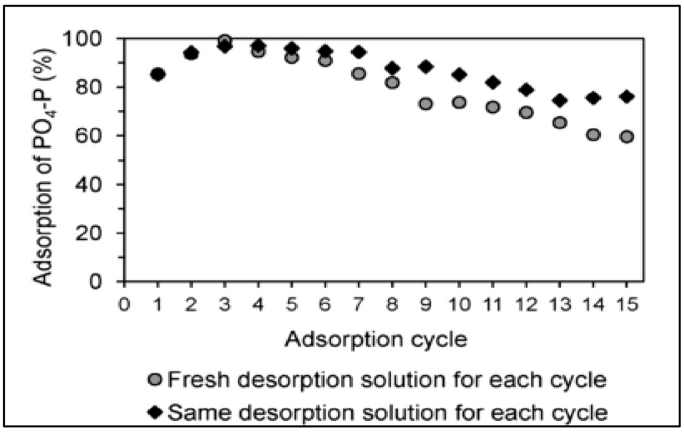

Figure 2 4. Adsorption efficiency after 15 cycles using 400 mg/L MgFeZr-LDH at pH 4,5 and 1 h contact time (Drenkova-Tuhtan *et al*, 2013).

2.3.4 Adsorptive removal of phosphate by Mg-Al and Zn-Al layered double hydroxides: Kinetics, isotherms and mechanism

Yang *et al*, 2014, performed experiments of adsorption kinetics, adsorption isotherms, effect of LDH dosages, contact time and pH. The phosphate removal was higher with ZnAl-LDH and achieved 95 % efficiency. A stock solution of 200 mg/L was prepared with KH_2PO_4 and 25 mL of this solution was used with the addition of the appropiate concentration of the LDH materials under shaking. If the pH had to be adjusted, solutions of 0,1 M HNO_3 or NaOH were used. The experiments were performed at room temperature and 1 h contact time

Regarding the results of LDH dosages, it was observed that the removal of phosphate increased with the quantity of LDH (0,02 to 0,16 g/L) and, the equilibrium (0,04 g/L adsorbent dosage), with around 97 % removal, was achieved with the ZnAl-LDH. Concerning the pH effect, it was observed that in the range of 6,0 to 9,0 more than 90 % of phosphate was adsorbed in both LDH materials.

The adsoption kinetics evaluates the adsorption efficiency between the adsorbent and the adsorbate. The experiments ran at room temperature showed an increase of phosphate removal in the first 20 min and achieved the maximum after 40 min. Both LDH materials had more than 95 % of adsorption efficiency, being the ZnAl-LDH with he higher (98,2 % after 40 min) as it can be observed in figure 2-5. For the adsorption isotherm, it was observed the best performance was achieved by the ZnAl-LDH.

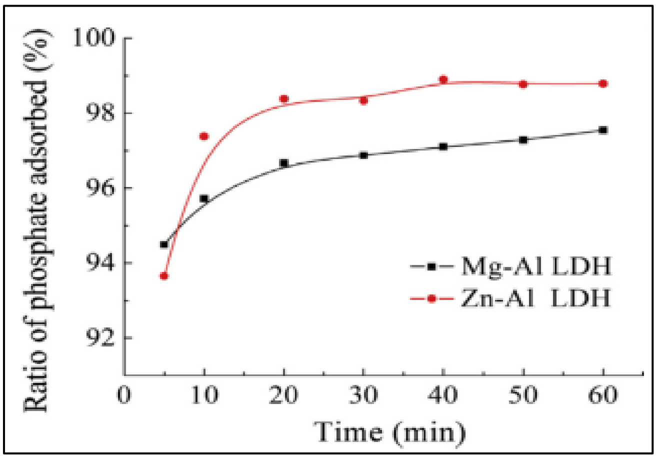

Figure 2 5. Phosphate adsorption onto ZnAl-LDH and MgAl-LDH vs the contact time (Yang *et al*, 2014).

Concerning the mechanism between the LDHs materials and the phosphate, it was determined the zeta potential and the FTIR. In the first analysis, it was found out that in the pH interval from 2 to 12, the dominant species were H_2PO^- and HPO_4^{2-}, which indicated that the first specie was easily adsorbed onto the LDHs surfaces of Mg-Al and Zn-AL. Due to the fact that the second specie is more negatively charged and because the surface sites of the LDHs are negatively charged as well, this cause an electrostatic repulsion between them which decreases the adsorption of phosphate onto the surfaces.

Regarding the second analysis, it was determined the FTIR spectras of the LDHs before and after adsorption. These spectras showed the adsorprion bands of O-H streching vibration (at 3436 cm^{-1}) and O-H bending vibration (a 1631 cm^{-1}) which meant the presence of interstitial water molecules. On the other hand, it was found out also the presence of the bonds of M-O (metal-oxygen) at 621 and 430 cm^{-1}. The band at 1039 cm^{-1} was attribued to the bending vibration of the phosphate adsorbed (P-O) and it appeared again after the adsorption of phosphate, indicating the possibility of the formation of an inner sphere surface complex of M-O-P, meaning that the M-OH exchange had occurred.

2.3.5 Kinetic, isotherm and thermodynamic investigations of phosphate adsorption onto core-shell Fe_3O_4-LDHs composites with easy magnetic separation assistance

Yan *et al*, 2015, studied three types of magnetic LDH composites consisting of a Fe_3O_4 core and a LDH shell: Fe_3O_4-ZnAl-LDH, Fe_3O_4-MgAl-LDH and Fe_3O_4-NiAl-LDH. The optimal parameters for the performance of the experiments were: Adsorbent dosage 2,0 g/L, pH 3,0 and a contact time of 60 min.

From KH_2PO_4, a stock solution was prepared with a concentration of 200 mg/L and for the development of the adsorption experiments, a more dilute solution was used and 0,05 g of adsorbent dosage of the three different magnetic core shells Fe_3O_4@LDHs, were added in 25 mL total reaction volume with an initial phosphate concentration of 40 mg/L. The mixture was shaken and then, the particles were separated magnetically.

Regarding the effect of adsorbent dosage, it was observed that the removal of phosphate increseased with the quantity of LDH (0,4 to 4 g/L) and reached the equilibrium at 2 g/L of adsorbent dosage, where Fe_3O_4-ZnAl-LDH showed the best adsorption capacity. The pH effect was measured in the range 3,0 to 12,0 and it was observed that the adsorption capacity decreased with increasing pH, where the maximum phosphate adsorption was reached at pH 3,0.

Concerning the adsorption kinetics, a fast and slow adsorption behavior was observed in the first 20 min of reaction for all three magnetic LDH composites. Nevertheless, each of them reached the maximum adsorption after 60 min (around 85 %), where Fe_3O_4-ZnAl-LDH showed the best adsorption capacity, as it can be seen in figure 2-6. The pseudo-first order of Lagergren (equation 3) and pseudo-second order of Ho (equation 4) were calculated in order to conclude which one fitted the data better (Yang *et al*, 2014).

$$\log\,(q_e - q_t) = log q_e - \frac{k_1}{2.303}t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where q_e and q_t (mg/g) are the phosphate amount adsorbed on the adsorbents at equilibrium and at time t, respectively; t (min) is the contact time, k_1 (1/min) and k_2 (g/(mg·min)) are the rate constant of pseudo-first and pseudo-second order kinetic models.

It was found out that the pseudo second order model fitted better due to the fact that the correlation coefficients (R^2) were higher (1,00; 0,99 and 0,99 for the composites of Fe_3O_4 with LDH material: ZnAl-LDH, MgAl-LDH and NiAl-LDH, respectively).

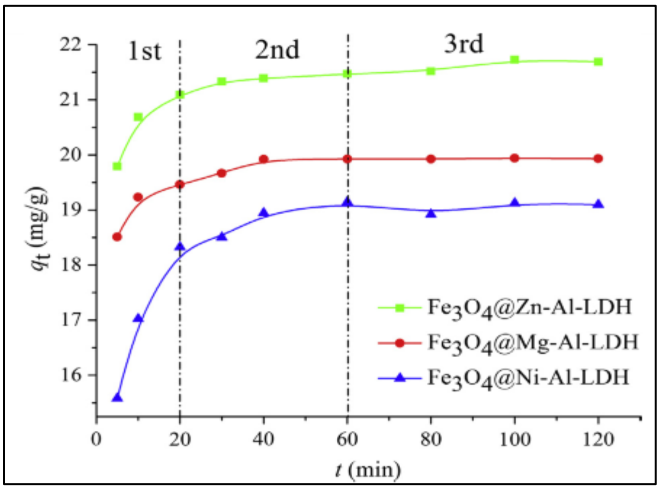

Figure 2 6. Phosphate adsorption on three core shell Fe_3O_4-LDH composites as a function of contact time (Yan *et al*, 2015).

The adsorption isotherm was measured at room temperature (25 °C), the adsorbent dosage was fixed to 2 g/L as well as the pH at 3,0. In general, the adsorption of phosphate increased with the increasing LDH concentration. The adsorption isotherm was fitted with two different adsorption models, Freundlich and Langmuir, equations 5 and 6, respectively (Yan *et al*, 2015):

$$logq_e = logk_{f+}\frac{lgC_e}{n} \qquad (5)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (6)$$

where C_e (mg/L) and q_e (mg/g) correspond to the equilibrium adsorbate concentration in the aqueous and solid phase. n is the constant that indicates the Freundlich isotherm curvature and K_f ((mg/g)/(mg/L)^n) is the Freundlich equilibrium constant, q_m (mg/m) is the maximum adsorption capacity and K_L (L/mg) is the Langmuir adsorption equilibrium constant (Yan *et al*, 2015). It was found out that the Langmuir model had a good fit because all R^2 were above 0,97.

Yang *et al*, 2015 analyzed the thermodynamic of the phosphate adsorption process. In order to know if this adsorption process was endothermic or exothermic, it was necessary to calculate the enthalpy change. The thermodynamic equilibrium constant (K_d) was obtained by plotting $ln(q_e/C_e)$ versus q_e and extrapolating q_e to zero. When the values of K_d were obtained, the equation 7 of Van´t Hoff was used in order to find the parameters of enthalpy (ΔH) and entropy (ΔS) change, which can be obtained by plotting $ln\ K_d$ versus $1/T$ (Yan *et al*, 2015).

$$lnK_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (7)$$

where R is the gas ideal constant (8,314 J/mol·K).

With this analysis, it was found out that phosphate adsorption processes on the three composites of Fe_3O_4 with ZnAl-LDH, MgAl-LDH and NiAl-LDH were endothermic because the enthalpy change was positive (41,8; 67,9 and 30,2 kJ/mol, respectively). It is important to mention that the calculation of K_d has to be done at equilibrium, which means at least 1 day of reaction according to previous studies (Lyubchik *et al*, 2004 and Yan *et al*, 2015).

In addition, with the obtained K_d values, it was possible to calculate the change in Gibbs free energy (ΔG) at each temperature with the following equation (Yan *et al*, 2015):

$$\Delta G = -RTlnK_d \qquad (8)$$

The results of the ΔG at the different temperatures on the three composites of Fe_3O_4 were all negative which means that the phosphate adsorption process was spontaneous.

Chapter 3: Experimental description

3.1. Equipment and materials

For the performance of this research project, equipment and materials from different laboratories at the Institute for Sanitary Engineering, Water Quality and Solid Waste Management (ISWA), the University of Stuttgart, Germany, were used.

The particle samples tested in the different experiments are the following:

Table 3 1. Chemical composition of the different particle samples.

Sample Name	**Chemical composition**
MS-34-A22	pure CaZnFeZr-LDH
MS-54-1	20 wt% CaZnFeZr-LDH. Magnetic particles were added first, followed by the addition of the metal salts for the LDH formation and then by the bulk NaOH solution necessary for the precipitation of the LDH at alkaline pH on the magnetic core.
MS-54-2	20 wt% CaZnFeZr-LDH. Magnetic particles were added first, followed by the addition of the metal salts and then by the NaOH solution drop by drop.
MS-54-3	20 wt% CaZnFeZr-LDH. Magnetic particles were added first, followed by the addition of the NaOH solution and then by the metal salts in bulk.
MS-54-4	20 wt% CaZnFeZr-LDH. Magnetic particles were added first, followed by the addition of the NaOH solution and then by the metal salts drop by drop.
MS-55	40 wt% CaZnFeZr-LDH. Magnetic microparticles with CaZnFeZr-LDH precipitated directly over the surface.
$Ca_9Zn_9Fe_3Zr_3$-LDH	Pure LDH, 200 mg/L.
MS-55-2	8 wt% CaZnFeZr-LDH on magnetic particles
MS-58-2	34,5 wt% ZnFeZr-LDH on magnetic particles
MS-58-3	32 wt% ZnFeZr-LDH on magnetic particles

3.2. Chemical reagents

All chemical reagents that were used in the different experiments are listed in table 3-2.

Table 3 2. Chemical reagents used in the different experiments.

Name	Chemical formula	Concentration
Different solutions of sodium hydroxide	$NaOH$	0,1; 0,3; 1 and 3 (mol/L)
Different solutions of sulphuric acid	H_2SO_4	0,1; 1 and 3 (mol/L)
Solution of sodium carbonate	Na_2CO_3	1 (mol/L)
Solution of sodium hydrogen carbonate	$NaHCO_3$	1 (mol/L)
Different solution of phosphoric acid	H_3PO_4	10, 100, 300 mg/L

3.3. Materials and methods

The wastewater (WW) used in all experiments was taken from the Secondary Settling Tank (SST) of the WWTP at ISWA, University of Stuttgart and was filtered by using a filter paper in a conical funnel. After this, a certain amount of WW was taken out and then spiked with a solution of phosphoric acid (1000 mg/L) in order to reach a concentration of 10 mg/L PO_4-P in the solution. For purposes of this work, the spiked wastewater will be called WW-PO_4-P solution. In every experiment, 100 mL of blind sample was taken from this WW-PO_4-P solution and the rest was used for the performance of the different experiments. The following parameters of the WW-PO_4-P solution were constantly measured: pH, temperature, conductivity and the phosphate concentration (photometrically according to DIN EN ISO 6678:2004).

3.3.1 Adsorption and desorption kinetics by using pure CaZnFeZr-LDH (sample MS-34-A22)

A- *Objective*

To find the adsorption and desorption efficiency of this specific pure LDH material in WW-PO_4-P in order to compare its performance with the same material after attaching it on the magnetic core, which will supposedly reduce the available surface area.

B- *Experimental description*

First experiment

a. *Adsorption kinetics of sample MS-34-A22*

A suspension of pure CaZnFeZr-LDH was received with a dry mass of 16,5 g/L. In order to achieve a concentration of 200 mg/L CaZnFeZr-LDH in the solution of WW-PO_4-P, 12,12 mL of the sample MS-34-A22 were added to 1000 mL of WW-PO_4-P solution and immediately the kinetics measurements were started. The kinetics reaction was performed at room temperature (23,1±1°C). The solution was mixed with a magnetic stirrer and the pH was regulated with a solution of 1 M H_2SO_4 in order to maintain the pH in the range of 7,0-8,0. Certain quantities of sample were taken at the predetermined times: 5, 10, 15, 20, 30, 45, 60 min and 1, 2, 3, 4, 5 and 24 h. From 5 to 30 min, 40 mL of sample were taken and from 45 min to 5 h min, 50 mL of sample were taken and the rest 500 mL were used for the 24 h sample.

At each sampling pH and temperature were measured. Each sample was centrifuged at 2500 rpm for 10 min and then, the supernatant liquid was filtered through a 0,45 µm membrane filter. Furthermore, the conductivity as well as the phosphate concentrations of the filtered solutions were measured spectrophotometrically according to DIN EN ISO 6678:2004.

b. Desorption kinetics of sample MS-34-A22

After the 24 h sampling, the particles which remained in the vessel were used for the performance of desorption kinetics. For this part, a desorption solution of 600 mL of 0,5 M NaOH (prepared with previously filtered WW) was used, 100 mL were taken as a blind sample and the parameters pH, temperature and conductivity were measured. The rest 500 mL of 0,50 M NaOH were added to the vessel with the pure LDH and the regeneration / desorption reaction started. The kinetics reaction was performed at room temperature (25,8±1°C). pH and temperature were recorded at the beginning as well as of every sample taking. The sample taking was carried out at the following times: 5 min (50 mL was taken). From 10 to 20 min, 40 mL of sample were taken, from 30 min to 3 h, 50 mL of sample were taken and finally, for the 20 h, 80 mL were left.

Each sample were centrifuged at 2500 rpm for 10 min and then filtered through a 0,45 µm membrane filter and afterwards, the conductivity as well as the phosphate concentrations of the filtered solutions were measured spectrophotometrically .

Second experiment (repetition)

a. Adsorption kinetic of sample MS-34-A22

The adsorption procedure was the same as before, with the following exceptions:

- 7,272 mL of MS-34-A22 sample was added on 500 mL of WW-PO_4-P solution.

- Contact time: 1 h.
- After 1 h, the pH and temperature were measured and afterwards, the solution was divided in two; this means, 250 mL of the solution was added into each vessel.
- After the reaction, the WW-PO_4-P was collected, centrifuged and filtered through a 0,45 µm membrane filter for the respective analysis.

b. *Desorption kinetic of sample MS-34-A22*

As was mentioned before, now two vessels contained pure LDH particles and these were used for the performance of two different desorption kinetics. Two desorption solutions of 0,5 M NaOH were prepared; one with 350 mL of WW taken from the SST effluent (filtered in advance) and the other with 350 mL of distilled water. The corresponding 100 mL of each fresh desorption solution were taken as a blind sample for analysis. Both desorption kinetics were carried out under the following predetermined times: 15 min, 30 min, 1 h, 2 h and 3 h, with 50 mL sample taken at each time. The pH and temperature of each sample were measured and then the sample was centrifuged and filtered through a 0,45 µm membrane filter. Afterwards, the conductivity as well as the phosphate concentrations of the filtered sample were measured spectrophotometrically.

3.3.2 Comparing the influence of the composite particles synthesis method on the PO_4-P adsorption performance

A- *Objective:*

To compare the influence of the particles synthesis method on PO_4-P adsorption where six different samples were used. A minimum of 90 % adsorption efficiency was required for selecting the preferred synthesis method and performing further experiments.

B- *Experimental description*

The variations in the synthesis method of the composite particles are different for each material, as was described on table 3.1.

For this experiment, six different vessels were filled with 200 mL of WW-PO_4-P solution. The corresponding amount of particle sample was added to achieve a LDH concentration of 200 mg/L in each reactor and adsorption reaction started. The solutions were mixed with a magnetic stirrer for 24 h at room temperature (24,0±1°C). The pH was regulated with a solution of 1 M

H_2SO_4 in order to maintain the pH in the range of 7,0-8,0. The pH and the temperature were measured at the beginning and at the end of the reaction.

After 1 h of adsorption reaction, pH and temperature were measured in each vessel and then the particles were separated from the treated solution by using a strong hand magnet followed by an extraction of the supernatant, as demonstrated in figure 3-1. Afterwards the solutions were filtered through a 0,45 µm membrane filter. The phosphate concentration was measured by photometrically. The same procedure was followed for the 24 h sampling, with the exception that additionally the conductivity of the filtered solutions was measured as well.

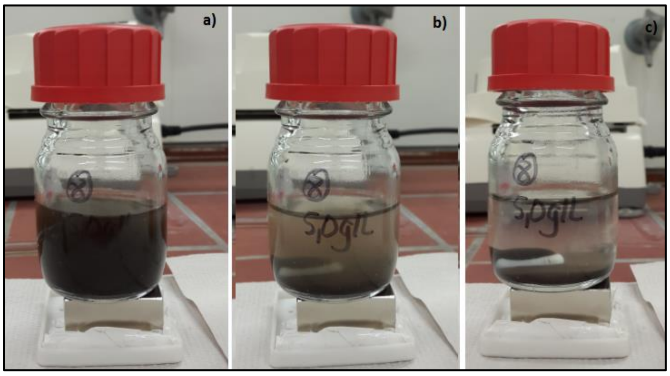

Figure 3 1. Separation of the magnetic particles by using a strong hand magnet.

3.3.3 Adsorption/Desorption cycles by using composite particles with 8,0 wt% Ca-ZnFeZr-LDH (sample MS-55-2) and different desorption solutions

A- Objective

To find the best desorption solution for the regeneration of the LDH-loaded composite particles and the ability to reuse them within 10 adsorption/desorption cycles in 3 different desorption solutions. Only the LDH material with the highest adsorption efficiency in the earlier investigations was used in this experiment.

A minimum of 90 % adsorption/desorption efficiency was required for selecting the preferred desorption solution for the regeneration of the particles and performing further experiments with it.

B- Experimental description

For the performance of the experiments, three vessels were filled with 200 mL of WW-PO_4-P solution.

The first adsorption cycle of each vessel started when 10 mL of the particles were dosed with a LDH concentration of 80 mg/L. The experiments were carried out at room temperature (23,0 °C±1) and the solutions were mixed with a magnetic stirrer. The pH was regulated with a solution of 1 M H_2SO_4 in order to maintain the pH in the range of 7,0-8,0. The contact time during the adsorption cycle was 1 hour. The pH and the temperature were measured at the beginning of the adsorption cycle and also at 1 h. After 1 h, the particles were separated by using a strong hand magnet and after approx. 10 min the supernatant was taken out and filtered with a 0,45µm membrane filter. The pH, temperature and conductivity of the filtered supernatant liquid were measured and afterwards the phosphate concentration was analyzed photometrically.

