Phosphate Sequestration from Aqueous Solutions Using a Zeolite in the Zinc form.

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Research

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Phosphate sequestration from aqueous solutions using a zeolite in
the zinc form

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Abstract
This work evaluated the ability of a modified zeolite to adsorb phosphates in aqueous solution. The zeolite used for this study was a modified faujasite impregnated with zinc chloride (Z-Zn) on its surface. The experiments were carried out in different stages. Adsorption was performed at different pH of the solution and the zeolitized material was found to be favorable for phosphate adsorption. The adsorption kinetics occurred after 240 minutes and reach the equilibrium, determining chemisorption reactions with a fit of the particular diffusion model ($D_p$) and pseudo second order, the Langmuir model was best adjusted through the isotherms. The adsorption and desorption process occurs best in the presence of HCl, the formation of residual phosphorous in the fractionation stage evidenced that the highest percentage was bound to metals such as Fe and Al.

Keywords: phosphate, adsorption, zinc, zeolite, kinetic, isotherm, Z-Zn (faujasite impregnated with zinc chloride).

1. Introduction
Among the important nutrients for the development of biota, phosphorus (P) is considered the limiting factor par excellence of phytoplankton productivity [1], in every ecosystem it is the limiting element because, depending on its concentration and presence determines the degree of biological productivity, in this way the concentration of total phosphorus has been traditionally used as an index of water quality and the trophic state of aquatic systems.

Due to the development of various types of detergents at the beginning of the twentieth century gave way to an evolution of the industrial sector for the manufacture of domestic cleaning products, the commercialization of phosphate detergents in various types and at the same time a problem or impact on the environment arose due to unaware of its consequences. Water bodies in the presence of phosphorus and its excess tend to increase
biological production, triggering the process called eutrophication, in this way a reduction in the availability of water resources, a decrease in the quality and quantity of water can occur. Another of the main problems associated with the use of phosphorus is found in those fertilizers that contain phosphates, also contributing to eutrophication, although this natural process finds an incentive given by artificial activities, it becomes a problem for bodies of water such as lakes and rivers that are close to agricultural areas where these products are used [1]. The presence of phosphorus in wastewater can occur in the form of ortho phosphates (PO$_4^{3-}$, HPO$_4^{2-}$, H$_2$PO$_4^{-}$, H$_3$PO$_4$), polyphosphates (P$_2$O$_7$) and as organic phosphorus. The ortho phosphates contribute total phosphorus to the wastewater, which with the polyphosphates and a small proportion of the organic phosphorus constitute all the soluble forms of phosphorus [2].

There is also a problem derived from phosphorus associated with its low availability in the form of phosphate rock and its decreasing purity, the presence of phosphorus in the soil is between 0.01% and 0.10% organically and varying from according to the soil and climates [3].

The problem of phosphorus was given by its low availability in the form of phosphoric rock and its decreasing purity, we consider that it is an essential biogenic element for living beings, so its activity is limiting in the ecosystem. The relationship between this element is related to organic matter, so the relationship between carbon and phosphorus is between 100 and 200, while the ratio between N/P varies between 10/1 and 10/2 [3].

In recent years, the interest in recycling phosphorus has increased; some governments have implemented measures to recover percentages of phosphorus from wastewater, as is the case of Sweden, which has established a recovery of 75% of the element [4]. The recovered phosphorus could thus be an alternative source of raw materials for the phosphate industry. As an example, one of the main phosphorus producers, Thermphos
International (Netherlands) has decided to replace 40 ton / yr of its raw material input P_2O_5 with recovered phosphorous materials. This company [4], is recycling calcium phosphate pellets produced by the Crystalactor process in a treatment plant in the Netherlands.

Some studies evaluated the use of certain materials for the removal of phosphorus from wastewater and the subsequent recovery or desorption of the element, in this case materials such as: zeolites, clays, modified aluminas in the presence of other compounds. With these antecedents, the present work evaluates the applicability of a zeolite modified with zinc for the adsorption of phosphates from aqueous solutions, considering that zeolites have some characteristics [5].

