

## Article

# Preparation of Synthetic Clays to Remove Phosphates and Ibuprofen in Water

Rosa Devesa-Rey , Jesús del Val, Jorge Feijoo , José P. González-Coma , Gonzalo Castiñeira and Lorena González-Gil 

Defense University Center at the Spanish Naval Academy, University of Vigo, Plaza de España 2, Marín, 36920 Pontevedra, Spain; jesusdv@cud.uvigo.es (J.d.V.); jfeijoo@cud.uvigo.es (J.F.); jose.gcoma@cud.uvigo.es (J.P.G.-C.); gonzalo.castineira@cud.uvigo.es (G.C.); lorena.gonzalez@cud.uvigo.es (L.G.-G.)

\* Correspondence: rosa.devesa.rey@cud.uvigo.es

**Abstract:** The main objective of this study consists in the synthesis of a layered double hydroxide (LDH) clay doped with magnesium and aluminum in order to test the removal of phosphates and ibuprofen in water. Two different LDH composites are assessed: oven-dried (LDH<sub>D</sub>) and calcined (LDH<sub>C</sub>). Single adsorptions of phosphate and ibuprofen showed up to 70% and 58% removal in water, when LDH<sub>C</sub> was used. A poorer performance was observed for LDH<sub>D</sub>, which presented adsorption efficiencies of 52% and 35%, respectively. The simultaneous removal of phosphate and ibuprofen in water showed that LDH<sub>C</sub> allows a greater reduction in the concentration of both compounds than LDH<sub>D</sub>. Phosphate adsorption showed a close agreement between the experimental and theoretical capacities predicted by the pseudo-second-order model, whereas ibuprofen fitted to a first-order model. In addition, phosphate adsorption showed a good fit to an intraparticle diffusion model and to Bangham model suggesting that diffusion into pores controls the adsorption process. No other mechanisms may be involved in ibuprofen adsorption, apart from intraparticle diffusion. Finally, phosphate desorption could recover up to 59% of the initial concentration, showing the feasibility of the recuperation of this compound in the LDH.

**Keywords:** eutrophication; hydrotalcite; adsorption; kinetics



**Citation:** Devesa-Rey, R.; del Val, J.; Feijoo, J.; González-Coma, J.P.; Castiñeira, G.; González-Gil, L. Preparation of Synthetic Clays to Remove Phosphates and Ibuprofen in Water. *Water* **2021**, *13*, 2394. <https://doi.org/10.3390/w13172394>

Academic Editor: Jiangyong Hu

Received: 30 July 2021

Accepted: 28 August 2021

Published: 30 August 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Phosphates are a critical element from a water quality point of view. Its concentration may be increased in water as a result of the hydrological and hydrochemical characteristics of the catchment site, land uses, or the presence of point sources of contamination, such as the use of detergents or wastewater. Phosphates in water may come from erosive processes or lixiviation [1] or to anthropogenic inputs, such as wastewater treatment plants (WWTPs), detergents, organic fertilizers, or other wastes [2].

An excess of this compound favors the excessive oxygen consumption in water, initiating its depletion and a eutrophication process that can even cause an anoxic situation in water [2,3]. Eutrophication is one of the main water quality problems, consisting in an excessive nutrient accumulation in water, typically nitrates and phosphates, which results in a series of undesirable damages to the environment (excessive algae growth, deterioration of the water quality, variation of the organoleptic properties, decrease of the light reaching the deeper layers, etc.) [4]. Phosphate sources to be controlled include the use of detergents, fertilizers, waste, and industrial effluents, among others.