The first desorption cycle of each vessel started when the respective desorption solutions were added into the respective reactor that contained the particles. In this case, 400 mL of desorption solution were added and the following desorption solutions were used: 1 M $NaHCO_3$, 1 M Na_2CO_3 + 1 M NaOH and 3 M NaOH, all prepared in distilled water. The contact time was 1 h and no pH regulation was done. It is important to mention that the pH and the temperature were measured at the beginning of desorption cycles and also at 1 h. After 1 h, the particles were separated as mentioned before but, in this case, only 30 mL of supernatant liquid was taken and then filtered with a membrane filter of 0,45 µm. The remaining supernatant liquid was stored in order to be reused in the next cycle for the purpose of increasing the phosphate concentration in the solution. The pH, temperature and conductivity of the filtered supernatant liquid were measured and afterwards the phosphate concentration was analyzed photometrically.

The procedures of adsorption and desorption cycles were repeated nine more times. However, due to the fact that some minimal volume of desorption solution can remain at the bottom of the vessels and rasise the pH when the next adsorption cycle started, it was necessary to regulate the pH by using a 3 M H_2SO_4 solution. From desorption cycle number six, the sample taking of supernatant liquid was reduced to 25 mL because the concentration of PO_4-P was higher and it was enough for the respective analysis.

3.3.4 pH effect on adsorption of phosphate by using two types of composite particles (samples MS-55-2 and MS-58-2)

A- *Objective*

To investigate the pH effect on the adsorption of phosphate in filtered wastewater solution spiked with H_3PO_4 and to find out which is the optimum pH value for such adsorption by using two types of magnetic particle-LDH materials.

B- *Experimental description*

The characteristics for each composite particle are described below:

a- MS-55-2: Composites particles with 8,0 wt% CaZnFeZr-LDH and 20 g/L dry substance.
b- MS-58-2: Composite particles with 34,5 wt% ZnFeZr-LDH and 37 g/L dry substance.

The pH effect on adsorption was investigated twice with the sample MS-55-2 and three times with the sample MS-58-2, in total five experiments. The description of each experiment is basically the same, with some changes in between, therefore, the first experiment with the sample MS-55-2 will be explained in detail and then, the respective changes will be mentioned. It is important to mentioned that all experiments were carried out at room temperature (23,0 °C±1).

First experiment (sample MS-55-2)

For the performance of the experiment, 10 vessels were filled with 100 mL of WW-PO_4-P solution. The studied pH ranges were the following: 3,0-3,5; 3,5-4,0; 4,5-5,0; 5,5-6,0; 6,5-7,0; 7,5-8,0; 8,5-9,0; 9,5-10,0; 10,5-11,0 and 11,5-12,0. To each vessel, 5 mL of particle sample MS-55-2 was added, corresponding to 1 g/L composite particles or 80 mg/L CaZnFeZr-LDH. Each vessel was mixed with a magnetic stirrer for 24 h and the pH was regulated with a solution of 1 M H_2SO_4 or 1 M NaOH in order to maintain the pH in the respective pH range. Sampling took place after 5 h of mixing and after 24 h at the end of the experiment. The pH and the temperature were measured at the beginning, at 5 h and at 24 h in each vessel. After the sampling, the particles were separated as described before and the supernatant liquid was filtered by using a 0,45 µm membrane filter and the conductivity and the phosphate concentration of the filtered samples were analyzed.

Second experiment (sample MS-55-2)

The performance of this experiment is the same as described before with the following exceptions:

- Vessels were filled with 50 mL of WW-PO_4-P solution.
- To each vessel; 1,5 mL of particle sample MS-55-2 were added, corresponding to 0,6 g/L composite particles or 48 mg/L CaZnFeZr-LDH.
- 25 mL sample was taken at 5 h and at 24 h.

First and second experiment (sample MS-58-2)

The performance of this experiment is the same as described before with the following exceptions:

- Two more pH values were considered: 2,0-2,5 and 12,5-13,0, due to this, 12 vessels were used.
- To each vessel; 0,500 mL of particle sample MS-58-2 were added, corresponding to 0,185 g/L composite particles or 64 mg/L ZnFeZr-LDH.

Third experiment (sample MS-58-2)

The performance of this experiment is the same as described before with the following exceptions:

- Two more pH values were considered: 2,0-2,5 and 12,5-13,0, due to this, 12 vessels were studied.
- To each vessel; 0,270 mL particle sample MS-58-2 were added, corresponding to 1,0 g/L composite particles or 345 mg/L ZnFeZr-LDH..
- 25 mL sample was taken at 5 h and at 24 h.
- The contact time was 30 min.

3.3.5 Effect of adsorbent dosage by using samples MS-58-2 and MS-58-3 at 22 °C

A- *Objective*

To study the effect of adsorbent dosage on the adsorption of phosphate on spiked filtered wastewater (10 mg/L PO_4-P) and spiked unfiltered wastewater (10, 100 and 300 mg/L PO_4-P). The experiments were performed at 22 °C with mixing by magnetic stirring and using two different composite particle-LDH materials.

B- *Experimental description*

Characteristics of sample MS-58-3: composite particles with 32 wt % ZnFeZr-LDH and 40 g/L dry substance. In this section, four experiments were carried out:

First and second experiments (Sample MS-58-2)

The first experiment used filtered WW and the second one unfiltered WW (both already spiked with the corresponding amount of 1000 mg/ L phosphoric acid in order to reach the 10 mg/L). The procedure for both is exactly the same, with the only difference being that in the unfiltered WW, two more points of LDH concentration were considered: 690 and 863 mg/L.

10 vessels were filled with 100 mL of WW-PO_4-P solution. The adsorption isotherm was developed at 22,0±1°C. The solution was mixed with a magnetic stirrer and the pH was regulated with a solution of 1 M H_2SO_4 in order to maintain their pH in the range of 7,0-8,0. Different particle volumes of sample MS-58-2 (34,5 wt% ZnFeZr-LDH) were added to each vessel in order to achieve ten different LDH concentrations: 9,0; 17; 35; 62; 86; 138; 173; 259; 345 and 518 mg/L.

The contact time was 24 h and sampling took place at 1 h and 24 h when 50 mL of sample were taken. The pH and temperature were measured at the beginning, at 1h and 24 h. As already explained, the particles were separated with a strong magnet, the supernatant liquid was filtered through a membrane filter of 0,45 µm and then the conductivity and the phosphate concentration of the filtered liquid were analyzed.

Third and fourth experiments (sample MS-58-3)

In both experiments, unfiltered WW was used; however the third experiment was spiked with phosphoric acid in order to reach a concentration of 100 mg/L PO_4-P and in the fourth experiment a concentration of 300 mg/L PO_4-P was used. The procedure for both is exactly the same as in the first and second experiments, with the only difference that in the fourth experiment another point of LDH concentration was added: 2000 mg/L.

These experiments were the same as described above, with the following exceptions:

- The vessels were filled with 50 mL of WW-PO_4-P solution in both experiments.
- The contact time was 1 h.
- The LDH concentrations were: 100; 300; 500; 700; 900; 1200; 1400 and 1600 mg/L.

3.3.6 Adsorption isotherm with sample MS-58-2 by using water bath at 15, 22, 35 and 50 °C

A- Objective

Develop phosphate adsorption isotherms with spiked filtered wastewater (10 mg/L PO_4-P) under different temperatures: 15, 22, 35 and 50 °C by using water bath and make a conclusion about the optimal temperature for the reaction.

B- Experimental description

The procedure of this experiment is exactly the same as described on section 3.3.5, first and second experiments (using filtered WW) with the following differences:

- Contact time only 1 h and sample taking of 100 mL.
- No pH regulation.
- A water bath was used in other to maintain the desired temperatures: 15 °C, 22 °C, 35 °C and 50 °C.

3.3.7 Adsorption and desorption kinetics by using sample MS-58-2

A- Objective

To execute an adsorption and a desorption kinetics reaction by using LDH-particles material in filtered and unfiltered WW solution, both spiked with H_3PO_4 (10 mg/L PO_4-P concentration) at room temperature and pH 7,5.

B- Experimental description

In this section, two experiments were performed: One with filtered WW and the other with unfiltered WW (both already spiked in order to reach an initial PO_4-P concentration of 10 mg/L). The procedure for both is exactly the same as described in section 3.3.1 with some differences that will are outlined below:

Filtered Wastewater

a. *Adsorption kinetics*

- A concentration of 345 mg/L ZnFeZr-LDH corresponding to 1 g/L particles was used. This means that 40,5 mL of particle sample was added to 1500 mL of WW-PO_4-P solution.

- The experiments were performed at room temperature (24,1±1°C).
- Sampling took place after 24 h when 1000 mL of sample was taken.
- A strong hand magnet was used for the separation of particles and afterwards the supernatant liquid was collected for analysis.

b. *Desorption kinetics*

- The following two desorption solutions of 500 mL each were used: 1 M NaOH prepared with tap water and 1 M NaOH prepared with distilled water.
- 50 mL sample was taken each time.
- The maximum contact time for each experiment was 3 h.

Unfiltered Wastewater

a. *Adsorption kinetics*

- A concentration of 863 mg/L ZnFeZr-LDH corresponding to 2,5 g/L particles was used. This means that 47,3 mL of particle sample was added to 700 mL of WW-PO_4-P solution.
- The experiment was performed at room temperature (24,3±1°C).
- Fom each reaction time, 50 mL sample was taken and for the 24 h, 150 mL were used.
- A strong hand magnet was used for the separation of the particles and the supernatant was collected for analysis.

b. *Desorption kinetics of sample*

- No desorption kinetics was performed for this unfiltered WW.

3.3.8. Effect of adsorbent dosage and adsorption/desorption cycles with a WW filtrate from the WWTP in Offenburg by using sample MS-58-3

A- Objective

To study the effect of adsorbent dosage on the adsorption of phosphate and perform 5 adsorption/desorption cycles with a wastewater filtrate from the struvite recovery facility at the WWTP in Offenburg, which was collected after acidic dissolution and filtration of the digested sludge, resulting in a significantly higher phosphate concentration in the filtrate used for the experiments (431 mg/L PO_4-P).

B- Experimental description

In this section, as was mentioned before, two experiments were performed and the sample MS-58-3 was used. The WW from Offenburg had a PO_4-P concentration of 431 mg/L and P-total concentration of 473 mg/L.

First experiment: Effect of adsorbent dosage

For the performance of this experiment, 3 vessels were filled with 50 mL of the Offenburg WW and different volumes of the sample MS-58-3 were added to each reactor in order to achieve the corresponding LDH-concentrations of 2000; 2500 and 3000 mg/L. The reactors were stirred for 1 h with a magnetic mixer without regulating the pH. Parameters as temperature and pH were measured at the beginning and at the end of the experiment. After 1 h, the particles were separated with a strong hand magnet and the phosphate concentration in the supernatant was analyzed photometrically.

Second experiment: Adsorption/desorption cycles

Two experiments were performed with the Offenburg WW in the same manner as described in section 3.3.3, with the following exceptions:

- Both vessels were filled with 50 mL of the Offenburg WW.
- 11,725 mL of the particles were dosage corresponding to a LDH concentration of 3000 mg/L.
- One experiment was performed without pH regulation during adsorption and in the other experiment pH was regulated to 7,0-7,3.
- The contact time during desorption was 20 min.
- Desorption samples of 5 mL were taken for the first 4 cycles and after the 5th cycle the rest of the desorption solution was available for analysis.
- After every desorption cycle, the particles were washed with 200 mL of distilled water and were reused in the next adsorption cycle.

Chapter 4: Results and discussion

4.1 Adsorption and desorption kinetics of pure CaZnFeZr-LDH (sample MS-34-A22)

The kinetics of phosphate adsorption and desorption in WW-PO_4-P was investigated in order to analyze the phosphate removal and recovery efficiency of pure CaZnFeZr-LDH. Based on the outcome of these experiments, it was concluded that CaZnFeZr-LDH is suitable for further experiments with composite particles by attaching the LDH material onto a magnetic core.

As mentioned in section 3.3.1, two experiments were performed. The first experiment demonstrates the phosphate adsorption kinetics, plotted in figure 4-1, where the removal of phosphate increased gradually in time and reached equilibrium at about 1440 min (24 h), where phosphate uptake was 99,5 %. In the second experiment the desorption kinetics was investigated. The first version of this experiment was performed with a desorption solution of 0,5 M NaOH prepared in a treated wastewater effluent. However, the maximum PO_4-P concentration found in the samples after desorption was only 0,250 mg/L, meaning that hardly any desorption of phosphate took place (only 2,7 %).

Therefore, a second version of this experiment was carried out, where two types of 0,5 M NaOH desorption solutions were used, one prepared in wastewater and the other in distilled water. This time the adsorption contact time was limited to 1 h because it was sufficient to reach > 95 % adsorption efficiency. The phosphate desorption kinetics in the 0,5 M NaOH solution prepared in WW had a very bad performance again, with efficiency values between 0,86 to 1,6 % only. In contrast, the phosphate desorption kinetics in the 0,5 M NaOH prepared in distilled water had a very good performance (see figure 4-1). The desorption of phosphate increased, reaching the maximum desorption after 1 h with an efficiency of 96,7 %.

According to Yan *et al,* 2015, the fast adsorption of phosphate onto the LDHs could be due to electrostatic attraction between the LDH material and the phosphate anions and afterwards, when the adsorption rate decreases, it is suggested that could be attributed to ion exchange and ligand exchange.

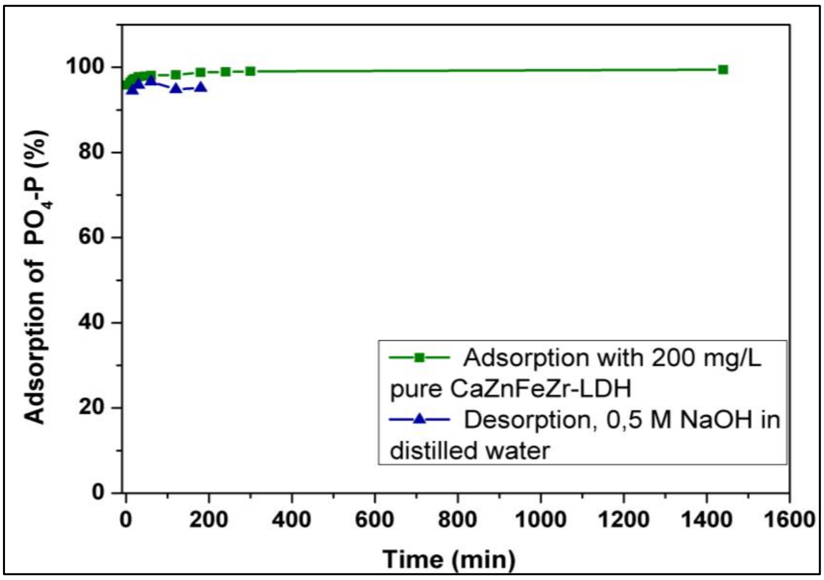

Figure 4. 1. Adsorption and desorption kinetics of phosphate onto/from pure CaZnFeZr-LDH as a function of contact time. Reaction conditions: pH=7,0-8,0 for adsorption and no pH regulation for desorption, temperature=22-25 °C.

Adsorption/desorption experiments mentioned above confirmed that CaZnFeZr-LDH has a good performance and is a suitable material which can be attached on magnetic particles for further experiments.

4.2 Comparing the influence of particles synthesis method on PO_4-P adsorption performance

A detailed analysis of the five composite particle samples used in the earlier experiments showed deviation of the LDH loading values from the theoretically calculated ones (20% or 40%) which were presented in section 3.3.2. The actual LDH mass loading fractions on the magnetic particles are the following:

a- MS-54-1= 3,9 wt% CaZnFeZr-LDH. Magnetic particles were added first, followed by the addition of the metal salts for the LDH formation and then by the bulk NaOH solution necessary for the precipitation of the LDH at alkaline pH on the magnetic core.

b- MS-54-2= 3,7 wt% CaZnFeZr-LDH. Magnetic particles were added first, followed by the addition of the metal salts and then by the NaOH solution drop by drop.

c- MS-54-3= 3,7 wt% CaZnFeZr-LDH. Magnetic particles were added first, followed by the addition of the NaOH solution and then by the metal salts in bulk.

- d- MS-54-4= 3,9 wt% CaZnFeZr-LDH. Magnetic particles were added first, followed by the addition of the NaOH solution and then by the metal salts drop by drop.
- e- MS-55= 7,6 wt% CaZnFeZr-LDH. Magnetic microparticles with CaZnFeZr-LDH precipitated directly over the surface.

It is important to mention that filtered WW-PO_4-P solution was used for the performance of these experiments.

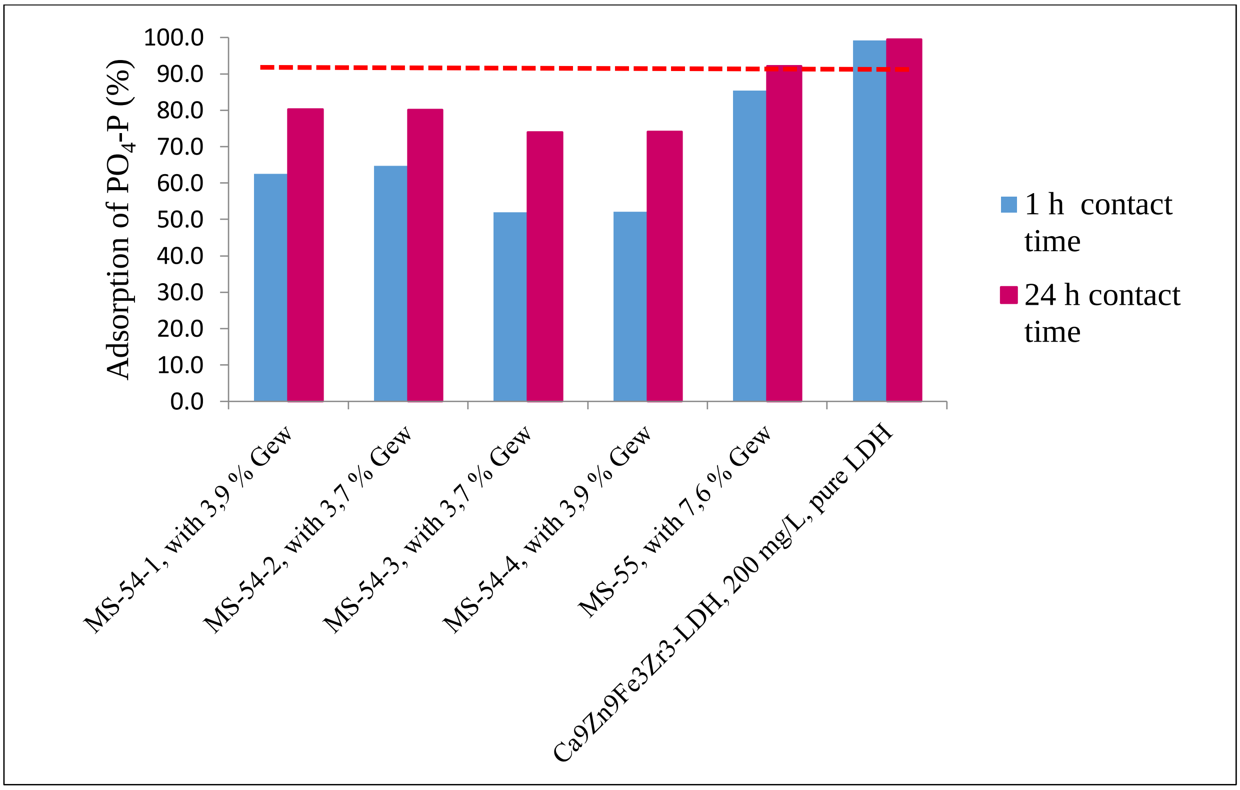

Figure 4. 2. Phosphate adsorption efficiency on five different composite particle-LDH materials and one pure LDH. Reaction conditions: pH= 7,0-8,0; T°= 24 °C; initial PO_4-P concentration= 10 mg/L; LDH concentration= 200 mg/L, contact time: 1 and 24 h.

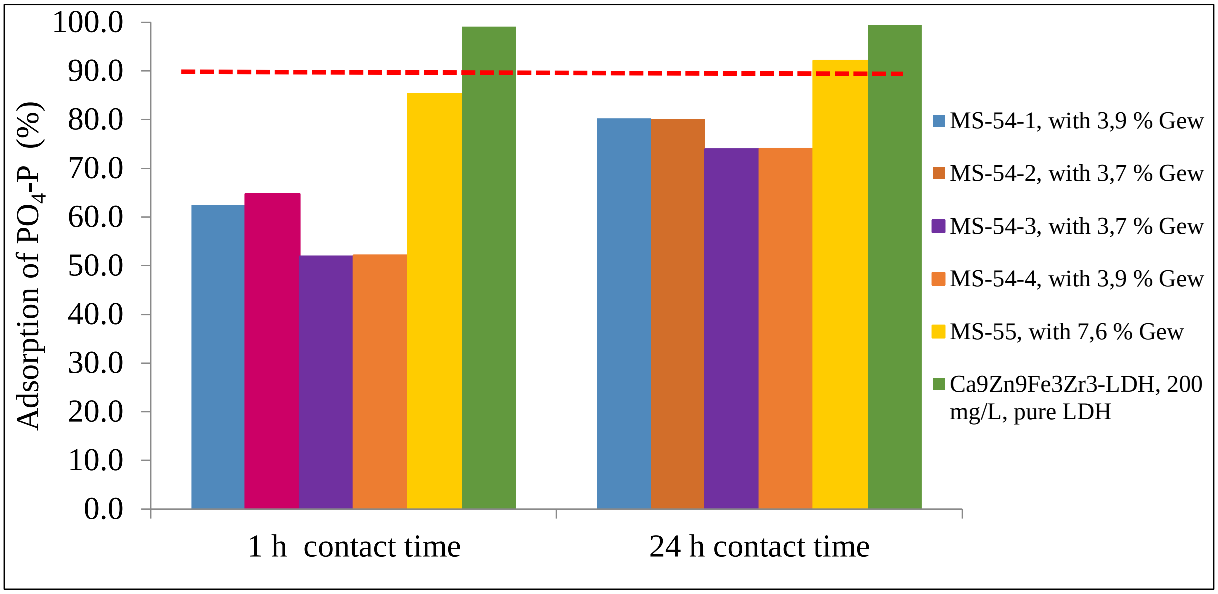

Figure 4. 3. Phosphate adsorption efficiency on five different composite particle-LDH materials and one pure LDH with contact times of 1 h and 24 h.