The use of zeolites for the adsorption and removal of certain chemical substances is due to their high adsorption capacity, ion exchange, low permeability, physical-chemical stability, and their high surface area [6]. Therefore the objectives of this study are: study the influence of pH and ions concentration on zeolites capacity removal, determine the equilibrium and kinetic sorption parameters, determine and evaluate their performance, sorption and desorption, as well as the phosphorus species present in the adsorbent.

## 2. Materials and methods

### 2.1. Analytical method

The concentration of phosphorus was analyzed by the vanadomolibdophosphoric acid colorimetric method (4500-P C) [7].

### 2.2. Zeolitization and modification of clays with ZnCl_2 by impregnation

The respective samples were made from a faujasite and impregnated with ZnCl_2, thus we increase the surface area to obtain an increase in phosphate adsorption capacity.
2.3. **Sample preparation, Faujasite synthesis:**

To get faujasita dissolve 55.5 g of hydrated nona sodium metasilicate in 222 g of water. 99 g of sodium aluminate was added in a controlled manner at room temperature and under stirring for 1 h until a homogeneous mixture was obtained, taking into account that the mixture becomes transparent and thick. It was left to age at room temperature for 24 h. The next step consists of subjecting it to a temperature of 90 °C for 8 h and then filtering under vacuum maintaining a pH of 7-8. It is left to dry at 90 °C for 24 h. Then the impregnation with zinc chloride was carried out, for which 30 g of faujasite was placed in 250 mL of 0.1 M ZnCl₂ solution.

2.4. **Determination of the point of zero charge (pzc)**

The zero charge point, in physical chemistry, is a concept related to the phenomenon of adsorption, and that describes the condition when the density of electric charge on a surface is zero. It is generally determined in relation to an electrolyte, and the pzc value was assigned to a specific substrate or colloidal particle. In other words, pzc is usually the pH value at which a solid immersed in an electrolyte exhibits net zero electrical charge on the surface.

Deionized water and a sodium chloride solution with two different concentrations (0.01 M and 0.05 M) are used. 25 mL of these solutions were placed in centrifuge tubes, the pH was adjusted to initial values: 3, 4, 5, 6, 7, 8, 9 and 10 and then 0.1 g of the Z-Zn. It was placed on the magnetic stirrer for 24 h and the pH measurement of each of the tubes were taken again and recorded.

2.5. **Effect of pH on sorption**

A phosphate solution prepared from concentrated sodium phosphate (20 mg L⁻¹) was used. 25 mL of this solution was placed in different centrifuge tubes, the pH was adjusted to initial values: 3, 4, 5, 6, 7, 8, 9 and 10 and 0.1 g of Z-Zn. It was placed on the
magnetic stirrer for 24 h. Subsequently, the mixture was filtered and centrifuged to measure the pH of each of the tubes again and the phosphate concentration was recorded.

2.6. Assessment of phosphate adsorption capacity

- Kinetics of phosphate adsorption:

In this study, the phosphate adsorption mechanism was evaluated using 0.1 g of Z-Zn in contact with 250 mL of a 25 mg L\(^{-1}\) phosphate solution at pH 7.5. This pH value was used on the basis that conventionally wastewater effluents register this value as part of their physicochemical properties. Aliquots of 5 mL were taken with time intervals between 30 seconds and 24 h. After filtered and centrifuged the solutions, the pH and phosphate concentration, both initial and final, are recorded.

- Phosphate adsorption isotherms:

The maximum adsorption concentration was determined using solutions of 5.10, 25.50, 100, 250, 500, 1000 and 2000 mg L\(^{-1}\) of phosphate at pH equal to 7.5. For which 25 mL of the prepared solutions were placed in centrifuge tubes with 0.1 g of the Z-Zn sample to carry out the adsorption in a period of 24 h. It was adjusted to a pH of 7.5 then when filtering the solutions the pH and the phosphate concentration were recorded, both at the beginning and at the end.

2.7. Determination of the phosphorus species in the adsorbent (fractionation)

The fractionation of phosphorus allows us to know and identify the fractions to which the phosphate adsorbed on the solid corresponds.