On the other hand, the increasing presence of pharmaceutical and personal care products (PPCPs) in wastewater is of great concern. The term PPCPs includes drugs, cleaning products, cosmetics, fragrances, and hormones. Their elimination in conventional WWTPs is very deficient because they are found in low concentration levels and because the treatment systems have not been specifically designed to eliminate this type of organic

micropollutants. However, their effects are worrying since continuous exposure can lead to endocrine system alterations, antibiotic resistance, or fetal exposure, among others [5,6]. There are still knowledge gaps on the ecotoxicity, sub-lethal effects, and effective treatment processes for PPCPs [7]. The treatment of pharmaceutical compounds is considered of great importance due to their recalcitrant nature, capacity to bioaccumulate, potential toxicity, and their alteration of the endocrine system [8]. Several studies have demonstrated the ability of bioreactors to remove these compounds from water, both by adsorption and by biotransformation or degradation, making it possible to optimize biological processes to jointly and efficiently remove both conventional (organic matter and nutrients) and emerging pollutants such as the PPCPs [9,10].

In this study, ibuprofen will be analyzed as a representative element of the family of pharmaceutical compounds. It is an anti-inflammatory drug sold in millions annually, without the need for a prescription and to practically all audiences. Actually, it is widely used in the treatment of ailments, both at home and in hospitals. Once administered to the patient, between 40 and 90% of the pill is eliminated through the urine, as the human body is not capable of metabolizing more than a small part of it, thus the rest goes to the sewage and will reach the WWTPs. The incomplete removal of PPCPs, such as ibuprofen, in different water and wastewater treatment processes results in the occurrence of PPCP compounds in various environmental compartments [7,11].

Adsorption is a good alternative for removing impurities from wastewater as it presents advantages such as flexibility, reduced cost, or simplicity, among others. Adsorbents widely employed in the literature include iron, active aluminum, fly ashes, ion exchange resins, active carbon, and clays [12–15]. These adsorbents exhibit some common characteristics such as strong physical and chemical bonds, selectivity, high volume adsorption, and a great capacity to develop the process efficiently.

Removal of phosphates and ibuprofen were tested in this study with a clay synthesized in the laboratory. Clays are a good option to act as purifiers of polluted waters of agricultural and industrial origin. They are based on phyllosilicates with good adsorbent properties, thanks to their accessible and expandable internal surfaces. Their negative electric charge structures undergo charge compensation by interlaminar cations, thus granting a great adsorption capacity.

Synthetic clays can be prepared in the laboratory to improve water treatment with a combination of cation layers, carbonate, and hydroxyl anions and water forming hexagonal or octahedral structures. Among the minerals included in this group, those derived from layered double hydroxides (LDH) with different intercalated anions may be employed to adsorb pollutants from the water [16]. LDH shows similarities in terms of structure, properties, and characteristics with hydrotalcite, a natural mineral composed of layers of magnesium and aluminum intercalated with carbonates and hydroxides. For this reason, LDH are often called hydrotalcite (HT)-type materials.

Layered double hydroxides are characterized by having a variable crystalline structure depending on the proportion of di- and trivalent metals. It is necessary to keep an adequate proportion, as higher proportions could generate a hydroxide of the trivalent cation, whereas lower ratios could form a divalent metal hydroxide [17], being the optimal ratio between  $M^{2+}/M^{3+}$  is 2:1 or 4:1.

Several authors found significant phosphate retention in LDH, which could be functionalized with biochar [18], achieving good results at an adsorbent dosage of 4 g/L. Zhu et al. [19] synthesized a Ca-Al-Fe LDH and could observe over 90% of phosphate removal in a 25 mg/L concentration after 30 min. Kim et al. [20] found phosphate adsorption of 68–73% of a solution of 16.31 mg/L after 24 h. Maia et al. [21] found effective adsorption at lower dosages and described the adsorption as a pseudo-second-order model, which could be affected by the presence of other anions in the sample.

In what concerns the pharmaceutical compounds, LDH has shown important adsorption capacity and catalytic activity as well as the possibility of a regeneration process, which could explain the importance of gaining knowledge of these compounds applied to

wastewater [22]. Santamaría et al. [23] proposed a synthesis ratio  $M^{2+}:M^{3+}$  for the adsorption of non-steroidal anti-inflammatory drugs and observed a good adsorbate-adsorbant affinity. In addition, Rosset et al. [24] found that acetylsalicylic acid on ZnAl layered double hydroxide could remove up to 90% of the solute and could be used for up to 6 cycles.