Figures 4-2 and 4-3 show that only pure CaZnFeZr-LDH could reach more than 90 % adsorption efficiency at both 1 h and 24 h contact time and LDH concentration of 200 mg/L. This was the criteria established to decide that this was the material suitable for further experiments. On the other hand, sample MS-55 almost achieved the 90 % adsorption efficiency after 1 h contact time (exactly was 85,4 %) and was beyond the 90 % limit (92,1 %) after 24 h contact time, making this also a good candidate. In contrast, samples MS-54-3 and MS-54-4 had the lowest phosphate adsorption efficiencies, for both contact times.

Apart from the selection of the best LDH-nanoparticles, the above experiments also present important aspects. The concentration of 200 mg/L of pure CaZnFeZr-LDH is optimal for the adsorption of phosphate. However, later LDH is attached on magnetic particles in order to facilitate separation of the particles due to their magnetic properties, but this reduces the available surface area of the LDH material. The best composite particle synthesis method is the one of sample MS-55 due to their high adsorption efficiency. This method is the one where the magnetic microparticles are functionalized with CaZnFeZr-LDH precipitated over the surface and this attachment is achieved by the use of ultrasound treatment, as was explained in section 2.3.2 (Mandel *et al*, 2013).

One of the possible explanations for the low performances of the other composite particle-LDH are the differences between the theoretical and actual LDH concentration measured after the synthesis of the materials. Because of this mismatch, the optimal concentration of LDH, i.e.200 mg/L, was not possible to be achieved in all the experiments.

Remarkable is that the adsorption was higher after 24 h, for all the samples. Nevertheless, due to economic reasons the idea in this project was to select system with high adsorption efficiency after 1 h contact time.

4.3 Adsorption/Desorption cycles by using composite particles with 8,0 wt % CaZnFeZr-LDH (sample MS-55-2) and different desorption solutions

The idea of this experiment was to find the best desorption solution out of 3 different proposed variations for the regeneration of the LDH-particles which were reused in tenth adsorption / desorption cycles.

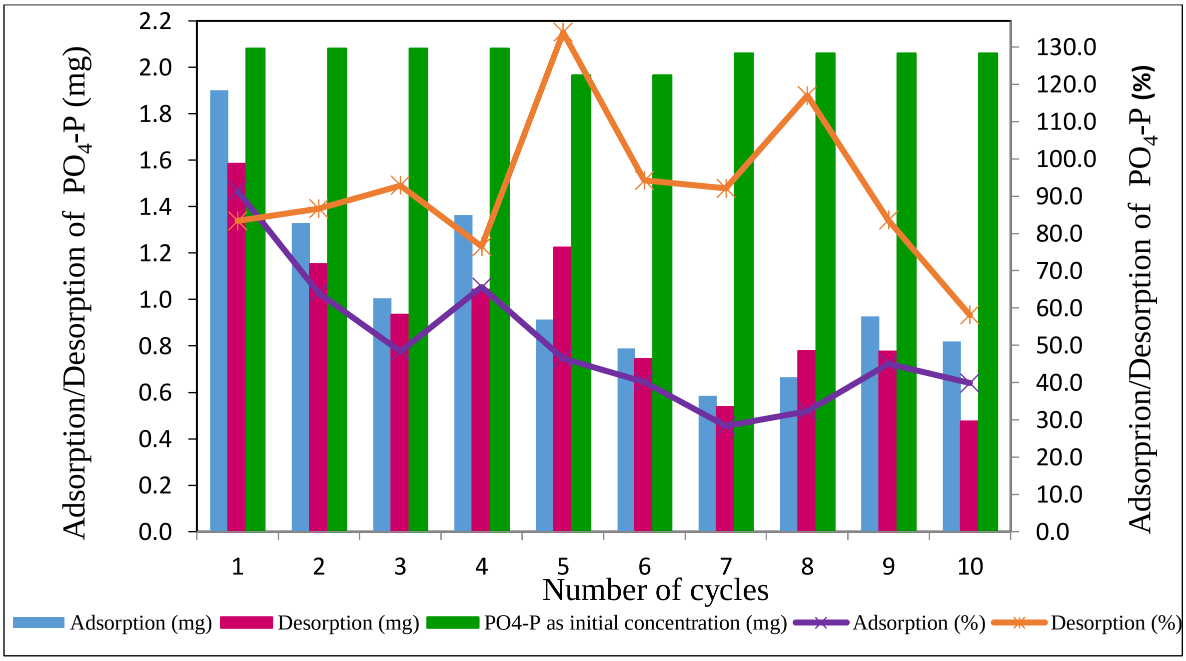

Figure 4. 4. Adsorption/desorption cycles of phosphate onto CaZnFeZr-LDH. Reaction conditions: Desorption solution **1 M $NaHCO_3$**. Contact time=1 h Ads/Des, Adsorption pH=7,0-8,0 and Desorption pH=8,0, LDH concentration=80 mg/L, T°=23-24 °C; initial PO_4-P mass=2,1; 1,9 and 2,1 mg per cycle.

Figure 4-4, shows the phosphate adsorption/desorption within ten cycles. At the beginning it presented better adsorption, only the first cycle reached the 90 % set as a minimum criterion in the previous section. The decrease in the adsorption with the number of cycles, as well as the fluctuations in the adsorption performance, can be attributed to the fact that the spiked WW used in the experiments was intermittently collected on 3 different days and each time the wastewater had different characteristics, such as different conductivities due to fluctuation in the concentration of anions. Especially, the adsorption of phosphate could be limited by the presence of the anion CO_3^{2-} -present in the $NaHCO_3$ desorption solution-, which competes with the phosphate for the adsorption sites on the LDH-particles.

The desorption values were higher than the adsorption, reaching efficiencies higher than 70 %. However, it can be seen that cycles 5 and 8 show efficiencies higher than 100 %. This could be due to some non-adsorbed phosphate residues which desorbed later. In total, 50,3 % of the dosed phosphate was adsorbed, from this 89,8 % from the adsorbed phosphate was desorbed afterwards.

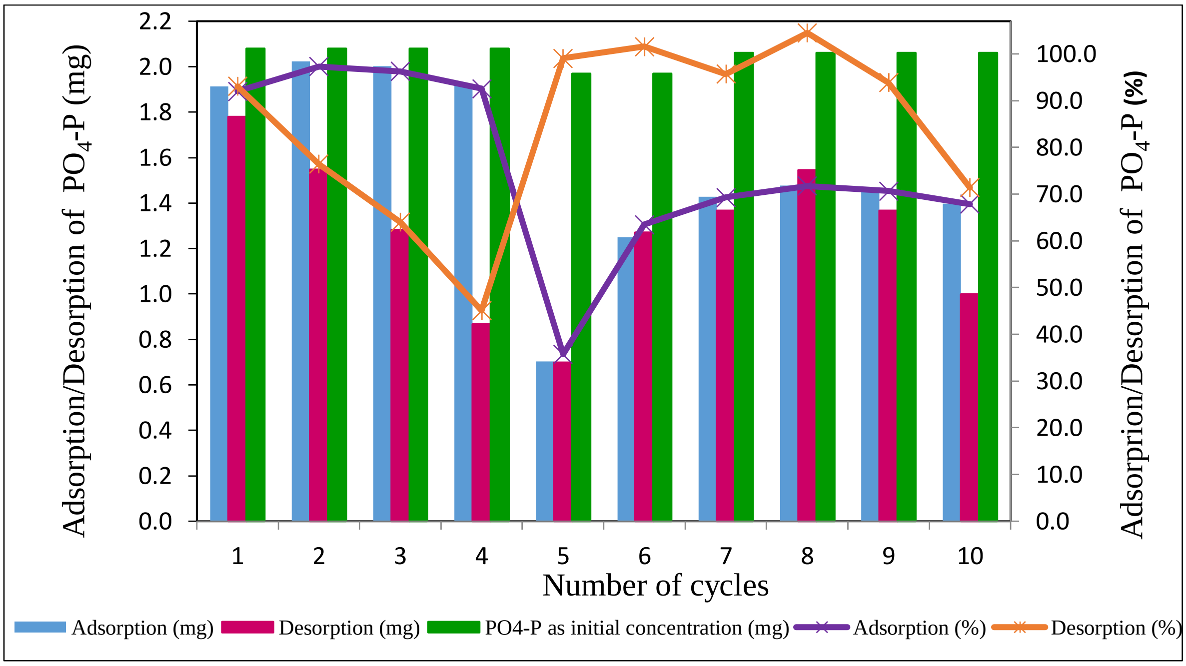

Figure 4. 5. Adsorption/desorption cycles of phosphate onto CaZnFeZr-LDH. Reaction conditions: Desorption solution **1 M NaOH + 1M Na_2CO_3**. Contact time= 1 h Ads/Des, Adsorption pH=7,0-8,0 and Desorption pH=13,0, LDH concentration=80 mg/L, T°=22-23 °C; initial PO_4-P mass=2,1;1,9 and 2,1 mg per cycle.

Figure 4-5 evidences that the adsorption increased when the desorption solution was 1 M NaOH + 1 M Na_2CO_3. The first four cycles had efficiencies higher than the 90 % “target value”, which shows a better performance compared to the previous experiment using $NaHCO_3$ solution. After the fifth cycle the adsorption efficiency dropped notably and the sample did not reach efficiencies greater than 70 % anymore. The performance drop in cycle 5 can be explained by the lower temperature and higher conductivity of the wastewater used in this particular cycle, where the temperature effect will be described in closer details in section 4.6.

In addition, it can be observed that from the fifth cycle onwards the desorption performance increase again showing a better overall performance that the previous experiment using $NaHCO_3$ as desorption solution. In total, 76,0 % of the phosphate dosed was adsorbed, in contrast to 50,3 % in the previous experiment. In contrary, desorption efficiency in this case was approximately 8% lower than in the case of $NaHCO_3$.

As mentioned in section 2.2, the LDHs have affinity for monovalent, divalent and trivalent anions. Due to the fact that the desorption solution contains OH^- and CO_3^{2-} anions, there is a synergetic effect which contributes to the better recovery of phosphate.

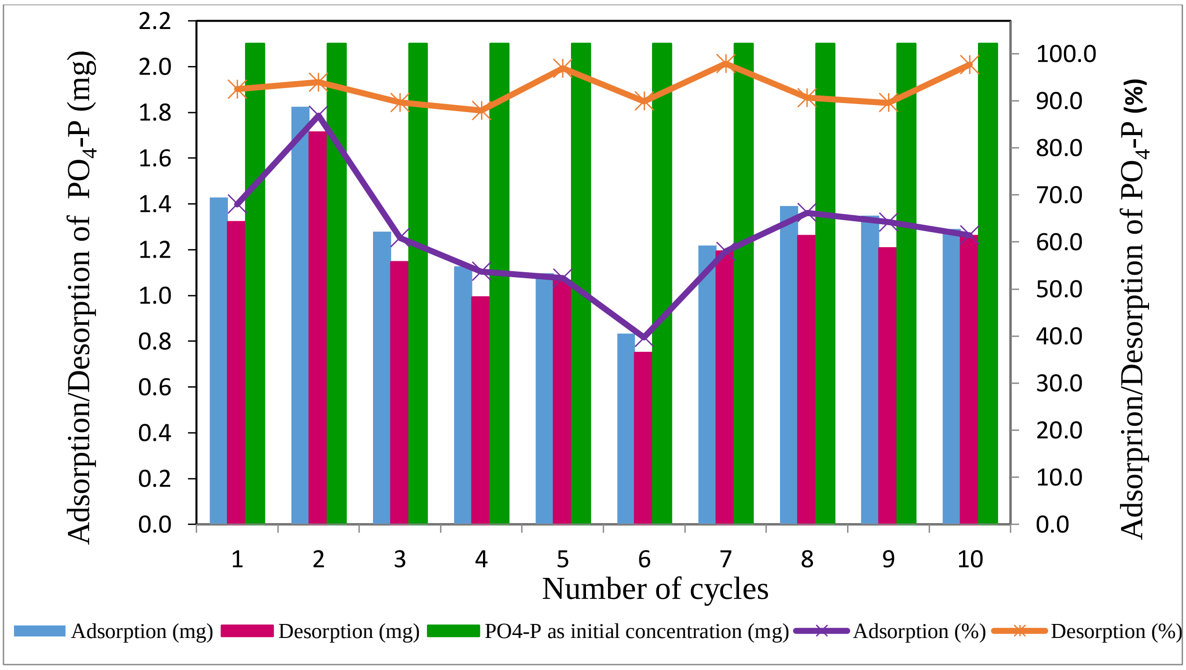

Figure 4. 6. Adsorption/desorption cycles of phosphate onto CaZnFeZr-LDH. Reaction conditions: Desorption solution **3 M NaOH**. Contact time= 1 h Ads/Des, Adsorption pH=7,0-8,0 and Desorption pH=13,3, LDH concentration=80 mg/L, T°=22-24 °C; initial PO_4-P mass=2,1 mg per cycle.

Figure 4-6, demonstrates that the adsorption decreased from cycle 1 to 6 and afterwards started to increase again. All adsorption cycles, with exception of cycle 2, had efficiencies of less than 70 % which is lower than the desired 90% and lower than the pure CaZnFeZr-LDH, mostly because of the higher conductivity of the wastewater and the fact that the particles were underdosed due to the discrepancy between the theoretical and actual LDH-loading values

It is important to mention that always the same spiked WW was used for the performance of all adsorption/desorption cycles. This WW had a higher conductivity (2680 µS/cm) than the WW used in the previous experiments (1000 µS/cm), that can be attributed to the higher concentration of chloride (680 mg/L) which may compete with the phosphate during adsorption. All the experiments in this section were done during winter season which can explain the higher amount of chloride derivate-salts use as snow etching products.
Additionally, it can be observed (figure 4-6) that throughout the desorption cycles, the performance was more uniform than in the other two experiments. All cycles reached desorption efficiencies close to 90 %.

In total 61,1 % phosphate was adsorbed, which is higher than the 50,3 % obtained in the experiment using 1 M $NaHCO_3$ as desorption solution, but less than in the experiment with 1 M NaOH + 1 M Na_2CO_3, (76,0 %). In contrast, from the total adsorbed phosphate 92,8 % was desorbed which is higher than the previous experiment. This means that the 3 M NaOH solution is the best desorption solution for the regeneration of the particles due to the higher concentration of OH^- anions. On the other hand, the adsorption performance is lower mostly due to the higher conductivity of the used WW, which makes it difficult to compare to the other 2 experiments.

4.4 pH effect on adsorption of phosphate by using two types of composite particles (samples MS-55-2 and MS-58-2)

Studying the pH effect on the adsorption of oxyanions by LDHs is subject of interest due to the fact that the adsorption depends on the dissociated oxyanion species which are a function of the pH. In this specific work, two types of LDH-particles were used: one composite particle material with 8,0 wt % CaZnFeZr-LDH and the other one with 34,5 wt % ZnFeZr-LDH.

In the case of the phosphate adsorption onto CaZnFeZr-LDH, the pH was varied from 3,0 to 12,0, figure 4-7.

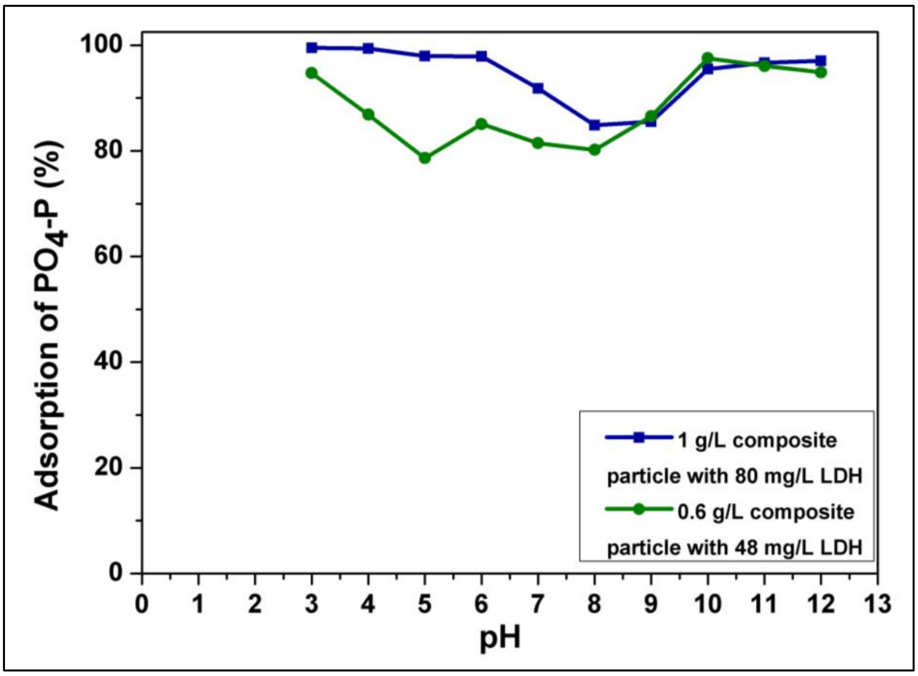

Figure 4. 7. Adsorption of phosphate onto CaZnFeZr-LDH on magnetic particles as a function of solution pH and particle concentration. Reaction conditions: T°= 21,5 °C; initial PO_4-P concentration= 10 mg/L; contact time= 24 h; filtered spiked WW.

Figure 4-7, shows that the phosphate uptake was higher when a concentration of 80 mg/L LDH was used, this is to be expected because higher concentration of LDH provides more adsorption sites and leads to a better performance. The maximum adsorption efficiency was 99,5 % at pH 3,0. Then there is a performance drop in the range pH 6-8; afterwards the phosphate uptake increases with increasing pH, reaching a maximum adsorption efficiency of 97,0 % at pH 12,0. The explanation of this tendency could be that from pH 3,0-6,0 outer-sphere complexes were formed, which involves formation of metal-ligand complexes between the surface hydroxyl groups (M-OH) of the LDH layers and the adsorbed phosphate anions (M-O-P) (Yan *et al*, 2015). In the pH range from 7,0 to 9,0 there was a decreased on the phosphate adsorption due to the fact that probably only ion exchange mechanism occurred and from pH 10,0 to 12,0 the phosphate adsorption increased because most probably the surface charge of the adsorbent was still positive and electrostatic attraction between the positive surface of the LDH and the negative PO_4^{3-} species occurred.

Regarding the experiment with 48 mg/L LDH, it can be said that the experiment follows the same trend of 80 mg/L LDH, with the difference that the minimum adsorption efficiency was obtained at pH 5,0 with 78,6 % and had a second drop at pH 8,0.

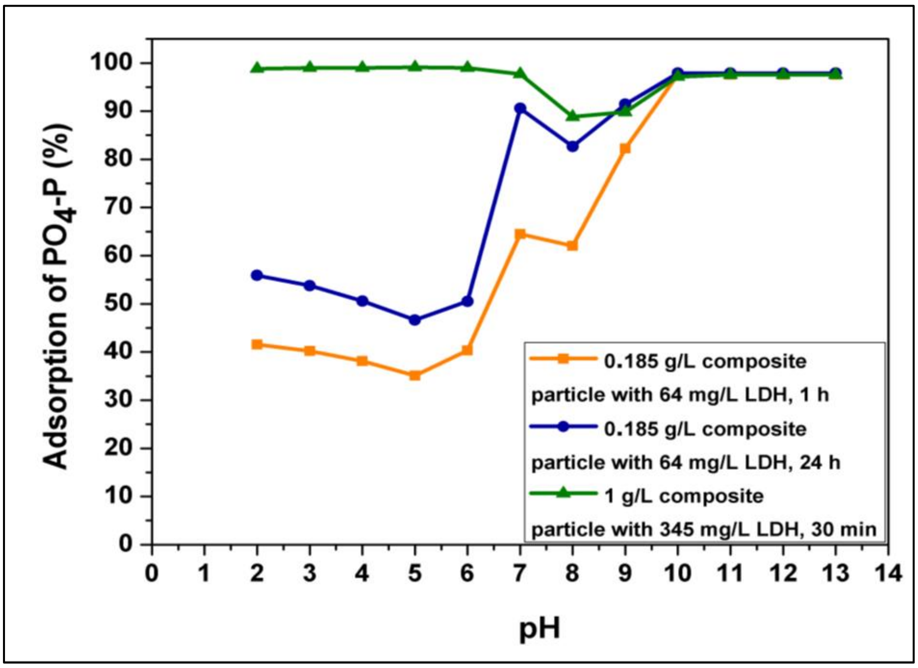

Figure 4. 8. Adsorption of phosphate onto ZnFeZr-LDH on magnetic particles as a function of solution pH. Reaction conditions: T°= 21-23 °C; initial PO_4-P concentration= 10 mg/L; filtered spiked WW.