The method described of Hieltjes and Lijklema according to Guaya et al [8] was used for the fractionation of phosphorus in the modified zeolite. 0.25 g of sample were placed in 25 mL of phosphate solution with a concentration of 25 mg L\(^{-1}\). To determine the fraction of freely bound phosphorus, during the first stage two consecutive extractions were carried out in 20 mL of 1 M NH\(_4\)Cl solution with a pH 7. The fraction of metals bound to
phosphorus was extracted consecutively on two occasions with 20 mL of 0.1 M NaOH solution followed by extraction in 1 M NaCl solution. Finally, two consecutive extractions are carried out in 20 mL of 0.5 M HCl, thus determining the phosphorus bound to zinc and other metals. In the case of residual phosphorus, it was calculated by mass balance between the absorbed phosphorus and the extracted fractions. The tests are done in duplicate and the data is reported.

2.8. Adsorbent regeneration evaluation

The purpose of this evaluation is to recover the phosphate already adsorbed, in this way it can be used in a next adsorption-desorption cycle. Phosphate adsorption was carried out at equilibrium using 0.1 g of modified zeolite in 25 mL of phosphate solution with a concentration of 20 mg L$^{-1}$ for 24 h. Subsequently, it was centrifuged and filtered to proceed with the washing and drying of this sample of saturated zeolite whose adsorption capacity is known. 15 mL of 0.01 M HCl (R1) solution and 15 mL of 0.01 M NaOH (R$^2$) solution were added to the separated solid, it is left under mechanical stirring for a further 24 h. At the end, for desorption, 25 mL of the phosphate solution were added to the last separated solid and it is subjected to a further 24 h of mechanical stirring for the subsequent reading of the results.

Previously, for this analytical section, 250 mL of phosphate solution at a concentration of 20 ppm, 100 mL of a 0.1 M HCl solution and 100 mL of a 0.1 M NaOH solution was prepared. After (next day), it is performed the separation of the solid and the liquid by centrifugation and the final concentration is read, also taking 3.5 mL of the filtered liquid, 0.5 mL of water and 1 mL of distilled water in each cell.
3. Results and discussion

3.1. Determination of the zero charge point.

As can be seen in Figure 1, the zero charge point (pH$_{pzc}$) intervenes with a vital role in the physicochemical reaction, the protons are adsorbed by the material (Z-Zn) in the contact time, in this way the pH of the Zinc-modified zeolite charges positively when pH < pH$_{pzc}$, favoring phosphate adsorption, Guaya et al [9]. Likewise, the phosphate anion will be repelled by Z-Zn when the surface has a negative charge, in this case pH > pH$_{pzc}$, for example 9 or 10. For this case, the pH$_{pzc}$ value of Z-Zn is 8.5. Comparing with bibliographic information on other types of adsorbents that have used zinc in their composition, data such as double hydroxides of zinc and aluminum are found in layers where the value of the zero charge point pH$_{pzc}$ is 10.05, Iftekhar et al [10].

Table 1 describes some important data on phosphate adsorption of various materials of a similar nature in relation to zeolite impregnated with zinc, among these the best isotherm and kinetic model are described. Some of these materials present results at different temperatures and concentrations; our research takes ambient temperature as a reference.

Figure 1 Zero charge point
3.2. **Effect of pH**

Phosphate adsorption on zinc-impregnated zeolites can occur through chemical and physical interactions, thus adsorption as a function of pH was represented in Figure 2.

The adsorption of phosphate by the modified zeolite occurs better when the solution has pH 3. According to the graph, the values are similar in pH 4 to 6 and pH 9 and 10; however, there is a variation in pH 7 and 8 promoting a reduction in phosphate elimination. Figure 3 describes the distribution of phosphate species as a function of pH.