Thus, efficiency in adsorption is related to pollutant removal, equilibrium features, but also to the kinetics of the process. The solute will be first transported into the water column, then will diffuse across the film surrounding the sorbent particles and next to the pores of the sorbent. One of these steps will be the slowest and will control the fate of the adsorption [25]. Pseudo-first and pseudo-second-order kinetics are among the most employed fittings employed in the literature. Equation (1) represents the linear form of the pseudo-first-order model [26]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

where  $q_e$  and  $q_t$  (both in mg/g) are the concentration of adsorbed phosphate and ibuprofen at equilibrium and at a defined time  $t$ , respectively, and  $k_1$  (1/min) is the rate constant of pseudo-first-order adsorption. The  $k_1$  parameter is the time-scaling factor whose value decides how fast the equilibrium in the system can be reached [27]. Some authors suggest that pseudo-second-order approximates better to the adsorption processes. Therefore, sorption kinetics were also described using a pseudo-second-order model following Equation (2) [28]:

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

where  $k_2$  (g/mg min) is the equilibrium rate constant of pseudo-second-order adsorption. If the pseudo-second-order kinetic equation is applicable, the plot of  $t/q_t$  against  $t$  should give a linear relationship, from which  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot. Plazinski et al. [27] described this adsorption as a chemical reaction occurring on the solid surface with the sorption rate being proportional to the actual solute concentration in the bulk solution and to the number of unoccupied adsorption sites. Azizian [29] proposed a relationship between pseudo-first and pseudo-second-order models, where the sorption process would obey a pseudo-first-order kinetic at high initial concentrations, while pseudo-second-order kinetics model would predominate at lower initial solute concentrations.

Chien and Clayton [30] developed an expression to evaluate the kinetics of phosphate sorption and release in soils (Equation (3)), where  $\alpha$  (min mg/g) was the initial sorption rate, and  $\beta$  (g/mg) was related to the extent of surface exposure and activation energy for chemisorption:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (3)$$

In order to determine whether the adsorption process is directed only by intraparticle diffusion or if it is more complex, an experiment will be fitted to the intraparticle diffusion model [31] following Equation (4):

$$q_t = k_p t^{0.5} + C \quad (4)$$

where,  $k_p$  is the intraparticle diffusion rate constant (mg/g min<sup>0.5</sup>) and  $C$  is the intercept (mg/g), and it is related to the thickness of the boundary layer. Other authors have found an influence of the intraparticle diffusion on phosphate removal [32,33], and this paper will also analyze the ibuprofen pattern.

Finally, following Equation (5), experimental data will be fitted to the Bangham model [34]:

$$\log \left[ \log \left( \frac{C_0}{C_0 - q_t m} \right) \right] = \log \left( \frac{k_0 m}{2.303 V} \right) + \alpha \log t \quad (5)$$

where,  $C_0$  is the initial adsorbent concentration in solution (mg/L),  $V$  is the solution volume (L),  $m$  is the weight of adsorbent used per liter of solution (g/L),  $q_t$  (mg/g) is the amount of adsorbent retained at time  $t$ , and  $\alpha$  ( $<1$ ) and  $k_0$  are constants. The Bangham model was tested to adsorb pharmaceutical compounds [35,36].

In this work, we hypothesize about the joint adsorption of phosphate and ibuprofen from wastewater. We focus our study on two compounds of environmental relevance: on the one hand, phosphates, which are released in large quantities and cause significant environmental degradation problems, such as eutrophication; and, on the other hand, ibuprofen, as a representative element of pharmaceutical compounds, whose progressive release to the environment causes toxicity, poisoning, or adaptation to antibiotics, among other effects. The main objectives are: to synthesize an LDH adsorbent doped with magnesium and aluminum and test it with organic and inorganic pollutants; to evaluate the adsorption capacity and the retention time; to fit the results to an adsorption model in order to improve our knowledge about the process; and, finally, to evaluate the recovery of phosphate after the adsorption process.