The behavior of ZnFeZr-LDH in the pH range 2,0-13,0 is shown in figure 4-8 which presents three pH experiments at three different contact times. Nevertheless, in two of them, the concentration of LDH was the same (64 mg/L), but the contact time was different (1 h and 24 h), and in the third one, a higher concentration of LDH was used (345 mg/L) and the contact time was reduced to 30 min. The phosphate uptake was higher when a concentration of 345 mg/L LDH was used, confirming that the higher concentration leads to better adsorption, regardless the type of LDH or the contact time.

The maximum adsorption efficiency was 99,1 % at pH 5,0. Is important to mentioned, that in the pH range 2,0-7,0 the adsorption of phosphate was constant, with adsorption efficiencies of 99,0 %. Afterwards, a drop can be observed at pH 8,0 where the phosphate adsorption decreases, however, after this pH the phosphate uptake increases again with the increasing of the pH and remained constant in the basic range, reaching a maximum adsorption efficiency of 97,6 % in the pH range 11,0-13,0.

Regarding the other two experiments with the same concentrations of LDH, the one with contact time of 24 h showed better phosphate adsorption, which can be explained with the fact that equilibrium state was achieved. Both experiments (1 h and 24 h contact time) followed the same trend, where in the acidic pH range, the phosphate uptake decreases with the increasing pH and after pH 5,0 started to increase till pH 7,0. Then a drop was observed at pH 8,0 and the explanation of this tendency could be attributed to the fact that in the pH range 6,0 to 8,0, phosphate exists in the form of monovalent and divalent species and adsorption was caused by ion exchange. However, LDH has more affinity for the divalent anions, and in this case a competition between the two different phosphate species takes place for the adsorption sites, which might have caused the drop.

After pH 8,0, the phosphate uptake started to increase again, reaching the maximum adsorption efficiency of 97,9 % in the pH range 10,0-13,0. In this pH range the phosphate species found are divalent and trivalent, wherein the LDH has more affinity to the trivalent anions, which can be easier to adsorb and this leads to an increase in the adsorption efficiency at higher pH. And, as described before, electrostatic bonding could happen between the phosphate and the LDH.

Additionally, it can be said that from the two types of LHD that were used, the CaZnFeZr-LDH had the higher phosphate uptake. This can be explained with the presence of an additional cation (calcium) within the LDH structure that contributes to increase in the positive charge of the LDH layers.

The WW-PO_4-P contains anions which may compete with phosphate during the adsorption, such as NO_3^-, CO_3^{2-}, SO_4^{2-} and Cl^-. As mentioned previously in this work, and also in the studies of Goh *et al*, 2008, the competition between anions follows the order $HPO_4^{2-}>SO_4^{2-}>CO_3^{2-}>NO_3^-$. This competition could be part of the explanation of the pH versus the phosphate adsorption behavior; Due to the fact that for the regulation of pH in the acidic range a 1 M H_2SO_4 was used, this increased the presence of the “competitor anions” in the system which lead to a drop in performance in the acidic pH range.

4.5 Effect of adsorbent dosage for the samples MS-58-2 and MS-58-3 at 22 °C

Study the effect of adsorbent dosage on the adsorption of phosphate in filtered and unfiltered WW is a subject of interest in order to find the optimal adsorbent dose for the removal of phosphate.

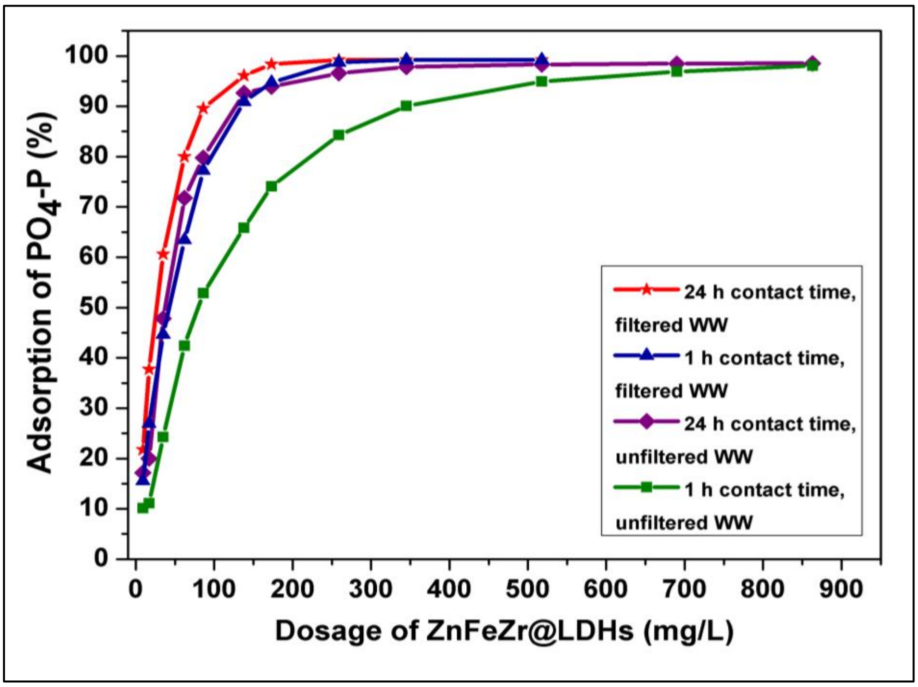

Figure 4. 9. Adsorption of phosphate onto ZnFeZr-LDH as a function of adsorbent dosage. Reaction conditions: T°= 22-23°C; initial PO_4-P concentration= 10 mg/L, pH=7,0-8,0.

According to figure 4-9, the phosphate adsorption efficiency was higher in filtered WW-PO_4-P solution, because the unfiltered WW contains more suspended solids (SS), which can clog the pores of the LDH material leading to a reduction of the contact surface area on the LDH available for the adsorption of phosphate.

To achieve a complete removal of the 10 mg/L PO_4-P, 259 mg/L LDH dosage and 24 h contact time was needed. The adsorption efficiency was 99,2 %. The tendency found for different times and concentrations was similar to the one observed in the previous section, wherein the increase of the adsorbent dose and the contact time lead to an increase in the adsorption efficiency. Based on these results, one can suggest the usage of 1 h contact time but at least 345 mg/L LDH dosage for the further experiments.

Regarding the experiment with unfiltered WW-PO_4-P solution, the maximum adsorption efficiencies found were 98,5 % and 98,1 % after 24 h and 1 h respectively, but with more than double concentration of particles in the case of the 1 h contact time (approximately 850 mg/L LDH). Therefore, it can be recommended that for raw unfiltered wastewater effluent, an LDH concentration of at least 800 mg/L LDH and contact time 1 h should be sufficient for the removal of 10 mg/L PO_4-P.

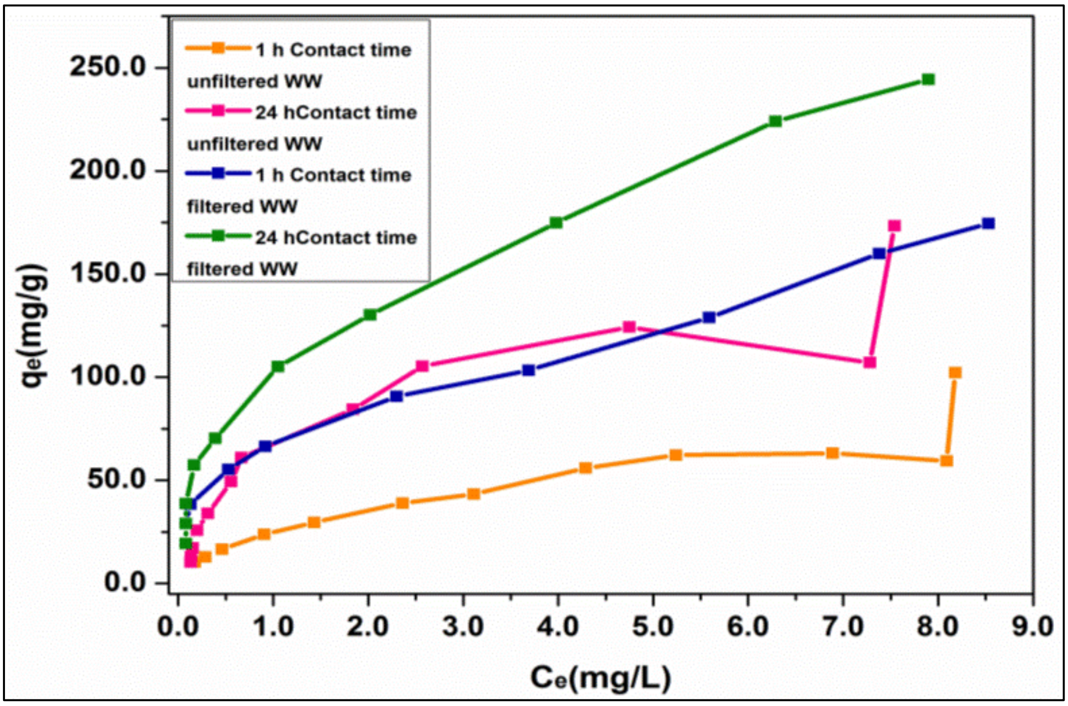

Figure 4. 10. Adsorption isotherms of phosphate onto ZnFeZr-LDH. Reaction conditions: T°= 22-23°C; initial PO_4-P concentration= 10 mg/L, pH=7,0-8,0.

An adsorption isotherm was developed and the filtered and unfiltered WW-PO_4-P solutions were compared (see figure 4-10). As explained before, the best performance for the phosphate uptake was observed when filtered WW was used and contact time of 24 h. It is important to remark, that for the contact time of 1 h, for both filtered and unfiltered WW, the reaction was not in equilibrium yet. Nevertheless, the 1 h isotherms were plotted just for the sake of comparison.

The adsorption isotherm was fitted with two different adsorption models, Freundlich and Langmuir, as was explained on the equations 5 and 6 in section 2.3.5. Figure 4-11 shows the fitted plots for both equilibrium models in a linearized form for the filtered and unfiltered WW samples. Equilibrium constants and correlation coefficients for the different cases are summarized in table 4-1.

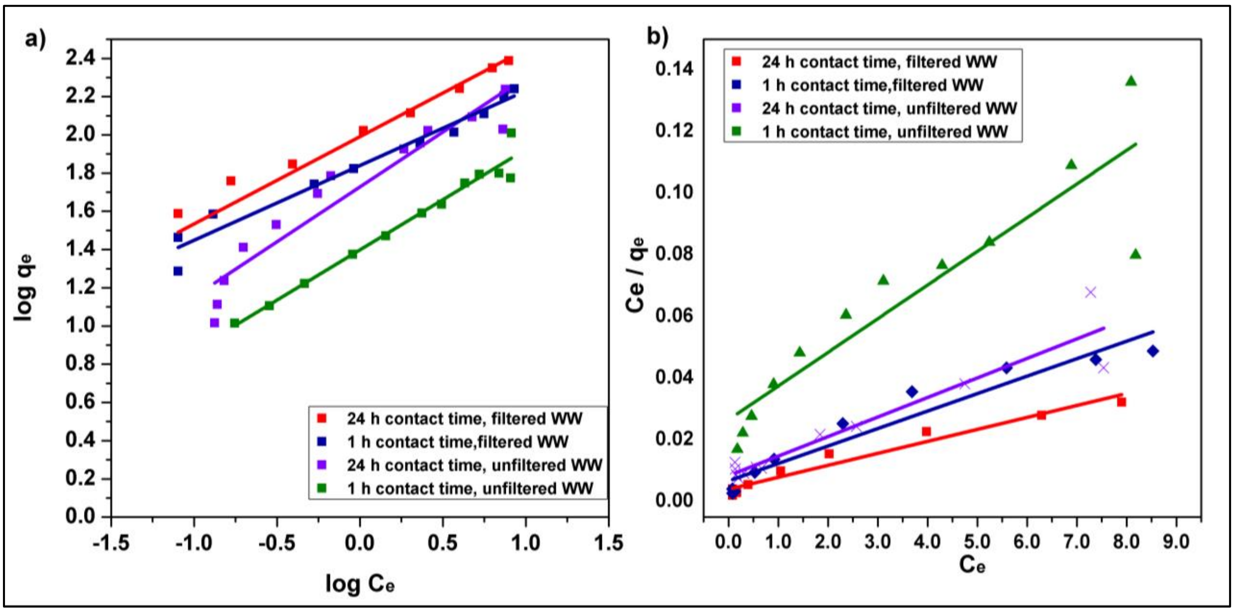

Figure 4. 11. Linear plots of Freundlich a) and Langmuir b) equations for the adsorption of phosphate onto ZnFeZr-LDH.

Table 4. 1**.** Freundlich and Langmuir parameters of the adsorption of phosphate onto the composite particle ZnFeZr-LDH material by using filtered and unfiltered WW-PO_4-P solution.

Model	**Parameter**	**Filtered WW, 1 h**	**Filtered WW, 24 h**	**Unfiltered WW, 1h**	**Unfiltered WW, 24 h**
Freundlich	K_f ((mg/g)/(mg/L)^n)	69,10	97,90	25,00	53,40
	n	2,55	2,19	1,90	1,74
	R^2	0,97	0,95	0,97	0,92
Langmuir	K_L (L/mg)	0,85	0,97	0,41	0,74
	q_m (mg/m)	175,40	256,40	91,70	158,70
	R^2	0,93	0,96	0,84	0,90

Langmuir isotherm suggests that a solid has a uniform surface, which does not have any interactions between the different adsorbed molecules, that the adsorbed molecules are fixed in a specific position and that the adsorption occurs only in monolayer. Meanwhile, Freundlich isotherm assumes that there are different position types of adsorption on the adsorbent and each one with different adsorption heat (Levine, 2004). From this two isotherms, Freundlich fitted better with correlation coefficients above 0,90 and also because it has been demonstrated in previous studies that there are different interactions between the LDHs (that contains Zn^{+2}, Fe^{+3} and Zr^{+4} ions) and the phosphates (electrostatic attraction, ion exchange and ligand exchange), as well as that the adsorption occurs in more than one layer (Chittrakar *et al*, 2007 and Yan *et al*, 2015).

The value of n in the Freundlich equation indicates a favorable adsorption process due to the fact that the n value is higher than 1 (Yang *et al*, 2015). The results for K_f indicate the Freundlich equilibrium constant is higher for both 1 h and 24 h on the filtered WW than in the unfiltered WW; as it was mentioned before this can be explained due to the fact that SS clog the pores of the LDH material leading to a reduction of the available contact area.

Similar to Freundlich, in Langmuir model, the constants values (K_L) were less than 1 in all the cases, which indicates a high affinity between the LDH (adsorbent) and the phosphates (adsorbate) (Lyubchik *et al*, 2004).

On the other hand, it was possible to calculate a dimensionless constant separation factor equilibrium parameter (R_L), explained in the following equation:

$$R_L = \frac{1}{(1+K_L C_0)} \quad (9)$$

where C_0 was the initial concentration (10 mg/L). This R_L states the possibility if the adsorption process will proceed, where: $R_L>1$ unfavorable; $R_L=1$ favorable (linear); $0 < R_L < 1$ favorable; $R_L=0$ irreversible and $R_L<0$ unfavorable (Yang *et al*, 2014). In this work it was found out that the values for filtered WW 1 h, filtered WW 24 h, unfiltered WW 1h and unfiltered WW 24 h were respectively 0,097; 0,094; 0,105 and 0,010, which means that for the particular adsorbent which was used (composite particles with ZnFeZr-LDH), the phosphate adsorption process was favorable.

In addition, for the Langmuir model, the adsorption capacity (q_m) was higher when a filtered WW and 24 h contact time were used. The obtained results were compared with the study of Yan *et al*, 2015 whose data were fitted better with the Langmuir model. The compared results are summarized in table 4-2.

Table 4. 2. Comparison of the phosphate adsorption capacity (q_m) on different LDH materials, based on Langmuir model.

Adsorbent	**Adsorption capacity (mg/g)**	**Reference**
ZnFeZr-LDH, filtered WW 1 h	175,40	This research
ZnFeZr-LDH, filtered WW 24 h	256,40	This research
ZnFeZr-LDH, unfiltered WW 1 h	91,70	This research
ZnFeZr-LDH, unfiltered WW 24 h	158,70	This research
Fe_3O_4@ZnAl-LDH	36,90	Yan *et al*, 2015
Fe_3O_4@MgAl-LDH	31,70	Yan *et al*, 2015
Fe_3O_4@ZnAl-LDH	26,50	Yan *et al*, 2015

As it can be seen in table 4-2, in this study better adsorption capacity was found, especially with the filtered WW at 24 h. It is important to mention, that in the work of Yan *et al*, 2015 adsorption equilibrium was reached within about 60 min and after this period the phosphate adsorption remained constant. As stated above, the results at 1 h were not in equilibrium. Despite of this fact, higher adsorption capacities were found in this project.

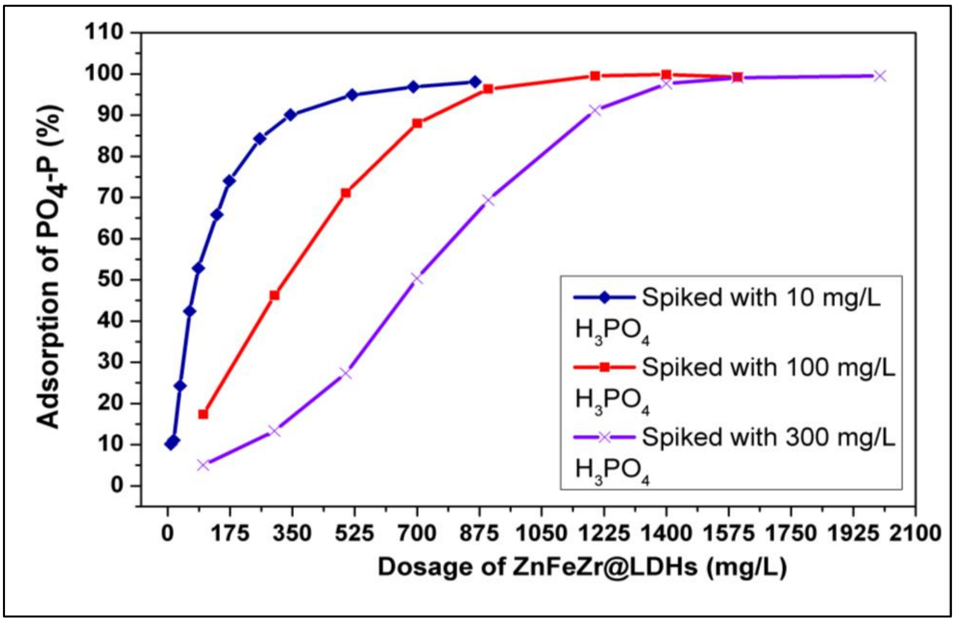

Figure 4.12. Adsorption of phosphate onto ZnFeZr-LDH as a function of LDH dosage and initial phosphate concentration in unfiltered WW. Reaction conditions: T°= 22-23°C; contact time= 1 h; pH=7,0-8,0 for the samples spiked with 10 and 100 mg/L PO_4-P and no pH regulation with the samples spiked with 300 mg/L PO_4-P.

Three unfiltered WW were used to compare the effect of H_3PO_4 dosage against its adsorption efficiency, figure 4-12. The unfiltered WW spiked with 10 mg/L H_3PO_4, required 863 mg/L of ZnFeZr-LDH in order to achieve the maximum phosphate uptake (98,1 %).

Regarding the unfiltered WW spiked with 100 mg/L H_3PO_4, the maximum removal of it was achieved when a concentration of 1400 mg/L ZnFeZr-LDH was used and the maximum phosphate uptake at this point was 99,9 %. On the other hand, for the unfiltered WW spiked with 300 mg/L H_3PO_4 it was necessary to use a concentration of 2000 mg/L ZnFeZr-LDH in order to achieve the maximum adsorption of phosphate which was 99,5 %.

Figure 4-12, shows that the adsorption curves for each WW were different, wherein the WW spiked with 10 mg/L PO_4-P, the adsorption occurs rapidly because the concentration of phosphate anions is less compared to the other two WW with 100 mg/L and 300 mg/L PO_4-P, leading to a rapid adsorption of phosphate onto the LDHs and that could be attributed to electrostatic attraction between the LDH and the phosphate anions. Meanwhile, the other two curves were more ¨linear¨ due to the fact that the concentration of phosphate is higher which took more time to be adsorbed onto the LDHs and that this adsorption could be attributed to ion exchange and/or ligand exchange.

4.6 Adsorption isotherm of samples MS-58-2 at 15 °C, 22 °C, 35 °C and 50 °C

Filtered WW-PO_4-P solution (10 mg/L H_3PO_4) was used for the performance of the adsorption isotherm under four different temperatures: 15, 22, 35 and 50 °C, by using water bath. The goal was to investigate which is the optimal temperature for the adsorption reaction.