In the acidic zone, electrostatic attraction of the phosphate anion was generated with the positive surface charge of the adsorbent (Z-Zn) in Eq. (1), while in the basic zone a repulsive effect of negative charges is generated Eq. (2). On the surface of the adsorbent (Z-Zn) another mechanism occurs during adsorption related to the basic zone associated with complexation reactions or formation of phosphate complexes that can be mono and bidentate in Eq. (3) [5].

\[
\begin{align*}
(1) \quad & \text{Z-Zn} \cong \text{MOH}^+ + \text{H}_2\text{PO}_4^- / \text{H}_2\text{PO}_4^2 \rightarrow (\cong \text{MOH}^+ \text{H}_2\text{PO}_4^- / \text{H}_2\text{PO}_4^+) \\
(2) \quad & \text{Z-Zn} \cong \text{MOH}^+ + \text{H}_2\text{PO}_4^- / \text{HPO}_4^- \rightarrow (\cong \text{MOH}^+ \ldots \text{H}_2\text{PO}_4^- \text{H}_2\text{PO}_4^- / \text{H}_2\text{PO}_4^2) \\
(3) \quad & \text{Z-Zn} \cong \text{MOH}^+ + \text{H}_2\text{PO}_4^- / \text{H}_2\text{PO}_4^2 \rightarrow \text{Z-Zn} \cong \text{MH}_2\text{PO}_4^+/ \text{H}_2\text{PO}_4^2 + \text{OH}^- 
\end{align*}
\]

The adsorption process allows reactive chemicals to bond to the surfaces of solids. Small particles, such as clay minerals, have a large specific surface area and thus physically tend to have a high adsorption capacity [11]. In some cases, these physical processes are accompanied by chemical reactions, which cause the precipitation of phosphorus from the soil solution into compounds with different degrees of solubility, known as chemisorption processes, in our case there was no formation of precipitates during the experiment, Guaya et al [12].
According to other investigations that evaluate the effect of pH in the removal of phosphates, where materials such as: natural clays, hydrated manganese oxide and bentonites are used, the performance of the Z-Zn material is similar reported by Guaya et al [8].

**Figure 2** Effect of pH on the adsorption of phosphates by Z-Zn

![Graph showing adsorption capacity vs. initial pH](image)

**Figure 3** Species of phosphate as a function on pH

![Graph showing species of phosphate vs. pH](image)

Fuente: [7]

3.3. *Phosphate isotherms*

The equilibrium uptake for phosphate was calculated using the Eq. (4):
\[ q_e = (C_o - C_e) x \frac{v}{w} \]

Where \( C_o \) (mg L\(^{-1}\)) and \( C_e \) (mg L\(^{-1}\)) represent the initial and equilibrium concentrations. In change, \( v \) (L) is the aqueous solution volume and \( w \) (g) is the mass of the zeolite. The phosphate equilibrium sorption was evaluated according to the Langmuir Eq. (5) and Freundlich Eq. (6) isotherms.

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{Q_m} \]

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]

Where \( Q_m \) (mg g\(^{-1}\)) is the maximum sorption capacity, \( K_L \) (L mg\(^{-1}\)) is the Langmuir sorption equilibrium constant and \( K_F \) (mg g\(^{-1}\))/(mg L\(^{-1}\)) is the Freundlich equilibrium sorption constant [9].

The data for the equilibrium in phosphate adsorption by the modified zeolite was better described according to the results of our system adjusting to the Langmuir isotherm. The results were shown in Table 2, where the value of \( R^2 \) was 0.98; it provides the appropriate experimental adsorption data according to this model, so chemisorption is the existing mechanism.

Therefore, the results suggest that the availability of affinity sites, are specific and equal, in the zeolite for monolayer and homogeneous sorption, in this case it would be of identical active centers capable of retaining a single sorbate molecule without interaction between these. The amount of available phosphorus is associated with the maximum adsorption value (\( Q_m \)). The results according to the Langmuir model show a value for \( Q_m \) of 27.5 mg g\(^{-1}\), similar to the experimental results shown in Figure 4. According to other studies, carried out under some conditions with temperature variation, there is a good adsorption capacity considering that work has been done with zinc ferrites and with cerium variations where the maximum result obtained
has been 41.63 mg $g^{-1}$ but with a fraction of the adsorbent [8]. For the case of the adsorption energy coefficient, $K_L$ of 0.0363, it is a favorable result, since the condition of the constant $K_L < 1$ is fulfilled [9].