## 2. Materials and Methods

### 2.1. Adsorbent Production and Preparation

Synthesis of LDH was carried out by co-precipitation of mixed solutions of 7.785 g of  $\text{Mg}(\text{NO}_3)_2$  and 3.727 g of  $\text{Al}(\text{NO}_3)_3$  in a 3:1 molar ratio. These solutions were added at a constant rating of 1 mL/min on a NaOH solution, stirred at 550 rpm. pH (HANNA, Edge pH) was monitored and corrected to a value of 10. Once the solutions were completely mixed, they were kept at continuous stirring for 4 h. The obtained dispersion was aged for 18 h, then filtered, washed, and oven-dried at 100 °C for 24 h. Finally, the synthesized composites were ground to attain 0.5–1.0 mm size. This compound was named in this study as oven-dried LDH, assigning it the acronym  $\text{LDH}_D$ .

Additionally, a fraction of this composite was subjected to calcination in a muffle for 2 h at 600 °C in order to evaluate the effect of calcination on the pollutant retention (named in this case as  $\text{LDH}_C$ ). A flowchart of the methodology followed in this study is shown in Figure 1.

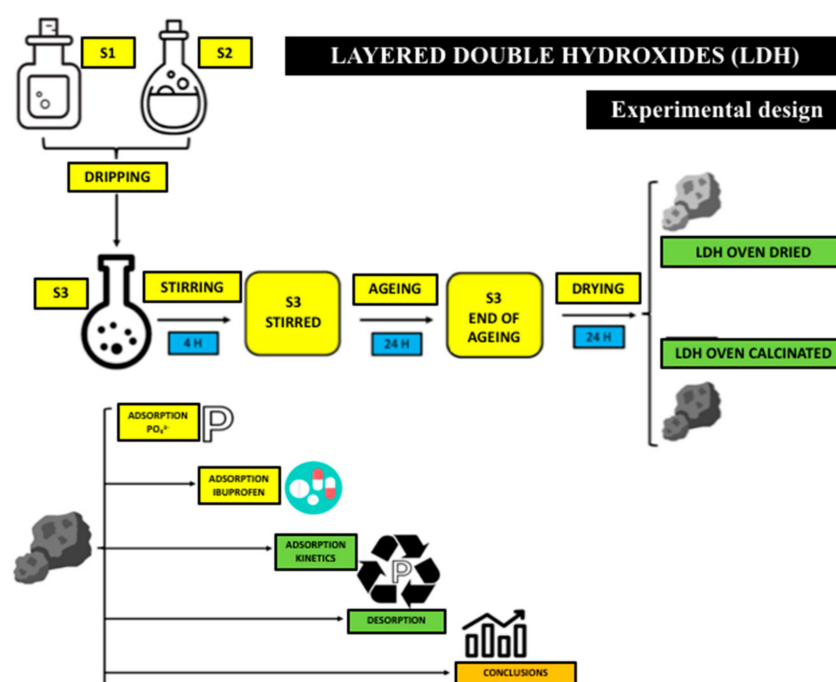


Figure 1. Flowchart illustrating the overall approach used in this study.

## 2.2. Materials and Solutions

Reagents employed in this study ( $\text{AlCl}_3$ ,  $\text{MgCl}_2$ ,  $\text{NaOH}$ ,  $\text{KH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , and ibuprofen) were purchased from Sigma Aldrich. To assess the adsorption of an organic and an inorganic compound by each LDH composite, different initial concentrations of phosphate and ibuprofen solutions were tested, varying the concentration from 2.5 to 20 mg/L.