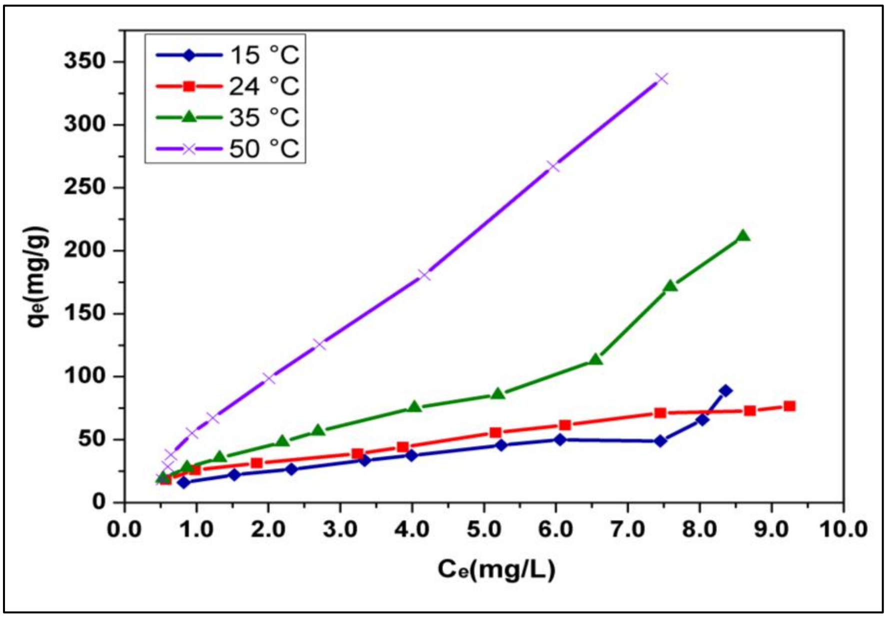

Figure 4.13. Phosphate adsorption isotherm for the ZnFeZr-LDH. q_e is the amount of adsorbed phosphate in mg/gLDH. C_e is the equilibrium concentration of phosphate in the solution. Reaction conditions: Contact time: 1 h; initial [PO_4-P] = 10 mg/L, pH=7,0-7,6 (not adjusted).

Figure 4-13 reveals that with the increase of temperature, the amount of adsorbed phosphate onto the ZnFeZr-LDH increases as well. This is attributed to the fact that this adsorption process is endothermic, as Yan *et al*, 2015 had reported.

Other studies also suggested that the surface sites are more reactive with the increase of temperature (Goh *et al*, 2008). In order to know about the thermodynamic parameters of the adsorption processes, it was used equation 7, as was explained before in section 2.3.5.

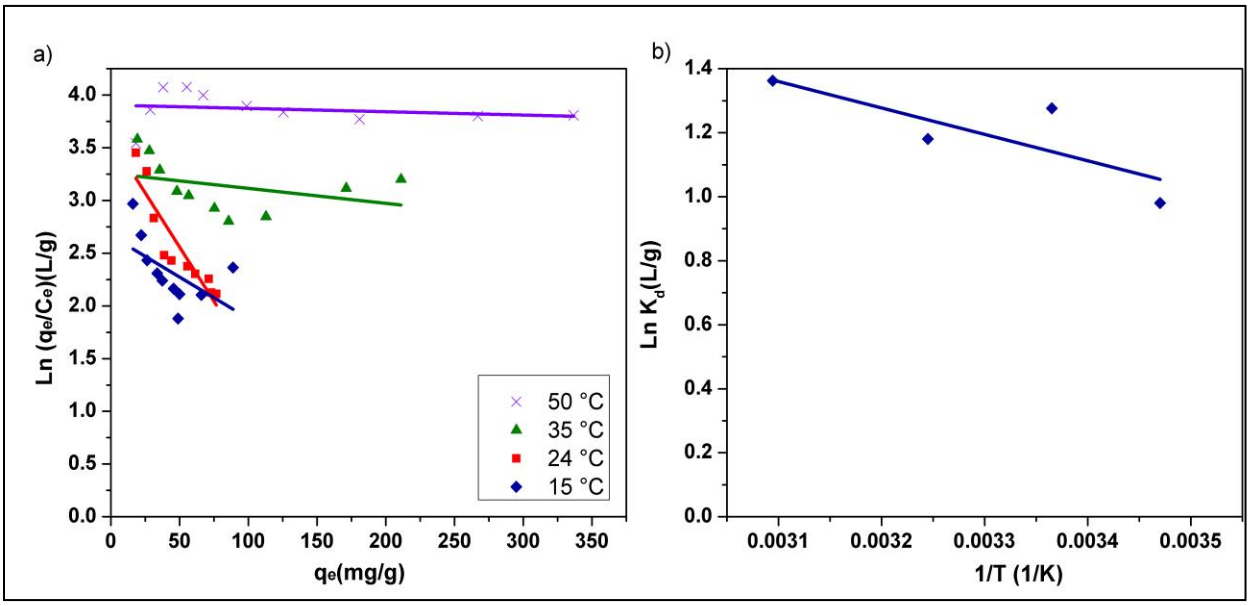

Figure 4. 14. Plots of a) *ln* (q_e/C_e) versus q_e for ZnFeZr-LDH at different temperatures and b) *ln* K_d versus $1/T$.

The values of K_d obtained as the intercept from figure 4-14a) at 15, 24, 35 and 50 °C, respectively were 2,67; 3,58; 3,25 and 3,90 L/g. Afterwards by plotting *ln* K_d versus $1/T$ (figure 4.14 b)), it was possible to calculate the values of enthalpy and entropy change from the slope and the intercept of the plot, which were ΔH=6,86 kJ/mol and ΔS=32,59 J/mol·K, respectively. With this information, it is possible to state the following (Lyubchik *et al*, 2004 and Yan *et al*, 2015):

- The enthalpy change was positive, meaning that adsorption is endothermic which is congruent with the literature.
- The entropy change was positive as well, which means that the degree of disorder increased with the increase of phosphate anions which moved from the liquid phase and adsorbed on the LDH materials.

Moreover, it was possible to calculate the change in Gibbs free energy (ΔG) at each temperature with the equation 8, described on section 2.3.5. The respective results of the ΔG at 15, 24, 35 and 50 °C were -2,35; -3,15; -3,03 and -3,66 kJ/mol, respectively. The negative results of ΔG indicate that the phosphate adsorption process was spontaneous and that with the increasing temperature, the spontaneity of the adsorption process was enhanced (Lyubchik *et al*, 2004).

In addition, the adsorption isotherms were fitted by two equilibriums models, Freundlich and Langmuir, as was described earlier in equations 5 and 6. In figure 4-15 the linear fitting for both equilibrium models at the four different temperatures can be seen. The respective results of equilibrium constants and correlation coefficients are summarized in table 4-3.

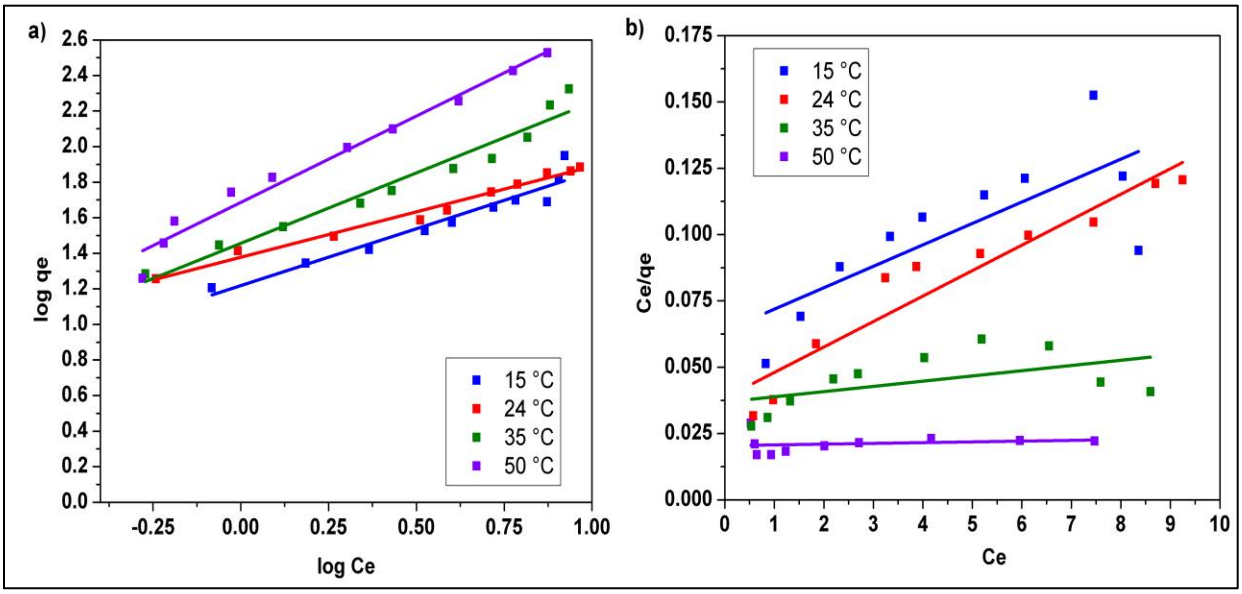

Figure 4. 15. Linear plots of a) Freundlich and b) Langmuir equations for the adsorption of phosphate onto ZnFeZr-LDH at four different temperatures.

Table 4. 3. Freundlich and Langmuir parameters of the adsorption of phosphate onto the composite particle ZnFeZr-LDH material at four different temperatures.

Model	**Parameter**	**15 °C**	**24 °C**	**35 °C**	**50 °C**
Freundlich	K_f ((mg/g)/(mg/L)^n)	16,50	23,90	25,60	48,50
	n	1,56	1,95	1,26	1,03
	R^2	0,93	0,98	0,96	0,97
Langmuir	K_L (L/mg)	0,13	0,25	0,05	0,01
	q_m (mg/m)	123,50	104,20	500,00	3333,33
	R^2	0,59	0,92	0,28	0,04

According to the correlation coefficients (table 4-3), Freundlich isotherm fitted better the data for the whole range of temperature studied. This is in agreement with what was expected and explained in section 4.5.

In this case, the value of $n>1$ in the Freundlich equation was also favorable for the phosphate adsorption process at all temperatures. The results of K_f indicate that the Freundlich equilibrium constant was the highest at 50 °C, confirming what was conclude with the thermodynamic analysis that higher temperatures are more favorable for the process.

The R_L values for 15 °C, 24 °C, 35 °C and 50 °C were respectively 0,1; 0,1; 0,3 and 0,7 which means that for this particular adsorbent which was used (composite particles with ZnFeZr-LDH), the phosphate adsorption process was favorable.

4.7 Adsorption and desorption kinetics of the sample MS-58-2

The adsorption and desorption kinetic were studied in this work using LDH-particles in filtered and unfiltered WW-PO_4-P solution at room temperature and pH=7,5.

Regarding the filtered WW, it can be seen in figure 4-16 that the removal of phosphate increased steadily through time and reached the equilibrium at about 240 min with a phosphate uptake of 99,0 %. In contrast, in the case of unfiltered WW, the uptake increased gradually for about 45 min, then it had a small dropt at approx. 60 min and after that the phosphate adsorption increased again reaching equilibrium after 1440 min with an efficiency of 99,8%.

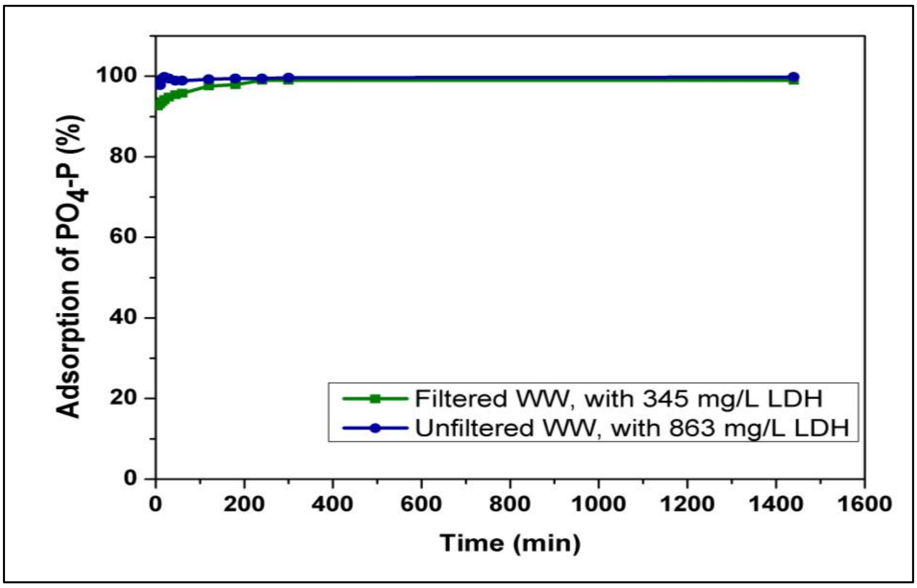

Figure 4. 16. Adsorption of phosphate onto ZnFeZr-LDH as a function of the contact time in filtered and unfiltered WW. Reaction conditions: pH=7,0; initial PO4-P concentration= 10 mg/L, Temperature=22-24 °C.

The pseudo-first order of Lagergren (equation 3) and pseudo-second order of Ho (equation 4) were calculated in order to conclude which one fitted the data better, as was described in section 2.3.5. Figure 4-17 shows the linear plots for both models. The respective results of k_1, k_2, q_e and R_2 are summarized in table 4-4.

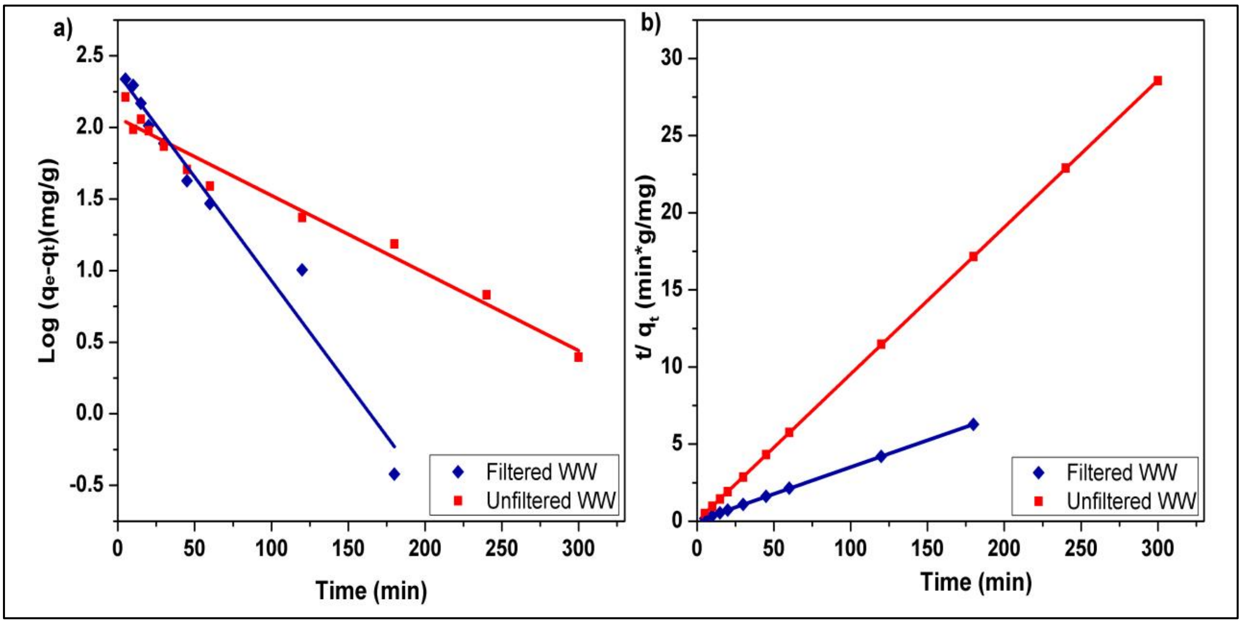

Figure 4. 17. Plots of a) *Log* (q_e-q_t) as a function of the contact time for the pseudo-first order model and b) T/q_t as a function of contact time for the pseudo-second order model.

Table 4. 4. Adsorption rate constants and correlation coefficients of pseudo-first and pseud-second order models for the adsorption of phosphate onto the composite particle ZnFeZr-LDH material in filtered and unfiltered WW.

Model	Parameter	Filtered WW	Unfiltered WW
Pseudo-first order	q_e (mg/g)	239,00	116,52
	k_1 (1/min)	0,033	0,012
	R^2	0,97	0,97
Pseudo-second order	q_e (mg/g)	28,74	10,50
	k_2 (g/(mg·min))	0,04	0,56
	R^2	1,00	1,00

Table 4-4, shows that the correlations coefficients were higher for the pseudo-second order than for the pseudo-first order model, therefore it could be said that for both, filtered and unfiltered WW, the phosphate adsorption followed principally the pseudo-second order model. This means that the adsorption process was mainly dominated by chemical adsorption or chemical bonding between the phosphate and the ZnFeZr-LDH active sites (Yan *et al*, 2015).

It is important to mention, that the q_e and equilibrium constants (k_1 and k_2) were higher for the filtered WW than for the unfiltered WW for both models and this is due to the fact that the unfiltered WW had more SS which hindered the adsorption of phosphate on the active sites of the LDH materials.

The desorption of phosphate as a function of contact time was also investigated and plotted in figures 4-18. Phosphate desorption efficiencies were better and higher when distilled water (DW) was used for the preparation of the desorption solution of 1 M NaOH, reaching values of 90 %, while with the tap water (TW) the desorption efficiency was between 37 % and 60 %. This difference could be ascribed to the fact that tap water contains ions and organic matter that could negatively affect the desorption of phosphate by forming different phosphate complexes.

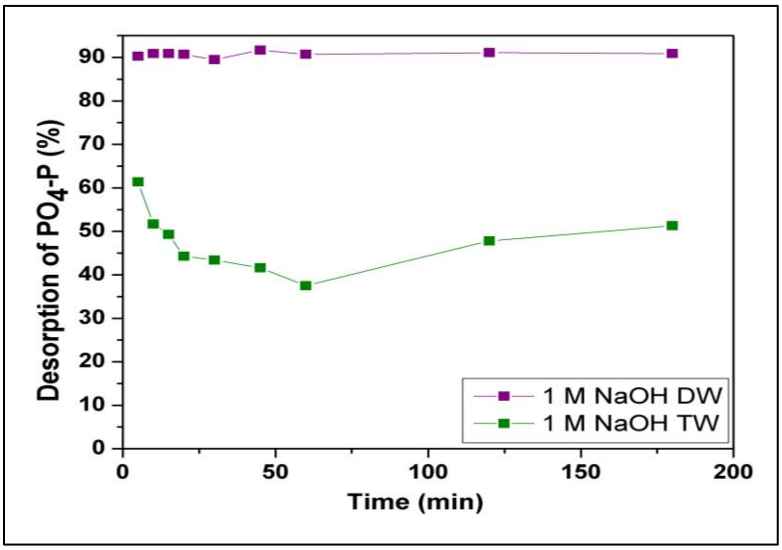

Figure 4. 18. Phosphate desorption from ZnFeZr-LDH as a function of the contact time in filtered using a) 1 M NaOH in DW and b) 1 M NaOH in TW as desorption solutions.

4.8 Effect of adsorbent dosage and adsorption/desorption cycles by using a WW filtrate from the WWTP in Offenburg (sample MS-58-3)

The goal of this experiment was to study the effect of adsorbent dosage on the adsorption of phosphate in a matrix with much higher phosphate concentration (figure 4-19) and perform 5 adsorption/desorption cycles with a wastewater filtrate from the struvite recovery facility at the WWTP in Offenburg, which was collected after acidic dissolution and filtration of the digested sludge, resulting in a significantly higher phosphate concentration in the filtrate used for the experiments (431 mg/L PO_4-P).

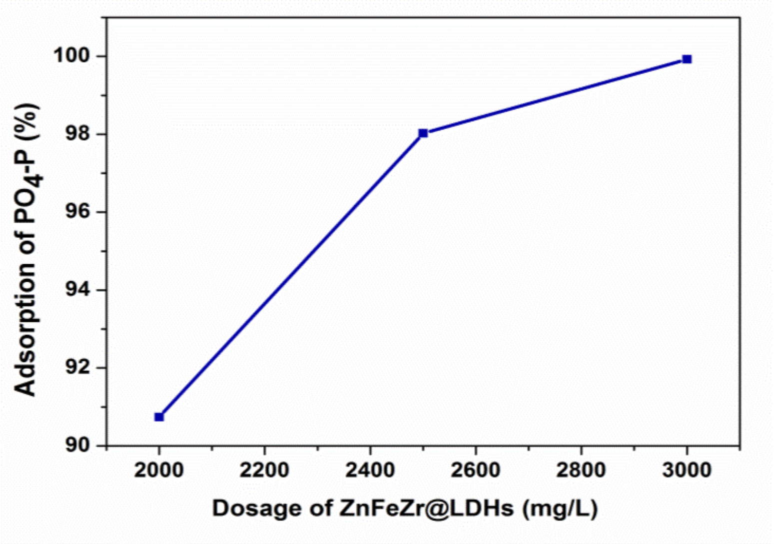

Figure 4. 19. Adsorption of phosphate onto ZnFeZr-LDH composite particles as a function of LDH dosage. Reaction conditions: T°= 25°C; initial [PO_4-P]=431 mg/L, contact time=1 h.

To achieve the removal of 431 mg/L PO_4-P present in the Offenburg WW, 3000 mg/L ZnFeZr-LDH dosage was needed. The adsorption efficiency was 99,9 %.

Comparing this result with the one presented in figure 4-12, one sees that for the removal of 300 mg/L PO_4-P in the unfiltered municipal WW effluent, it was necessary to use a concentration of 2000 mg/L ZnFeZr-LDH in order to achieve the maximum adsorption of phosphate, which was 99,5 %. Nevertheless, using this same concentration of ZnFeZr-LDH in the Offenburg WW, a very good phosphate uptake of 90,7% was achieved. In general, the higher the concentration of phosphate and competing substances in a WW, the higher the LDH concentration should be in order to achieve better removal of phosphate.