**Figure 4** Experimental isotherm equilibrium for phosphate by Z - Zn

3.4. **Kinetic study**

The kinetic adsorption of the phosphate ion on Z-Zn, as shown in Figure 5, describe that equilibrium was reached at 240 min. So the data fit was applied to the pseudo first, second order and particular diffusion models.

**Figure 5** Z–Zn Phosphate kinetic adsorption curve
Two adsorption kinetic models, the pseudo first order and the pseudo second order models, were used to describe our experimental data [13]. The pseudo first order model uses this Eq. (7):

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]

Where \(q_e\) and \(q_t\) are the phosphate adsorbed per unit mass of adsorbente (mg g\(^{-1}\)) at equilibrium and the reaction time \(t\) (min). \(k_1\) is the rate constant (min\(^{-1}\)), this Eq. (8):

\[
\ln (q_e - q_t) = \ln q_e - k_1t
\]

The pseudo second order model may be represented by Eq. (9):

\[
\frac{dq_t}{dt} = K_2^* (q_e - q_t)^2
\]

Where \(K_2\) is the rate constant (g (mg.min\(^{-1}\))), after integration and rearrangement, it may be linearized by Eq. (10) [14]:

\[
q_t = \frac{q_e^2 * K_2 t}{1 + q_e K_2 t}
\]

The kinetic models of pseudo first order and pseudo second order were used to describe the experimental data.

Table 3 shows the results obtained. According to the value of \(R^2\), the pseudo second order model was better adjusted, in this way it is inferred that the adsorption is a chemisorption process [14]. During the process, the particular diffusion model also controlled part of the process. According to the experimental data, an \(R^2\) value of 0.93 was obtained, which indicates that the entire sorption process was divided into two linear regions. A first moment in which the phosphate solution surrounds the zeolite particle and a second moment in which the phosphate diffuses towards the nucleus of the adsorbent.
There is information on the speed of the phosphorus reaction processes on solid surfaces, adsorption experiments given in different periods of time show that the phosphorus disappeared from the solution in the first 24 h is due to rapid adsorption processes which are reversible and occur on the surface of solids [15]. There is a quantity of phosphorus that disappears from the solution in later periods of time through slow processes that are not totally reversible [16].

In this model, the species originally in the solution phase must diffuse through the liquid layer surrounding the adsorbent particle, transferring through the solution / particle interface, diffusing throughout most of the adsorbent particle and possibly interacting with a remainder on the surface of the adsorbent.

This particular diffusion pattern crosses the internal structure of the adsorbent pores, for this the structure of the same must be homogeneous porous.

For purposes of comparison with results obtained in other investigations where materials composed of zinc have been used, in the case of ferrites impregnated with zinc where the value of $q_e = 3.13 \text{ mg g}$ at room temperature [14].

In this case, if there is a process controlled by adsorption in the pores, the sorption speed will be directly proportional to the concentration of the solute [17].

3.5. Phosphate adsorption and desorption

For the process of adsorption and desorption of phosphates, NaOH and HCl solutions were used respectively, in Figure 6 it is shown.
Table 4 summarizes the phosphate desorption efficiency of the charged zeolites using NaOH and HCl in the first sorption-desorption cycle.

These results reveal that the desorption of phosphate was effective in the presence of 0.1 M HCl solution since it was observed that it was possible to recover up to 57%; while in the case of 0.1 M NaOH solution a recovery of 25% was obtained.

The most common way for the desorption of phosphates consists in the addition of a base, usually NaOH, being able to recover sodium phosphate in the solution; However, in this study there was a better adsorption and desorption capacity in the presence of HCl, this may be due to the basicity capacity of the zeolite. Commonly, for strong base anions, the use of high concentration hydrochloric acid is recommended for the desorption of phosphates [12].

In some cases the desorption is carried out in columns in the presence of 1 M HCl solution, in this way the exchangers can be regenerated and reused, also obtaining equations that determine the adsorption capacity of the exchangers, the amount of phosphate adsorbed and the amount recovered, (Huitrón, 2009). The adsorption process in some cases is not reversible since, due to chemisorption, most of the phosphate is bound to the adsorbent. Other studies demonstrate...
the applicability of other solutions for desorption such as: NaCl, KOH, NaOH in different concentrations, obtaining percentages of 79% with NaCl and 93.99% with KOH, [8].