## 2.3. Batch Adsorption Experiments

Adsorption experiments were carried out in 100 mL Erlenmeyer flasks placed in orbital shakers at room temperature and 150 rpm shaking speed. Different experiments were carried out to compare the efficiency of oven-dried ( $\text{LDH}_\text{D}$ ) or calcined hydrotalcite ( $\text{LDH}_\text{C}$ ). Given the efficiency observed in the literature [37,38], a high solid:liquid ratio was tested and, thus 1:200 ( $w/v$ ) was analyzed both for phosphates and ibuprofen, and the time of treatment was set at 42 min based on a set of preliminary results carried out. Experiments were performed with solutions of phosphate and ibuprofen separately. Finally, an adsorption experiment was tested with a solution of both compounds. Then, the samples were taken, and the dispersions were filtered by a microsyringe (0.45  $\mu\text{m}$ ). To determine the phosphate concentration of the filtrate, it was selected a wavelength of 690 nm in a spectrophotometer (model UV/VIS Spectrometer Lambda XLS, PerkinElmer, Waltham, MA, USA), determined by the molybdenum blue method. Ibuprofen was measured in filtered samples at a wavelength of 220 nm in the spectrophotometer. Ibuprofen adsorption measurements were registered by using an UV/VIS Lambda XLS double beam spectrophotometer (Perkin Elmer, USA) with a fixed slit width (1.5 mm) and 1 cm quartz cells. All experiments were run in triplicate.

## 2.4. Kinetic Study of Pollutant Adsorption

Adsorption behavior was analyzed by performing a kinetic analysis carried out by means of batch adsorption experiments. Erlenmeyer flasks were placed in an orbital shaker at 150 rpm and 25 °C, using 0.125 g and a starting concentration of 20 mg/L. Aliquots were extracted at 1, 5, 10, 20, and 40 min for analysis of phosphates and ibuprofen and filtered through a 0.45  $\mu\text{m}$  pore size membrane before analyzing.

The adsorption capacity for the  $\text{LDH}_\text{C}$  was calculated at each time,  $q_t$  (mg/g), following Equation (6):

$$q_t = \frac{(C_0 - C_t) \cdot V}{W} \quad (6)$$

where  $C_0$  and  $C_t$  (mg/L) are the concentrations of phosphate or ibuprofen in the solution before and after treatment, respectively,  $V$  is the volume of the wastewater used during batch experiments (L) and  $W$  (g) is the mass of  $\text{LDH}_\text{C}$ .

The percentage of phosphate or ibuprofen removed from wastewater was calculated, both for  $\text{LDH}_\text{D}$  and  $\text{LDH}_\text{C}$ , following Equation (7):

$$\text{Pollutant removal (\%)} = \left(1 - \left(\frac{C_t}{C_0}\right)\right) \times 100 \quad (7)$$

The difference between the initial concentration and the one measured in solution will offer the adsorbed concentration. Therefore, on the basis of the phosphate or ibuprofen removed after treatment of wastewater, the adsorption capacity of each LDH used was calculated.

Kinetic adsorption onto the  $\text{LDH}_\text{C}$  was studied using different kinetic models: pseudo-first-order [26], pseudo-second-order [28], Chien–Clayton model [30], intraparticle diffusion [31], and Bangham model [34].

## 2.5. Study of the Recovery of the Adsorbate

On completion of the adsorption process, the adsorbent composite was recovered from the solution with centrifugation at 4000 rpm for 2 min followed by microfiltration.

Experiments of phosphate recovery were carried out by adding 5 mL of distilled water to the solid. Only LDH<sub>C</sub> was employed, as it showed the best results in the previous experiment. Batch desorption was carried out for 10 min at 150 rpm in an orbital shaker. The adsorbent was then separated from the distilled water by filtration, and the released phosphate was measured in a spectrophotometer using the method described above.