Table 4. 5**.** Freundlich and Langmuir parameters of the adsorption of phosphate onto the composite particle ZnFeZr-LDH.

Model	**Parameter**	**Offenburg WW**
Freundlich	K_f ((mg/g)/(mg/L)^n)	153,70
	n	12,30
	R^2	0,97
Langmuir	K_L (L/mg)	0,72
	q_m (mg/m)	278
	R^2	0,99

According to the correlation coefficients (table 4-5), both Freundlich and Langmuir isotherms adjusted good for the Offenburg WW. The value of n in the Freundlich was n>1, therefore the phosphate adsorption process was favorable. Regarding to Langmuir model, the K_L was less than 1, which indicates a high affinity between the LDH (adsorbent) and the phosphates (adsorbate) (Lyubchik *et al*, 2004). The R_L was 0,1 meaning that the phosphate adsorption process carried out was favorable.

As was mentioned before, fifth adsorption/desorption cycles were run. The first experiment was carried out without pH regulation during adsorption. Figure 4-20 shows that the adsorption and desorption efficiencies in cycle 1 were high: 99,8 % and 100 %, respectively. Nevertheless, from cycle 2 on, a decrease on the desorption of phosphate could be observed and this is due to the fact that the pH was not regulated in any adsorption cycle, were the pH value in cycle 1 was pH=6,30, but in cycles 2-5 it was pH=12,40 which was caused by the transfer of the unwashed particles carrying OH^- groups from the desorption solution (pH 13,0) after every regeneration cycle. Therefore, there was no significant change in pH between adsorption (pH=12,4) and desorption (pH=13) which hindered the desorption process and the particles kept adsorbing phosphate even during the desorption phase. In total 91,6 % of the dosed phosphate was adsorbed and from this only 16,4 % was desorbed afterwards.

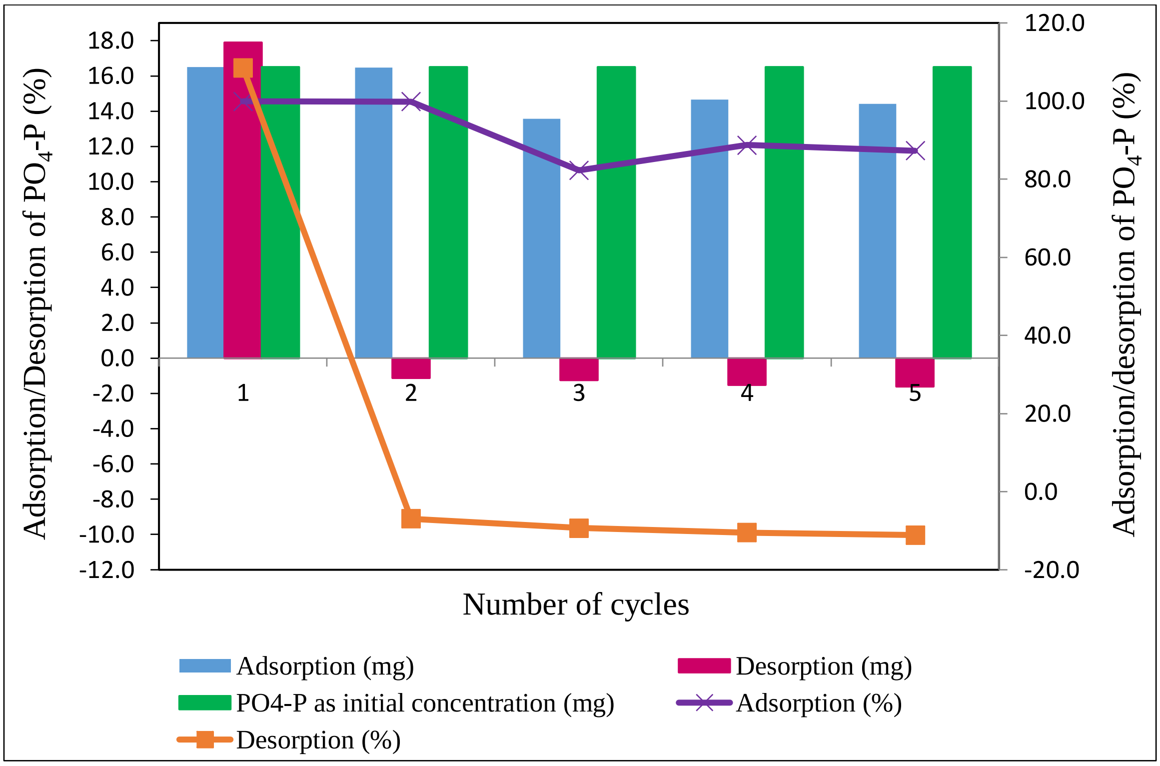

Figure 4. 20. Adsorption/desorption cycles of phosphate onto ZnFeZr-LDH. Reaction conditions: Desorption solution= 1 M NaOH. Contact time= 1 h Ads/Des, no pH regulation in Adsorption and pH=13,0 in Desorption, LDH concentration=3000 mg/L, T°=25-30 °C; initial PO_4-P mass per cycle=16,5 mg (corresponding to 431 mg/L).

Then the experiment was repeated, but this time it was taken into account that pH has to be regulated in the range pH=7-8 during adsorption. Fresh composite particles were used and they were washed with distilled water after every desorption cycle. Figure 4-21 demonstrates a good performance of phosphate adsorption in all cycles, where in total 94,2 % of the dosed phosphate was adsorbed and from this 73,0 % was desorbed.

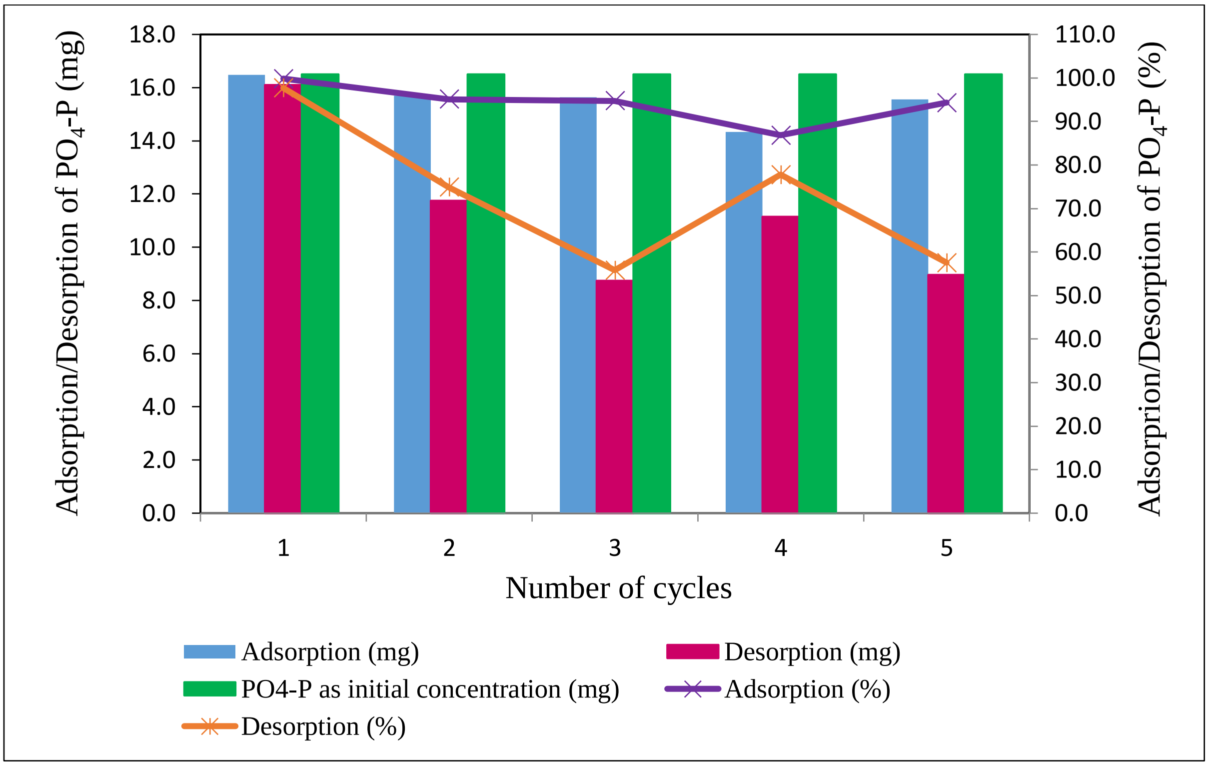

Figure 4. 21. Adsorption/desorption cycles of phosphate onto ZnFeZr-LDH. Reaction conditions: Desorption solution= 1 M NaOH. Contact time= 1 h Ads/Des, pH=7,0-7,2 in Adsorption and pH=13,0 in Desorption, LDH concentration=3000 mg/L, T°=25-29 °C; initial PO_4-P mass per cycle=16,5 mg (corresponding to 431 mg/L).

Chapter 5: Conclusions and recommendations

5.1 Conclusions

It was found that the phosphate adsorption and desorption kinetics for a pure CaZnFeZr-LDH reached maximum adsorption efficiency of 99,5 % after 24 h and the best desorption performance was when a desorption solution of 0,5 M NaOH in distilled water was used, with an efficiency of 96,7 % after 1 h contact time.

The pure CaZnFeZr-LDH reached phosphate adsorption efficiencies above 90 % after 1 h and 24 h. The sample MS-55 (composite particles with 7,6 wt% CaZnFeZr-LDH) achieved 85,4 % and 92,1 % adsorption efficiencies after 1 h and 24 h, respectively. This means that the sample MS-55 it is suitable for the adsorption of phosphate.

For the regeneration of the composite particles, the best performance was observed with the 3 M NaOH desorption solution. However, when this NaOH was used, the adsorption efficiency decreased a little bit

Regarding the influence of pH, it was found that the pH affects the phosphate adsorption. In the case of CaZnFeZr-LDH, it is better to work in the acidic pH range, while if ZnFeZr-LDH is used, it is better to work in basic pH.

For the removal of 10 mg/L PO_4-P in filtered WW, the best phosphate uptake was with a ZnFrZr-LDH dosage of 259 mg/L with 99,2 % efficiency after 24 h. For the unfiltered WWs spiked with 3 different concentrations of PO_4-P: 10, 100 and 300 mg/L, the phosphate uptake was respectively: 98,1; 99,9 and 99,5 %, with a ZnFrZr-LDH dosage of: 863; 1400 and 2000 mg/L. Additionally, the adsorption isotherms in filtered and unfiltered WW with 10 mg/L PO_4-P fitted better with the Freundlich isotherm because the correlation coefficients were above 0,90, concluding that the adsorption process occurs in multilayers.

The increase in temperature enhanced the amount of adsorbed phosphate onto the LDH material. It was found that the adsorption process was spontaneous and endothermic by calculating ΔG and ΔH, respectively.

For the filtered WW, the adsorption kinetics reached its equilibrium after 3 h, while with the unfiltered WW equilibrium was achieved after 4 h. For both filtered and unfiltered WW, the adsorption kinetics fitted better with a pseudo-second order model. For the desorption kinetics, the best performance was when 1M NaOH in distilled water was used.

The best adsorbent dosage for the removal of 431 mg/L PO_4-P in the Offenburg WW (99,9 %) was 3000 mg/L ZnFeZr-LDH. Both Freundlich and Langmuir isotherm models fitted well the experimental data. Five adsorption/desorption cycles were performed with the Offenburg WW. Two important aspects were observed: a) It was necessary to regulate the pH during adsorption in order to improve the regeneration of the particles when desorption solution was added and b) washing the regenerated particles after each desorption cycle enhanced the adsorption/desorption cycles performances.

5.2 **Recommendations**

Considering the pH effect on the adsorption process, it is suggested to perform the same pH experiment with composite particles with 345 mg/L LDH and contact times of 1 h and 24 h in order to compare with the results obtained for 30 min contact time.

It will be interesting to investigate the effect of adsorbent dosage on unfiltered WW spiked with 10 mg/L PO_4-P with more LDH dosage points in order to define the maximum adsorption efficiency and to compare it with the results obtained in the unfiltered WW which was spiked with 100 and 300 mg/L PO_4-P.

It is recommended to run adsorption kinetics with the filtered WW, spiked with 10 mg/L PO_4-P, with a ZnFeZr-LDH concentration of 863 mg/L and to compare the results with the experiment performed with unfiltered WW under the same conditions.

It will be interesting to carry out adsorption/desorption cycles in filtered and unfiltered WW (10 mg/L PO_4-P) with composite particles that contain ZnFeZr-LDH with a concentration of 80 mg/L but regenerating them in 1 M and 3 M NaOH in distilled water.

Finally, it is suggested to perform more experiments with the Offenburg WW, such as adsorption and desorption kinetics, pH effect, temperature effect and further adsorption/desorption cycles.

Chapter 6: Bibliography

Cai, P.; Zheng, H.; Wang, C.; Ma, H.; H, J.; Pu, Y. & Liang, P. (2012). Competitive adsorption characteristics of fluoride and phosphate on calcined Mg-Ale-CO_3 layered double hydroxides. Journal of Hazardous Materials 213-214 (2012) 100-108. DOI:10.1016/j.jhazmat.2012.01.069.

Cheng, X.; Huang, X.; Wang, X.; Zhao, B.; Chen, A. & Sun, D. (2009). Phosphate adsorption from sewage sludge filtrate using zinc-aluminum layered double hydroxides. Journal of Hazardous Materials 169 (2009) 958-964. DOI:10.1016/j.jhazmat.2009.04.052.

Cheng, X.; Huang, X.; Wang, X. & Sun, D. (2010). Influence of calcination on the adsorptive removal of phosphate by Zn-Al layered double hydroxides from excess sludge liquor. Journal of Hazardous Materials. 177 (2010) 516-523. DOI:10.1016/j.jhazmat.2009.12.063.

Chitraka,R.; Tekuza, S.; Sonoda, A.; Sakane, K.; Ooi, K. & Hirotsu, T. (2006). Selective adsorption of phosphate from seawater and wastewater by amorphous zirconium hydroxide. Journal of Colloid and Interface science 297, 426-433. DOI:10.1016/j.jcis.2005.11.011.

Chitraka,R.; Tekuza, S.; Sonoda, A.; Sakane, K.; Ooi, K. & Hirotsu, T. (2007). Synthesis and phosphate uptake behavior of Zr4+ incorporated MgAl-layered double hydroxides. Journal of Colloid and Interface science 313, 53-63. DOI:10.1016/j.jcis.2007.04.004.

Cooper, J.; Lombardi, R.; Boardman, D. & Carliell-Marquet, C. (2011). The future distribution and production of global phosphate rock reserves. Resources, Conservation and Recycling 57 (2011) 78-86. DOI:10.1016/j.resconrec.2011.09.009.

Cordell, D.; Drangert, J.O. & White, S. (2009). The story of phosphorus: Global food security and food for through. Global Environmental Change 19, 292-305. DOI:10.1016/j.gloenvcha.2008.10.009.

Cordell, D. & White, S. (2011). Peak Phophorus: Claryfying the Key Issues of a Vigorous Debate about Long-Term Phosphorus Security: A Review. Sustainability. 3, 2027-2049. DOI: 10.3390/su3102027.

Das, J.; Patra, J.; Baliarsingh, N. & Parida, K.M. (2006). Adsorption of phosphate by layered double hydroxides in aqueous solutions. Applied Clay Science. 32 (2006) 252-260. DOI:10.1016/j.clay.2006.02.005.

De Ridder, M.; De Jong, S.; Polchar, J. & Lingemann, S. (2012). Risks and Opportunities in the Global Phosphate Rock Market.
Web site:http://www.phosphorusplatform.eu/images/download/HCSS_17_12_12_Phosphate.pdf
Date of consultancy: June 2nd, 2015.

Desmidt, E.; Pinoy, L.; Ghyselbrecht, K.; Van der Bruggen, B.; Rabaey, K.; Zhang, Y.; Verstraete, W. & Meesschaert, B. (2015). Global Phosphorus Scarcity and Full-Scale P-Recovery Techniques: A Review. Critical Reviews in Environmental Science and Technology, 45:336–384. DOI: 10.1080/10643389.2013.866531.

Drenkova-Tuhtan, A.; Mandel, K.; Paulus, A.; Meyer, C.; Hutter, F.; Gellermann, C.; Sextl, G.; Franzreb, M. & Steinmetz, H. (2013). Phosphate recovery from wastewater using engineered superparamagnetic particles modified with layered double hydroxide ion exchangers. Water Research 47 (2013) 5670-5677. http://dx.doi.org/10.1016/j.watres.2013.06.039.

DWA Working Group CEC 1.1. (2013). Recovery of valuable materials from waste water and sewage sludge. Web site: http://www.deutsche-phosphor-plattform.de/content/dam/iwks/DeuPP/Phosphor%20Sonderdruck-KEK-1-1.pdf Date of consultancy: June 4th, 2015. DOI: 10.3242/kae2013.10.001.

Ewert, O.; Hermanussen, C.; Kabbe, C.; Mele, C.; Niewersch, H.; Paillard, E.; Wagenbach A. & Stemann J. (2014). Sustainable sewage sludge management fostering phosphorus recovery and energy efficiency. Web site: http://www.p-rex.eu/fileadmin/P-REX-Reserach/Downloads/P-REX_D_5_online.pdf Date of consultancy: June 4th, 2015.

Goh, K.H.; Lim, T.T. & Dong, Z. (2008). Application of layered double hydroxides for removal of oxyanions: A review. Water Research 42 (2008) 1343-1368. DOI:10.1016/j.watres.2007.10.043.

Jeffery, G.H.; Bassett, J.; Mendham, J. & Denney, R.C. (1989). Textbook of Quantitative Chemical Analysis. 5th Edition. Longman Scientific & Technical. Page: 186.

Kalmykova, Y.; Palme, U.; Karlfeldt Fedje, K. & Yu, S. (2015). Total Material Requirement Assessment of Phosphorus sources from Phosphate ore and urban sinks: Sewage Sludge and MSW incineration fly ash. Int. J. Environ. Res., 9 (2): 561-566. ISSN: 1735-6865.

Koilraj, P. & Kannan, S. (2010). Phosphate uptake behavior of ZnAlZr ternary layered double hydroxides through surface precipitation. Journal of Colloid and Interface Science 341 (2010) 289-297. DOI:10.1016/j.jcis.2009.09.059.

LAGA (Bund/Länder-Arbeitsgemeinschaft Abfall), 2010. Evaluation of Options for the Sustainable Use of Secondary Phosphorus Reserves. Ministerium Für Unwelt, Klima und Energiewirtschaft. Web-site: http://www.laga-online.de Date of consultancy: June 4th, 2015.

Levine, I. (2004). Fisicoquímica. 5th Edición. Volumen 1. McGRAW-HILL/INTERAMERICANA DE ESPAÑA, S. A U. Madrid. Pages: 485-487.

Lyubchik, S.; Lyubchik, A.; Galushko, O.; Tikhonova, L.; Vital, J.; Fonseca, I. & Lyubchik, S. (2004). Kinetics and Thermodynamics of the Cr(III) adsorption on the activated carbon from co-mingled wastes. Colloids and Surfaces A: Physicochem. Eng. Aspects 242 (2004) 151–158. DOI:10.1016/j.colsurfa.2004.04.066.

Martin, B. (2010). Removal and Recovery of Phosphorus from Municipal Wastewater using a Ferric Nanoparticle Adsorbent. PhD Thesis. School of Applied Science, Department of Sustainable Systems, Center for Water Science. Cranfield University. Web site link: http://core.ac.uk/download/pdf/140404.pdf Date of consultancy: November 4th, 2014.

Mandel, K.; Drenkova-Tuhtan, A.; Hutter, F.; Gellermann, C.; Steinmetz, H. & Sextl, G. (2013). Layered double hydroxide ion exchangers on superparamagnetic micropaticles for recovery of phosphate from waste water. J. Mater. Chem, 2013, 1, 1840-1848. DOI: 10.1039/c2ta00571a.

Meyer, C. (2014). Lecture: Water Softening. Summer Semester. University of Stuttgart.

Nieminen, J. (2010). Phosphorus Recovery and Recycling From Municipal Wastewater Sludge. Master Thesis. Aaltpo University. Web site: http://www.sswm.info Date of consultancy: June 4th, 2015.

Panasiuk, O. (2010). Phosphorus Removal and Recovery from Wastewater using Magnetite. Master of Science Thesis. Royal Institute of Technology. Stockholm, Sweden. Web site: http://www.diva-portal.org/smash/get/diva2:473397/FULLTEXT01.pdf Date of consultancy: November 4th, 2014.

Parsons, S. & Smith, J. (2008). Phosphorus Removal and Recovery from Municipal Wastewaters. Elements, Vol. 4, pp 109-112. DOI: 10.2113/GSELEMENTS.4.2.109.

Rittmann, B.E.; Mayer, B.; Westerhoff, P. & Edwards, M. (2011). Capturing the lost of phosphorus. Chemosphere 84 (2011) 846-853. DOI:10.1016/j.chemosphere.2011.02.001.

Van Kauwenbergh, S. (2010). World Phosphate Rock Reserves and Resources. IFDC. Web site: http://pdf.usaid.gov/pdf_docs/PNADW835.pdf Date of consultancy: June 2nd, 2015.