3.6. Fractionation of phosphorus species

According to the fractionation of phosphorus according to the results presented in Table 5, from the Z-Zn, it was found that the phosphorus with the highest presence is the one bound to the metals Al and Zn. Secondly, the labile phosphor is bound to the adsorbent through electrostatic forces; these results would indicate that the adsorbents have limited reusability. Third, phosphorus is bound to alkaline earth through reactions presumably due to the precipitation of phosphate compounds. Therefore, given its low regeneration and after carrying out a cost-benefit analysis, the possibility of using it as a soil improvement material could be studied. Thus, being a material that could manage the fertilization carried out in the short term on the parameters that determine the availability of the nutrient in the soil such as quantity, capacity and intensity [16].

4. Conclusions

The need to recover the phosphate anion from aqueous solutions has influenced the development of this work where the application of a zeolite modified with zinc as an adsorbent is exposed. The study of the zero charge point shows that the adsorbent is favorable for the adsorption of phosphates in real wastewater under the pH conditions in the range of 7-8. The isotherm better fits the Langmuir model with maximum adsorption capacity of 27.5 mg g⁻¹. In addition, the adsorption kinetics conforms to the pseudo second order model, which indicates that the process was governed by chemisorption in a time of 240 minutes.

As for the fractionation of phosphorus from Z-Zn, it was found mostly bound to metals Zn, Fe and Al, secondly, labile phosphorus and finally to phosphorus bound to alkaline earth. During
the adsorption and desorption cycle in the presence of HCl it provides a better recovery of the zeolite in view of the basicity of the zeolite. Given that there is a low regeneration of the zeolite, the cost-benefit relationship must be evaluated in the applicability of the large-scale process and thus obtain a concentrate that can be use in soil improvement.

Declarations

Availability of data and materials

The data used to support the findings of this study are available from the corresponding author upon request.

Competing interests

The authors declare that they have no competing interests.

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This work was carried out with own funds.

Author’s contributions

Diana Guaya planned, supervised and conducted the experiments and project. Lenin Loayza performed the experiments, interpreted results, conclusions, and prepared the manuscript.

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### Table 1 Comparison chart of phosphate adsorption capacity of different adsorbents

| Sorbent                        | Description                                                        | T (ºC) | Fracción | Langmuir isotherm parameters | Kinetic parameters | Reference |
|--------------------------------|--------------------------------------------------------------------|--------|----------|------------------------------|-------------------|-----------|
|                                |                                                                    |        |          |                              |                   |           |
| Faujasita                      | 
| 
| ZnCl₂ modified faujasite       | 25                    | 0.0364 | 27.5     | 0.98                         | Pseudo second order | 5.87      | 0.41     | 0.98     | This study |
| Zinc Ferrite                   | Zinc Ferrite (ZnFe₂O₄) by solvothermal technique at different temperatures. | 25        | 0.5304 | 5.2329 | 0.9895                         | Pseudo second order | 0.0073 | 3.13 | 0.999 | |
|                                | Zinc ferrite with cerium incorporated with temperature application. | 35      | 0.6352 | 5.5726 | 0.9918                         |                    | 0.0077 | 3.36 | 0.9996 | [14] |
|                                | 45                    | 0.6233 | 6.2842  | 0.993                         |                    | 0.0078 | 3.52 | 0.9997 | |
| Zinc Ferrite                   | Zinc – aluminium layered double hydroxides with temperature application. | 10      | 0.53 | 5.233 | 0.99 | Pseudo second order | 0.00058 | 18.99 | 0.9951 | |
|                                | 25                    | 0.495  | 9.083   | 0.996                         |                   | 0.00072 | 22.88 | 0.9993 | [15] |
|                                | 45                    | 0.538  | 24.01   | 0.994                         |                   | 0.00099 | 25.81 | 0.9984 | |
|                                | 0.24                  | 29.94   | 1       |                   |                   | 0.365 | 1.245 | 0.999 | |
|                                | 0.48                  | 41.632  | 0.999 |                   |                   | 0.75 | 0.844 | 0.999 | |
|                                | 1                     | 24.041  | 2.6 | 0.996 |                   |                   | 1 | 0.365 | 0.999 | |
|                                | 25                    | 256.73  | 2.59 | 0.997 |                   |                   | 55 | 4.979 | 0.611 | |
|                                | 35                    | 414.23  | 2.68 | 0.998 |                   |                   | 50 | 0.844 | 0.892 | |
|                                | 45                    | 523.57  | 2.72 | 0.999 |                   |                   | 1 | 0.365 | 1.245 | |
|                                | 55                    | 4.979   | 0.611 | 1 |                   |                   | 1 | 0.844 | 0.892 | |
|                                | 0.50                  | 0.844   | 0.892 | 0.999 |                   |                   | 0.365 | 1.245 | 0.999 | |
|                                | 0.75                  | 2.68    | 2.72 | 0.999 |                   |                   | 1 | 0.365 | 1.245 | |
### Table 2 Parameters of the isotherm for the adsorption of phosphate in Z–Zn