Yan, L.G.; Yang, K.; Shan, R.R.; Wei, J.; Yu, S.J. Yu, H.Q. & Du, B. (2015). Kinetic, isotherm and thermodynamic investigations of phosphate adsorption onto core-shell Fe_3O_4@LDHs composites with easy magnetic separation assistance. Journal of Colloid and Interface Science 448 (2015). 508-516. http://dx.doi.org/10.1016/j.jcis.2015.02.048

Yang, K.; Yan, L-G.; Yang, Y-M.; Yu, S.J.; Shan,R.R.; Yu, H-Q. Zhu, B.C. & Du. B. (2014). Adsorptive removal of phosphate by Mg-Al and Zn-Al layered duble hydroxides: Kinetics, isotherms and mechanism. Separation and Purification Technology 124 (2014) 36-42. http://dx.doi.org/10.1016/j.seppur.2013.12.042

Yuan, Z.; Pratt, S. & Batstone, D. (2012). Phospohorus recovery from wastewater through microbial processes. Current opinion in Biotechnology, 23: 878-883. DOI: 10.1016/j.copbio.2012.08.001.

Appendix with the experimental data

Appendix A1. Experiment: Adsorption and desorption kinetic by using pure CaZnFeZr-LDH, sample MS-34-A22.

Table A1-1. Experimental data obtained in the phosphate adsorption kinetic in 200 mg/L pure CaZnFeZr-LDH.

Wastewater	**Contact time (h)**	**pH**	**T (°C)**	**1M H_2SO_4 (ml)**	**Volume (ml)**	**Cn PO_4-P (mg/l)**
Wastewater	0,00	7,62	21,50	-	1000	9,44
MS-34-A22 5 min	0,08	7,65	21,70	-	40	040
MS-34-A22 10 min	0,17	7,69	21,70	-	40	0,33
MS-34-A22 15 min	0,25	7,71	21,80	-	40	0,29
MS-34-A22 20 min	0,33	7,72	22,00	-	40	0,25
MS-34-A22 30 min	0,50	7,75	22,10	-	40	0,21
MS-34-A22 45 min	0,75	7,81	22,40	-	50	0,20
MS-34-A22 1 h	1	7,87	22,60	-	50	0,18
MS-34-A22 2 h	2	8,0	23,30	0,2	50	0,17
MS-34-A22 3 h	3	7,88	23,90	0,1	50	0,11
MS-34-A22 4 h	4	8,00	25,10	0,05	50	0,09
MS-34-A22 5 h	5	9,97	25,60	0,1	50	0,09
MS-34-A22 24 h	24	7,80	25,70	-	500	0,05

Table A1-2. Experimental data obtained in the phosphate desorption kinetic in 0,5 M NaOH in WW.

Wastewater	**Contact time (h)**	**pH**	**T (°C)**	**Volume (ml)**	**Cn PO_4-P (mg/l)**
0,5 M NaOH in WW	0,00	13,03	25,90	500	0,25
MS-34-A22 5 min	0,08	13,31	25,40	50	0,25
MS-34-A22 10 min	0,17	13,32	25,50	40	0,25
MS-34-A22 15 min	0,25	13,32	25,50	40	0,25
MS-34-A22 20 min	0,33	13,31	25,70	40	0,25
MS-34-A22 30 min	0,50	13,3	25,80	50	0,25
MS-34-A22 45 min	0,75	13,31	25,90	50	0,25
MS-34-A22 1 h	1	13,30	26,00	50	0,25
MS-34-A22 2 h	2	13,24	26,30	50	0,25
MS-34-A22 3 h	3	13,26	26,40	50	0,25
MS-34-A22 10 h	20	13,12	26,00	80	0,25

Table A1-3. Repetition: Experimental data obtained in the phosphate adsorption kinetic in 200 mg/L pure CaZnFeZr-LDH.

Wastewater	**Contact time (h)**	**pH**	**T (°C)**	**1M H_2SO_4 (ml)**	**Volume (ml)**	**Cn PO_4-P (mg/l)**
Wastewater	0,00	7,62	22,50	-	500	9,49
MS-34-A22	1,00	8,08	23,20	-	500	0,15

Table A1-4. Experimental data obtained in the phosphate desorption kinetic 0,5 M NaOH prepared in wastewater (WW) and in distilled water (DW).

	Contact time (h)	**pH**	**T(°C)**	**Volume (ml)**	**Cn PO_4-P (mg/l)**
0,5 M NaOH in WW	0,00	12,99	24,5	250	0,08
MS-34-A22 15 min	0,25	13,01	24,6	50	0,15
MS-34-A22 30 min	0,50	13,03	24,7	50	0,14
MS-34-A22 1 h	1	13,04	25	50	0,12
MS-34-A22 2 h	2	13,01	25,6	50	0,08
MS-34-A22 3 h	3	13,00	25,6	50	0,09
0,5 M NaOH in DW	0,00	13,16	24	250	0,11
MS-34-A22 15 min	0,25	13,23	24,4	50	8,83
MS-34-A22 30 min	0,50	13,22	25,1	50	8,96
MS-34-A22 1 h	1	13,18	25,6	50	9,03
MS-34-A22 2 h	2	13,12	27,7	50	8,86
MS-34-A22 3 h	3	13,12	27,5	50	8,89

Appendix A2. Experiment: Comparing the influence of particles synthesis method on PO_4-P adsorption performance.

Table A2-1. Experimental data obtained for the comparison of particles synthesis method.

Sample	0 h		1 h		24 h		1 M H_2SO_4 (ml)	Conductivity (µS/cm)	PO_4-P WW (mg/L)	PO_4-P 1 h (mg/L)	PO_4-P 24 h (mg/L)
	pH	T (°C)	pH	T (°C)	pH	T (°C)					
MS-54-1	7,41	24,40	7,18	24,10	7,46	23,70	0,13	853	9,75	3,65	1,92
MS-54-2	7,39	24,00	7,19	24,80	7,46	23,20	0,13	861	9,75	3,44	1,94
MS-54-3	7,36	24,10	7,13	25,10	7,39	23,10	0,13	853	9,75	4,69	2,54
MS-54-4	7,34	24,30	7,21	24,90	7,46	23,40	0,13	852	9,75	4,67	2,53
MS-55	7,76	24,00	7,21	24,50	7,48	23,50	0,19	935	9,75	1,43	0,77
Pure CaZnFeZr-LDH	7,41	21,80	7,60	23,90	7,77	24,20	-	997	9,385	0,082	0,050

Appendix A3. Experiment: Adsorption/Desorption cycles by using the sample MS-55-2 with a composite particle with 8,0 wt % CaZnFeZr-LDH under different desorption solutions.

Table A3-1. Experimental data obtained in the phosphate adsorption /desorption cycle by using the desorption solution of 1 M $NaHCO_3$.

Cycle	0 h		1 h		1 M H_2SO_4 (ml/L)	Conductivity (uS/cm)	PO_4-P WW (mg/L)	PO_4-P 1 h (mg/L)
	pH	T(°C)	pH	T(°C)				
1	7,28	22,80	7,90	24,30	0,00	1131	10,40	0,89
2	8,39	24,50	7,86	25,50	0,75	2160	10,40	3,75
3	8,28	25,10	7,35	24,00	1,50	2380	10,40	5,37
4	8,79	24,00	7,26	24,60	1,50	2310	10,40	3,58
5	8,79	22,50	7,59	23,40	1,50	2310	9,83	5,26
6	8,87	21,90	7,66	23,00	1,50	2400	9,83	5,88
7	8,32	24,10	7,2	24,40	1,50	2830	10,30	7,38
8	8,2	23,70	7,86	24,10	0,75	2740	10,30	6,97
9	8,8	22,20	7,36	22,80	1,50	2750	10,30	5,66
10	9,17	23,10	7,75	23,40	2,25	3160	10,30	6,20

Cycle	0 h		1 h		Conductivity (uS/cm)	Desorption Solution (ml)	Sample quantity (mL)	PO_4-P, 1 h (mg/L)
	pH	T(°C)	pH	T(°C)				
1	8,03	23,20	8,05	24,50	52100	400	32	3,96
2	8,17	24,40	8,18	25,50	52200	368	32	7,09
3	8,33	25,10	8,28	25,80	50600	336	32	9,87
4	8,43	23,70	8,38	24,60	50700	304	32	13,30
5	8,49	23,00	8,45	23,90	50200	272	32	17,80
6	8,51	23,00	8,52	23,60	50100	240	25	20,90
7	8,57	23,30	8,56	23,90	49100	215	25	23,40
8	8,68	23,50	8,61	24,30	48600	190	25	27,50
9	8,71	23,00	8,67	24,00	48100	165	25	32,20
10	8,67	23,00	8,73	23,80	47700	140	140	35,60

Table A3-2. Experimental data obtained in the phosphate adsorption /desorption cycle by using the desorption solution of 1 M Na_2CO_3 + 1 M NaOH.

Cycle	**0 h**		**1 h**		**1 M H_2SO_4 (ml/L)**	**Conductivity (uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**
	pH	**T(°C)**	**pH**	**T(°C)**				
1	7,30	23,20	7,84	24,40	0,00	1129	10,40	0,84
2	11,62	25,00	7,7	25,50	12,75	4920	10,40	0,28
3	11,76	25,20	7,74	26,40	15,75	5830	10,40	0,39
4	11,80	23,30	7,56	24,80	15,75	5740	10,40	0,77
5	11,71	22,10	7,41	23,10	12,00	5340	9,83	6,33
6	11,70	22,30	7,36	23,30	13,50	5020	9,83	3,60
7	11,51	24,00	7,61	24,90	12,00	5050	10,30	3,16
8	11,38	23,00	7,73	24,40	9,75	4510	10,30	2,91
9	11,34	22,10	7,36	23,20	9,00	4310	10,30	3,02
10	11,43	21,60	7,38	22,80	9,75	4750	10,30	3,31

Cycle	**0 h**		**1 h**		**Conductivity (uS/cm)**	**Desorption Solution (ml)**	**Sample quantity (mL)**	**PO_4-P, 1 h (mg/L)**
	pH	**T(°C)**	**pH**	**T(°C)**				
1	12,97	23,30	13,03	24,50	178400	400	30	4,45
2	12,94	24,60	13,00	25,50	178400	370	30	8,63
3	12,88	25,20	12,93	26,00	176600	340	30	12,40
4	12,84	23,60	13,01	24,70	176000	310	31	15,20
5	12,89	23,00	13,09	24,10	174200	279	30	17,70
6	12,91	22,30	12,96	23,80	172200	249	25	22,80
7	12,83	23,00	13,01	24,20	172500	224	26	28,90
8	12,89	23,20	12,99	24,60	171300	198	25	36,70
9	12,77	23,00	13,00	24,40	171300	173	24	44,60
10	12,72	22,80	13,03	24,40	167600	149	149	51,30

Table A3-3. Experimental data obtained in the phosphate adsorption /desorption cycle by using the desorption solution of 3 M NaOH.

Cycle	**0 h**		**1 h**		**1 M H_2SO_4 (ml/L)**	**Conductivity (uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**
	pH	**T(°C)**	**pH**	**T(°C)**				
1	7,22	21,60	7,79	23,40	0,000	2560	10,50	3,36
2	11,86	22,10	7,68	23,50	9,200	6020	10,50	1,38
3	12,04	22,50	7,67	23,80	16,500	5230	10,50	4,11
4	12,04	22,30	7,69	23,40	15,000	5180	10,50	4,86
5	12,06	21,40	7,78	23,00	13,500	4990	10,50	5,01
6	12,03	22,10	7,79	23,10	15,300	5310	10,50	6,33
7	12,36	23,20	7,68	22,70	15,300	5300	10,50	4,41
8	12,17	23,10	7,65	23,90	13,500	4880	10,50	3,55
9	11,67	23,40	7,21	24,40	13,500	4970	10,50	3,76
10	11,89	22,00	7,90	22,60	13,800	4920	10,50	4,05

Cycle	**0 h**		**1 h**		**Conductivity (uS/cm)**	**Desorption Solution (ml)**	**Sample quantity (mL)**	**PO_4-P, 1 h (mg/L)**
	pH	**T(°C)**	**pH**	**T(°C)**				
1	13,08	22,20	13,33	22,90	374000	400	30	3,30
2	12,96	22,60	13,2	23,50	375000	370	30	7,93
3	13,26	23,20	13,22	23,60	372000	340	30	11,30
4	12,98	21,40	13,3	22,10	370000	310	30	14,50
5	12,91	22,30	13,21	23,10	368000	280	30	18,30
6	12,87	21,10	13,26	22,80	366000	250	25	21,30
7	12,77	23,00	13,36	23,30	365000	225	25	26,60
8	12,96	23,10	13,3	24,00	362000	200	25	32,90
9	12,88	23,50	13,27	24,40	365000	175	25	39,80
10	12,73	22,60	13,3	23,40	357000	150	150	48,20

Table A3-4. Experimental data obtained in the different WW that were used for the different cycles.

				Photometric	Ion chromatographie					
	pH	T (°C)	Conductivity (uS/cm)	PO$_4$-P (mg/L)	PO$_4$-P (mg/L)	Cl$^-$ (mg/L)	S0$_4$-S (mg/L)	NO$_3$-N (mg/L)	NO$_2$-N (mg/L)	F$^-$ (mg/L)
🟦 WW	7,53	22,30	1206	10,40	7,18	216	69,10	6,09	<0,20	<0,50
🟩 WW	7,13	22,40	1537	9,83	10,20	278	90,70	12,70	0,42	<0,50
🟥 WW	7,02	24,00	2170	10,30	9,92	512	81,80	8,10	<0,20	0,50
🟧 WW	13,36	22,40	2680	10,50	10,10	685	85,30	7,10	<0,20	<0,50

Appendix A4. Experiment: pH effect on adsorption of phosphate by using two types of composite particles, samples MS-55-2 and MS-58-2

Table A4-1. Experimental data obtained in pH effect on phosphate adsorption by using the composite particles MS-55-2 with 80 mg/L LDH I 24 h contact time.

pH	**0 h**		**5 h**		**24 h**		**1 M H_2SO_4 (ml/L)**	**1 M NaOH (ml/L)**	**Conductivity (uS/cm)**	**PO$_4$-P WW (mg/L)**	**PO$_4$-P 24 h (mg/L)**
	pH	**T(°C)**	**pH**	**T(°C)**	**pH**	**T(°C)**					
3,0-3,5	3,05	21,40	3,38	21,60	3,27	21,80	3,40	-	1567	10,30	0,05
3,5-4,0	3,51	21,30	3,55	21,50	3,56	21,60	1,87	-	1560	10,30	0,06
4,5-5,0	4,58	21,30	4,56	21,60	4,82	21,60	1,71	-	1605	10,30	0,21
5,5-6,0	5,64	21,40	5,64	21,60	5,82	21,60	0,66	-	1474	10,30	0,22
6,5-7,0	6,59	21,40	6,76	21,60	6,83	21,60	0,90	-	1219	10,30	0,84
7,5-8,0	7,57	21,30	7,50	21,70	7,65	21,60	-	0,10	1206	10,30	1,56
8,5-9,0	8,53	21,20	8,76	21,90	8,65	21,00	-	0,81	1165	10,30	1,49
9,5-10,0	9,52	21,40	9,66	22,00	9,62	21,40	-	4,33	1330	10,30	0,4
10,5-11,0	10,56	21,50	10,66	22,10	10,63	21,60	-	11,00	1895	10,30	0,34
11,5-12,0	11,56	21,50	11,72	22,30	11,55	21,70	-	18,30	3130	10,30	0,30

Table A4-2. Experimental data obtained in pH effect on phosphate adsorption by using the composite particles MS-55-2 with 48 mg/L LDH in 24 h contact time.

pH	**0 h**		**5 h**		**24 h**		**1 M H_2SO_4 (ml/L)**	**1 M NaOH (ml/L)**	**Conductivity (uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 24 h (mg/L)**
	pH	**T(°C)**	**pH**	**T(°C)**	**pH**	**T(°C)**					
3,0-3,5	3,05	22,70	3,13	22,10	3,35	21,60	3,40	-	1525	10,20	0,54
3,5-4,0	3,50	22,30	3,50	21,30	3,68	21,70	2,04	-	1412	10,20	1,34
4,5-5,0	4,69	21,80	4,55	21,60	4,52	21,70	1,70	-	2060	10,20	2,18
5,5-6,0	5,87	21,60	5,76	21,60	5,94	21,70	1,36	-	1398	10,20	1,52
6,5-7,0	6,75	21,60	6,50	21,50	6,77	21,60	1,30	-	1173	10,20	1,89
7,5-8,0	7,83	21,60	7,52	21,10	7,75	21,70	-	0,46	1255	10,20	2,02
8,5-9,0	8,67	21,70	9,00	21,20	8,62	21,60	-	0,96	1131	10,20	1,37
9,5-10,0	9,63	21,50	9,84	21,20	9,86	21,60	-	2,84	1500	10,20	0,25
10,5-11,0	10,68	21,40	10,80	21,60	10,75	21,50	-	6,08	1706	10,20	0,40
11,5-12,0	11,64	21,40	11,80	21,60	11,75	21,60	-	32,80	3920	10,20	0,52

Table A4-3. Experimental data obtained in pH effect on phosphate adsorption by using the composite particles MS-58-2 with 64 mg/L LDH in 24 h contact time.

pH	**0 h**		**5 h**		**24 h**		**1 M H_2SO_4 (ml/L)**	**1 M NaOH (ml/L)**	**Conductivity (uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 24 h (mg/L)**
	pH	**T(°C)**	**pH**	**T(°C)**	**pH**	**T(°C)**					
2,0-2,5	2,31	21,80	2,33	22,20	2,28	22,40	5,57		3870	11,90	5,25
3,0-3,5	3,05	21,70	3,14	22,00	3,11	22,20	2,70	-	1533	11,90	5,50
3,5-4,0	3,64	21,70	3,56	21,90	3,55	22,20	2,10	-	1313	11,90	5,88
4,5-5,0	4,68	21,70	4,58	22,80	4,73	22,20	2,14	-	1216	11,90	6,35
5,5-6,0	5,52	21,70	5,57	22,00	5,72	22,20	1,68	-	1191	11,90	5,89
6,5-7,0	6,61	21,60	6,56	22,10	6,96	22,20	1,09	-	1129	11,90	1,12
7,5-8,0	7,76	21,30	7,50	21,90	7,88	22,00	0,24	-	1073	11,90	2,06
8,5-9,0	8,73	21,50	8,81	22,00	8,67	22,10	-	0,52	1076	11,90	1,02
9,5-10,0	9,80	21,50	9,80	22,00	9,60	22,00	-	1,91	1095	11,90	0,25
10,5-11,0	10,8	21,50	10,85	21,90	10,6	22,00	-	4,10	1274	11,90	0,25
11,5-12,0	11,72	21,50	11,75	22,00	11,67	22,20	-	12,70	1690	11,90	0,25

Table A4-4. Experimental data obtained in pH effect on phosphate adsorption by using the composite particles MS-58-2 with 64 mg/L LDH in 1 h contact time.

	0 h		**1 h**		**1 M H_2SO_4 (ml/L)**	**1 M NaOH (ml/L)**	**Conductivity (uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**
pH	**pH**	**T(°C)**	**pH**	**T(°C)**					
2,0-2,5	2,36	23,10	2,38	22,40	5,10		3360	10,20	5,96
3,0-3,5	3,25	23,30	3,38	21,80	2,40	-	1396	10,20	6,10
3,5-4,0	3,63	23,10	3,71	21,70	2,10	-	1278	10,20	6,31
4,5-5,0	4,62	22,80	4,87	22,00	2,20	-	1194	10,20	6,62
5,5-6,0	5,72	22,70	5,94	22,00	1,65	-	1168	10,20	6,09
6,5-7,0	6,72	22,40	6,88	21,90	0,75	-	199	10,20	3,62
7,5-8,0	7,71	22,20	7,92	22,00	-	0,21	1083	10,20	3,87
8,5-9,0	8,76	22,00	8,70	21,80	-	0,70	1085	10,20	1,81
9,5-10,0	9,80	22,00	9,78	22,00	-	2,10	1124	10,20	0,25
10,5-11,0	10,83	22,00	10,77	21,90	-	4,20	1299	10,20	0,25
11,5-12,0	11,70	22,00	11,68	21,80	-	10,50	2610	10,20	0,25

Table A4-5. Experimental data obtained in pH effect on phosphate adsorption by using the composite particles MS-58-2 with 345 mg/L LDH in 30 min contact time.

	0 h		**30 min**		**1 M H_2SO_4 (ml/L)**	**1 M NaOH (ml/L)**	**Conductivity (uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 30 min (mg/L)**
pH	**pH**	**T(°C)**	**pH**	**T(°C)**					
2,0-2,5	2,25	23,50	2,29	23,00	7,20		3970	10,20	0,12
3,0-3,5	3,22	23,50	3,38	23,80	5,60	-	1701	10,20	0,10
3,5-4,0	3,50	23,20	3,78	23,50	3,80	-	1469	10,20	0,10
4,5-5,0	4,65	23,00	4,93	23,50	4,20	-	1400	10,20	0,090
5,5-6,0	5,56	23,20	5,84	23,30	3,20	-	1313	10,20	0,10
6,5-7,0	6,55	23,10	6,67	23,30	1,60	-	1096	10,20	0,23
7,5-8,0	7,65	22,80	7,94	23,50	-	0,36	1007	10,20	1,14
8,5-9,0	8,73	22,80	8,77	22,70	-	1,00	1037	10,20	1,04
9,5-10,0	9,80	22,90	9,70	22,90	-	2,80	1077	10,20	0,29
10,5-11,0	10,71	22,90	10,69	22,80	-	4,60	1277	10,20	0,25
11,5-12,0	11,71	22,90	11,73	23,10	-	13,20	3030	10,20	0,25

Appendix A5. Experiment: Effect of adsorbent dosage by using magnetic stirrer and samples MS-58-2 and MS-58-3 at 22 °C.

Table A5-1. Experimental data obtained in the adsorbent dosage effect on phosphate adsorption by using the composite particles MS-58-2 with 1 and 24 h contact time and pH regulation (7,0-8,0).

	LDH Cn (mg/L)	**0 h**		**1 h**		**24 h**		**1 M H_2SO_4 (ml/L)**	**Conductivity 1 h (uS/cm)**	**Conductivity 24 h (uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**	**PO_4-P 24 h (mg/L)**
Quantity of particles		**pH**	**T(°C)**	**pH**	**T(°C)**	**pH**	**T(°C)**						
Wastewater	0	7,19	23,90	-	-	-	-	-	1087	1087	10,10	10,10	10,10
0,025 g/L particles	9	7,28	23,90	7,69	22,50	7,93	22,30	0,06	1079	1076	10,10	8,53	7,90
0,05 g/L particles	17	7,31	23,50	7,64	22,30	7,89	22,20	0,06	1077	1068	10,10	7,38	6,29
0,10 g/L particles	35	7,41	23,10	7,78	22,30	7,98	22,60	0,11	1073	1068	10,10	5,59	3,98
0,18 g/L particles	62	7,47	22,90	7,85	22,20	7,88	22,00	0,10	1072	1060	10,10	3,69	2,02
0,25 g/L particles	86	7,66	22,70	7,84	22,20	7,93	22,20	0,11	1065	1062	10,10	2,30	1,05
0,40 g/L particles	138	7,75	22,50	7,82	22,20	7,97	22,20	0,14	1069	1070	10,10	0,92	0,39
0,50 g/L particles	173	7,85	22,30	7,88	22,20	7,91	22,10	0,17	1070	1073	10,10	0,53	0,17
0,75 g/L particles	259	7,99	22,30	7,92	22,10	7,91	22,20	0,19	1077	1082	10,10	0,13	0,08
1,00 g/L particles	345	8,00	22,30	7,85	22,20	7,94	22,10	0,28	1083	1088	10,10	0,08	0,08
1,50 g/L particles	518	8,05	22,20	7,76	22,10	7,94	22,10	0,28	1093	1089	10,10	0,08	0,08

Table A5-2. Experimental data obtained in the adsorbent dosage effect on phosphate adsorption by using the composite particles MS-58-2 with 1 and 24 h contact time and pH regulation (7,0-8,0).

	LDH Cn (mg/L)	**0 h**		**1 h**		**24 h**		**1 M H_2SO_4 (ml/L)**	**Conductivity 1 h(uS/cm)**	**Conductivity 24 h (uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**	**PO_4-P 24 h (mg/L)**
Quantity of particles		**pH**	**T(°C)**	**pH**	**T(°C)**	**pH**	**T(°C)**						
Wastewater	0	7,19	-	-	-	-	-	-	1086	1086	9,10	9,10	9,10
0,025 g/L particles	9	7,00	22,30	7,19	23,00	7,29	23,50	0,14	1070	1072	9,10	8,18	7,54
0,05 g/L particles	17	7,01	22,00	7,13	22,90	7,28	23,50	0,14	1071	1070	9,10	8,09	7,28
0,10 g/L particles	35	7,00	21,80	7,28	22,90	7,21	23,20	0,11	1072	1071	9,10	6,89	4,75
0,18 g/L particles	62	6,96	22,50	7,21	22,90	7,28	23,00	0,16	1068	1068	9,10	5,24	2,57
0,25 g/L particles	86	6,97	22,60	7,21	22,90	7,29	23,20	0,14	1069	1069	9,10	4,29	1,84
0,40 g/L particles	138	6,95	22,80	7,22	22,80	7,22	23,00	0,17	1067	1070	9,10	3,11	0,67
0,50 g/L particles	173	7,01	22,60	7,17	22,90	7,32	22,90	0,16	1069	1075	9,10	2,36	0,56
0,75 g/L particles	259	6,97	22,70	7,15	22,90	7,34	23,00	0,17	1073	1079	9,10	1,43	0,31
1,00 g/L particles	345	6,97	22,60	7,13	22,90	7,37	22,80	0,19	1075	1086	9,10	0,91	0,20
1,50 g/L particles	518	6,92	22,60	7,12	22,80	7,32	22,70	0,19	1082	1092	9,10	0,46	0,15
2,00 g/L particles	690	6,90	22,70	7,13	22,90	7,37	22,70	0,17	1089	1092	9,10	0,29	0,14
2,50 g/L particles	863	6,90	22,70	7,14	22,80	7,33	22,60	0,17	1098	1100	9,10	0,18	0,13

Table A5-3. Experimental data obtained in the adsorbent dosage effect on phosphate adsorption by using the composite particles MS-58-3 with 1 h contact time and pH regulation (7,0-8,0).

	LDH Cn (mg/L)	**0 h**		**1 h**		**1 M H_2SO_4 (ml/L)**	**Conductivity 1 h(uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**
Quantity of particles		**pH**	**T(°C)**	**pH**	**T(°C)**				
Wastewater	0	5,414	21,40	-	-	-	907	90,00	90,00
0,313 g/L particles	100	5,84	24,50	6,13	23,70	-	892	90,00	74,40
0,94 g/L particles	300	6,02	24,00	6,30	23,50	-	862	90,00	48,40
1,56 g/L particles	500	6,12	25,20	6,60	23,40	-	832	90,00	26,00
2,19 g/L particles	700	6,33	24,70	6,83	23,40	-	827	90,00	10,80
2,81 g/L particles	900	6,60	25,20	7,07	23,40	0,01	835	90,00	3,31
3,75 g/L particles	1200	7,02	24,10	7,09	23,20	0,12	904	90,00	0,42
4,38 g/L particles	1400	7,18	23,10	7,05	23,20	0,21	967	90,00	0,12
5,0 g/L particles	1600	7,31	23,60	7,07	23,20	0,27	999	90,00	0,70

Table A5-4. Experimental data obtained in the adsorbent dosage effect on phosphate adsorption by using the composite particles MS-58-3 with 1 h contact time and no pH regulation.

	LDH Cn (mg/L)	**0 h**		**1 h**		**1 M H_2SO_4 (ml/L)**	**Conductivity 1 h(uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**
Quantity of particles		**pH**	**T(°C)**	**pH**	**T(°C)**				
Wastewater	0	2,61	25,30	-	-	-	2050	278,00	278,00
0,313 g/L particles	100	2,66	25,70	2,70	23,70	-	1733	278,00	264,00
0,94 g/L particles	300	3,04	25,70	3,30	23,50	-	1190	278,00	241,00
1,56 g/L particles	500	4,35	25,30	4,42	23,40	-	1027	278,00	202,00
2,19 g/L particles	700	4,80	24,70	4,64	23,40	-	930	278,00	138,00
2,81 g/L particles	900	4,90	24,60	4,91	23,40	-	845	278,00	85,100
3,75 g/L particles	1200	5,08	24,30	5,61	23,20	-	761	278,00	24,500
4,38 g/L particles	1400	5,22	23,60	6,06	23,20	-	752	278,00	6,550
5,0 g/L particles	1600	5,32	23,60	6,37	23,20	-	743	278,00	2,64
6,25 g/L particles	2000	5,53	23,50	6,61	23,20	-	758	278,00	1,31

Appendix A6. Experiment: Adsorption isotherm of samples MS-58-2 at 15 °C, 22 °C, 35 °C and 50 °C

Table A6-1. Experimental data obtained on phosphate adsorption isotherm at 15 °C with 1h contact time and no pH regulation.

	LDH Cn (mg/L)	0 h		1 h		Conductivity 1 h(uS/cm)	PO_4-P WW (mg/L)	PO_4-P 1 h (mg/L)
Quantity of particles		**pH**	**T(°C)**	**pH**	**T(°C)**			
Wastewater	0	7,32	-	-	-	998	9,16	9,16
0,025 g/L particles	9	7,40	12,00	7,49	16,60	990	9,16	8,36
0,05 g/L particles	17	7,42	13,10	7,48	16,50	993	9,16	8,04
0,10 g/L particles	35	7,37	13,40	7,48	17,90	990	9,16	7,45
0,18 g/L particles	62	7,39	12,20	7,46	17,50	989	9,16	6,06
0,25 g/L particles	86	7,38	12,10	7,47	17,00	986	9,16	5,24
0,40 g/L particles	138	7,36	12,00	7,47	16,80	987	9,16	3,99
0,50 g/L particles	173	7,37	12,20	7,44	16,60	986	9,16	3,34
0,75 g/L particles	259	7,35	12,70	7,45	16,30	987	9,16	2,32
1,00 g/L particles	345	7,32	11,70	7,41	16,20	990	9,16	1,53
1,50 g/L particles	518	7,28	11,60	7,39	16,20	996	9,16	0,83

Table A6-2. Experimental data obtained on phosphate adsorption isotherm at 24 °C with 1h contact time and no pH regulation.

	LDH Cn (mg/L)	0 h		1 h		Conductivity 1 h(uS/cm)	PO_4-P WW (mg/L)	PO_4-P 1 h (mg/L)
Quantity of particles		**pH**	**T(°C)**	**pH**	**T(°C)**			
Wastewater	0	7,22	24,40	-	-	996	9,94	9,94
0,025 g/L particles	9	7,17	24,90	7,49	24,40	995	9,94	9,25
0,05 g/L particles	17	7,40	25,20	7,49	24,30	993	9,94	8,70
0,10 g/L particles	35	7,40	24,70	7,49	24,30	990	9,94	7,45
0,18 g/L particles	62	7,41	24,70	7,51	24,10	986	9,94	6,13
0,25 g/L particles	86	7,40	24,50	7,5	24,20	985	9,94	5,16
0,40 g/L particles	138	7,35	24,40	7,50	24,20	984	9,94	3,87
0,50 g/L particles	173	7,37	24,30	7,51	24,20	982	9,94	3,24
0,75 g/L particles	259	7,33	24,20	7,51	24,30	985	9,94	1,84
1,00 g/L particles	345	7,31	24,30	7,46	24,30	986	9,94	0,98
1,50 g/L particles	518	7,25	24,20	7,42	24,30	989	9,94	0,57

Table A6-3. Experimental data obtained on phosphate adsorption isotherm at 35 °C with 1h contact time and no pH regulation.

	LDH Cn (mg/L)	**0 h**		**1 h**		**Conductivity 1 h(uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**
Quantity of particles		**pH**	**T(°C)**	**pH**	**T(°C)**			
Wastewater	0	7,04	34,90	7,56	35,50	999	10,50	10,50
0,025 g/L particles	9	7,21	34,90	7,57	34,90	1004	10,50	8,60
0,05 g/L particles	17	7,26	34,90	7,48	34,90	1000	10,50	7,59
0,10 g/L particles	35	7,31	35,00	7,49	34,80	987	10,50	6,55
0,18 g/L particles	62	7,34	34,90	7,44	34,80	985	10,50	5,19
0,25 g/L particles	86	7,30	34,90	7,43	34,90	979	10,50	4,03
0,40 g/L particles	138	7,3	34,70	7,47	34,80	980	10,50	2,69
0,50 g/L particles	173	7,28	34,80	7,46	35,00	980	10,50	2,19
0,75 g/L particles	259	7,28	34,80	7,43	35,10	982	10,50	1,32
1,00 g/L particles	345	7,22	34,70	7,38	34,90	985	10,50	0,87
1,50 g/L particles	518	7,04	34,90	7,56	35,50	988	10,50	0,54

Table A6-4. Experimental data obtained on phosphate adsorption isotherm at 50 °C with 1h contact time and no pH regulation.

	LDH Cn (mg/L)	**0 h**		**1 h**		**Conductivity 1 h(uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**
Quantity of particles		**pH**	**T(°C)**	**pH**	**T(°C)**			
Wastewater	0	-	-	-	-	1005	10,50	10,50
0,025 g/L particles	9	7,20	48,00	7,59	48,00	991	10,50	7,47
0,05 g/L particles	17	7,44	48,10	7,56	48,00	983	10,50	5,96
0,10 g/L particles	35	7,44	47,70	7,56	48,10	977	10,50	4,17
0,18 g/L particles	62	7,43	47,70	7,52	47,50	974	10,50	2,71
0,25 g/L particles	86	7,42	48,00	7,53	48,50	973	10,50	2,01
0,40 g/L particles	138	7,40	48,00	7,54	48,20	976	10,50	1,23
0,50 g/L particles	173	7,38	48,00	7,53	47,90	980	10,50	0,94
0,75 g/L particles	259	7,36	47,70	7,53	47,90	980	10,50	0,65
1,00 g/L particles	345	7,31	47,70	7,51	48,00	983	10,50	0,60
1,50 g/L particles	518	7,21	47,80	7,55	48,60	970	9,94	0,53

Appendix A7. Experiment: Adsorption and desorption kinetics of the sample MS-58-2

Table A7-1. Experimental data obtained on the phosphate adsorption kinetic on filtered WW and using 345 mg/L ZnFeZr-LDH and pH regulation.

Wastewater	Contact time (h)	pH	T(°C)	1M H_2SO_4 (mL)	Volume (mL)	Conductivity (uS/cm)	Cn PO_4-P (mg/L)
Wastewater	0,00	7,27	24,00	-	1500	1013	10,10
MS-34-A22 5 min	0,08	7,54	23,80	-	40	1031	0,75
MS-34-A22 10 min	0,17	7,57	23,90	-	40	1027	0,69
MS-34-A22 15 min	0,25	7,57	23,90	0,020	40	1023	0,64
MS-34-A22 20 min	0,33	7,57	23,90	0,010	40	1026	0,59
MS-34-A22 30 min	0,50	7,58	24,00	0,020	40	1026	0,53
MS-34-A22 45 min	0,75	7,57	24,00	0,030	50	1031	0,46
MS-34-A22 1 h	1	7,57	24,10	0,020	50	1033	0,43
MS-34-A22 2 h	2	7,54	24,40	0,080	50	1041	0,25
MS-34-A22 3 h	3	7,57	24,60	0,060	50	1040	0,21
MS-34-A22 4 h	4	7,56	24,80	0,060	50	1045	0,10
MS-34-A22 5 h	5	7,56	25,00	0,060	50	1045	0,10
MS-34-A22 24 h	24	7,47	23,10	0,080	1000	1059	0,10

Table A7-2. Experimental data obtained on the phosphate desorption kinetic on filtered WW when 1 M NaOH prepared in tap water was used.

Wastewater	Contact time (h)	pH	T°©	1M H_2SO_4 (mL)	Volume (mL)	Cn PO_4-P (mg/L)
Blind 1M NaOH	0,00	13,03	25,40	500	181200	<0,25
MS-34-A22 5 min	0,08	13,14	24,50	500	177800	6,14
MS-34-A22 10 min	0,17	13,18	24,60	450	177500	5,17
MS-34-A22 15 min	0,25	13,20	24,60	400	177500	4,93
MS-34-A22 20 min	0,33	13,20	24,70	350	177600	4,43
MS-34-A22 30 min	0,50	13,21	24,70	300	177100	4,34
MS-34-A22 45 min	0,75	13,21	24,80	250	177300	4,16
MS-34-A22 1 h	1	13,16	25,00	200	177300	3,75
MS-34-A22 2 h	2	13,13	25,60	150	177300	4,78
MS-34-A22 3 h	3	13,13	25,70	100	176900	5,13

Table A7-3. Experimental data obtained on the phosphate desorption kinetic on filtered WW when 1 M NaOH prepared in distilled water was used.

Wastewater	**Contact time (h)**	**pH**	**T°©**	**1M H_2SO_4 (mL)**	**Volume (mL)**	**Cn PO_4-P (mg/L)**
Blind 1M NaOH	0,00	13,02	25,40	500	182700	<0,25
MS-34-A22 5 min	0,08	13,13	24,00	500	178400	9,03
MS-34-A22 10 min	0,17	13,18	24,10	450	178200	9,09
MS-34-A22 15 min	0,25	13,21	24,10	400	178200	9,09
MS-34-A22 20 min	0,33	13,23	24,20	350	178100	9,07
MS-34-A22 30 min	0,50	13,25	24,30	300	178100	8,95
MS-34-A22 45 min	0,75	13,26	24,50	250	178300	9,17
MS-34-A22 1 h	1	13,25	24,70	200	177700	9,07
MS-34-A22 2 h	2	13,14	25,40	150	177400	9,11
MS-34-A22 3 h	3	13,14	25,90	100	177400	9,09

Table A7-4. Experimental data obtained on the phosphate adsorption kinetic on unfiltered WW and using 863 mg/L ZnFeZr-LDH and pH regulation.

Wastewater	**Contact time (h)**	**pH**	**T(°C)**	**1M H_2SO_4 (mL)**	**Volume (mL)**	**Conductivity (uS/cm)**	**Cn PO_4-P (mg/L)**
Wastewater	0,00	7,19	24,20	-	700	1086	9,10
MS-34-A22 5 min	0,08	7,09	21,70	0,1	50	1102	0,15
MS-34-A22 10 min	0,17	7,05	21,70	0,06	50	1111	0,20
MS-34-A22 15 min	0,25	7,08	21,90	0,02	50	1090	0,05
MS-34-A22 20 min	0,33	7,08	22,00	0,04	50	1111	0,02
MS-34-A22 30 min	0,50	7,07	22,40	0,03	50	1119	0,05
MS-34-A22 45 min	0,75	7,09	22,90	0,05	50	1126	0,10
MS-34-A22 1 h	1	7,07	23,50	0,14	50	1138	0,10
MS-34-A22 2 h	2	7,08	25,30	0,10	50	1164	0,07
MS-34-A22 3 h	3	7,06	26,50	0,07	50	1189	0,05
MS-34-A22 4 h	4	7,07	27,40	0,04	50	1201	0,05
MS-34-A22 5 h	5	7,07	27,90	0,01	50	1210	0,04
MS-34-A22 24 h	24	7,05	27,80	-	150	1234	0,02

Appendix A8. Experiment: Effect of adsorbent dosage and adsorption/desorption cycles by using a WW of the WWTP from Offenburg by using the sample MS-58-3

Table A8-1. Experimental data obtained on the effect of adsorbent dosage on the phosphate adsorption on the Offenburg WW.

Quantity of particles	**LDH Cn (mg/L)**	**Particle dosis (ml/50 mL)**	**0 h**		**1 h**		**Conductivity 1 h(uS/cm)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**
			pH	**T(°C)**	**pH**	**T(°C)**			
Wastewater	0,00	0,00	4,00	25,00	-	-	14980	431,00	431,00
6,25 g/L particles	2000	7,82	5,50	25,00	5,62	25,70	11540	431,00	39,90
7,81 g/L particles	2500	9,77	5,57	25,30	5,86	26,40	11280	431,00	8,52
10,94 g/L particles	3000	11,73	5,65	25,00	6,24	25,80	10980	431,00	0,31

Table A8-2. Experimental data obtained on adsorption/desorption cycles of the Offenburg WW without pH regulation on adsorption cycles.

Adsorption cycle	**0 h**		**1 h**		**Conductivity (uS/cm)**	**1M H_2SO_4 (mg/L)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**
	pH	**T(°C)**	**pH**	**T(°C)**				
1	5,67	26,00	6,30	25,40	10940	-	330,00	0,20
2	10,86	25,70	10,67	25,70	11960	-	330,00	0,40
3	12,35	25,20	12,40	27,20	22900	-	330,00	58,50
4	12,17	25,90	12,36	27,80	22500	-	330,00	37,10
5	12,12	26,20	12,39	28,20	24400	-	330,00	41,80
Desorption cycle	**0 h**		**1 h**		**Conductivity (uS/cm)**	**Desorption solution (mL)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L) pH**
	pH	**T(°C)**	**pH**	**T(°C)**				
1	12,6	25,70	12,63	25,60	159500	100	5	179
2	12,5	24,90	12,71	25,30	135200	95	5	167
3	12,43	26,50	12,79	27,10	114400	90	5	153
4	12,28	27,20	12,77	27,60	92800	85	5	135
5	12,45	27,60	12,84	28,40	74300	80	5	115

Table A8-3. Experimental data obtained on adsorption/desorption cycles of the Offenburg WW with pH regulation on adsorption cycles.

Adsorption cycle	**0 h**		**1 h**		**Conductivity (uS/cm)**	**1M H_2SO_4 (mg/L)**	**PO_4-P WW (mg/L)**	**PO_4-P 1 h (mg/L)**
	pH	**T(°C)**	**pH**	**T(°C)**				
1	5,958	26,80	6,560	28,70	10900	-	330,00	0,48
2	6,996	27,90	7,286	29,30	11800	0,040	330,00	16,10
3	7,092	28,90	7,295	29,80	12830	0,412	330,00	17,30
4	7,028	26,20	7,148	25,70	12940	0,190	330,00	43,40
5	7,050	25,70	7,108	26,30	12070	0,140	330,00	18,70
Desorption cycle	**0 h**		**1 h**		**Conductivity (uS/cm)**	**Desorption solution (mL)**	**Sample quantity (mL)**	**PO_4-P 1 h (mg/L)**
	pH	**T(°C)**	**pH**	**T(°C)**				
1	12,60	25,70	12,63	25,60	159500	100	5	150
2	12,50	24,90	12,71	25,30	135200	95	5	251
3	12,43	26,50	12,79	27,10	114400	90	5	318
4	12,28	27,20	12,77	27,60	92800	85	5	391
5	12,45	27,60	12,84	28,40	74300	80	5	452