| Sorbent  | $Q_m$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $R^2$ | $K_F$ (mg g$^{-1}$) | $R^2$ |
|----------|---------------------|----------------------|-------|----------------------|-------|
| Z–Zn     | 27.5                | 3.64E-02             | 0.98  | 1.72E-04             | 0.10  |

### Table 3 Kinetic parameters for the removal of phosphate from Z - Zn

| Sorbent  | $Q_e$ (mg g$^{-1}$) | $k_I$ 1 h$^{-1}$ | $R^2$ | $Q_e$ (mg g$^{-1}$) | $k_2$ (mg (g h$^{1/2}$)$^{-1}$) | $R^2$ | $k_{i1}$ (mg (g h$^{1/2}$)$^{-1}$) | $R^2$ | $k_{i2}$ (mg (g h$^{1/2}$)$^{-1}$) | $R^2$ |
|----------|---------------------|------------------|-------|---------------------|---------------------------------|-------|---------------------------------|-------|---------------------------------|-------|
| Z–Zn     | 0.30                | 0.16             | 0.86  | 0.41                | 5.87                            | 0.98  | 0.13                            | 0.89  | 0.05                            | 0.67  |

| Model       | Kinetic parameters | Adsorbent results |
|-------------|--------------------|--------------------|
| HPDF        | $D_f$ (m$^2$ h$^{-1}$) | 2.33E-08           |
| Film diffusion | $R^2$         | 0.86               |
| HPDM        | $D_p$ (m$^2$ h$^{-1}$) | 1.7E-09            |
| Particle diffusion | $R^2$     | 0.93               |

### Table 4 Efficiency of the adsorption and desorption of phosphate on Z - Zn

| Model  | Kinetic parameters | Adsorbent results |
|--------|--------------------|--------------------|
| HCl    | Sorption (mg g$^{-1}$) | 0.30               |
|        | Desorption (mg g$^{-1}$) | 0.17               |
| NaOH   | Sorption (mg g$^{-1}$) | 0.28               |
|        | Desorption (mg g$^{-1}$) | 0.07               |
Table 5 Results of the fractionation of the Z–Zn phosphorus

| Qad mg PO₄³⁻ g⁻¹ | P-labil | P-metals (Zn) Fe, Al | P-alkaline earth Na, K, Mg, Ca |
|------------------|---------|---------------------|--------------------------------|
|                  | NH₄Cl   | NaOH                | HCl               |
| 0.50 ± 0.0       | 25.5% ± 2.4% | 56.8% ± 4.3%    | 17.8% ± 4.3% |
| 0.50 ± 0.1       | 29.4% ± 2.3% | 52.3% ± 2.4%    | 18.3% ± 5.0% |
Figure 1

Zero charge point
Figure 2

Effect of pH on the adsorption of phosphates by Z-Zn
Figure 3

Species of phosphate as a function on pH
Figure 4
Experimental isotherm equilibrium for phosphate by Z - Zn

Figure 5
5 Z–Zn Phosphate kinetic adsorption curve

Figure 6
Representation of the adsorption and desorption capacity of phosphate in the presence of HCl and NaOH