### 3. Results and Discussion

#### 3.1. Formulation of an Adsorbent Composite for Removing Phosphates and Ibuprofen from Wastewater

Table 1 shows the pollutant adsorption tests, carried out using both LDH<sub>D</sub> (oven-dried LDH) and LDH<sub>C</sub> (calcined LDH), for different initial concentrations of phosphate. Adsorption was lower for the LDH<sub>D</sub>, with average adsorption of 52.5% and no significant variations between treatments. However, LDH<sub>C</sub> adsorbed an average of 70% of phosphate, with the maximum adsorption observed at the highest tested concentration, 20 mg/L, where the adsorption reached a percentage of 77.3%.

**Table 1.** Adsorption results for hydrotalcite when testing phosphate solutions from 2.5 to 20 mg/L.  $C_0$  and  $C_t$  refer to initial and final concentration, respectively. Variation coefficients (%) of triplicates were under 10% in all cases.

$C_0$ (mg/L)	LDH <sub>D</sub> (Oven-Dried)		LDH <sub>C</sub> (Calcined)	
	$C_t$ (mg $PO_4^{3-}$ /L)	Adsorption (%)	$C_t$ (mg $PO_4^{3-}$ /L)	Adsorption (%)
2.5	1.1	55.4	1.4	57.8
5	2.6	47.8	3.6	71.2
10	5.0	49.8	7.3	73.5
20	8.6	56.8	15.5	77.3

Structurally, there was a significant difference between oven-dried and calcined LDH. Moustafa et al. [39] analyzed the Zeta potential of Zn-Fe LDH nanoparticles and confirmed the high stability of the solid as well as the electrostatic interaction between the metals and the pollutant. The zero-point charge of Mg/Al-LDH showed a positive surface, which benefits the phosphate adsorption, although it is pH-dependent [40]. Oven drying forms the hydrotalcite-like compounds, which lose the layered structure when it is treated above 450–500 °C, forming bimetallic oxides [41]. However, calcined LDH has a “memory effect,” which enables the reconstruction of its original structure after hydration and immobilizes hazardous anions for balancing the charge, which could occur by intercalation and surface sorption [42,43]. Although calcination is usually carried out at high temperatures, there are studies that report that treatments at 280 °C, in FeCuNi-LDH, produce a larger surface area compared with treatments at 550 °C [44]. In addition, an important effect to be considered is the inhibitory effect on the sorption due to coexisting anions in the environment [42].

Regarding ibuprofen adsorption onto the LDH<sub>C</sub> and LDH<sub>D</sub> composites (Table 2), results showed the same pattern as phosphates, with the highest adsorption achieved when using the LDH<sub>C</sub>. Average adsorption of 58% was observed in this case, whereas adsorption decreased to an average of 35% when using LDH<sub>D</sub>.



**Table 2.** Adsorption results for hydrotalcite when testing ibuprofen solutions from 2.5 to 20 mg/L. Adsorption refers to the percentage of ibuprofen retained by the solid with respect to the initial concentration in the solution. Variation coefficients (%) of triplicates were under 10% in all cases.

$C_0$ (mg/L)	LDH <sub>D</sub> (Oven-Dried)		LDH <sub>C</sub> (Calcined)	
	$C_t$ (mg ibuprofen/L)	Adsorption (%)	$C_t$ (mg ibuprofen/L)	Adsorption (%)
2.5	0.8	32.0	1.3	52.0
5	2.2	44.0	2.2	44.0
10	2.7	27.0	6.9	69.0
20	7.5	37.5	13.5	67.5

MgAl-LHD has shown its potential as a drug carrier, typically intercalating solutes in the layer space during co-precipitation [45], leading to an increase of inner space from 7.89 Å to 14.71 Å. Therefore, sorption capacity may differ when ibuprofen is added to the solution after LDH has been synthesized, as ibuprofen may exceed the space available for solute assimilation. Scarce studies have been found related to ibuprofen removal from water using LDH. Kumari et al. [46] tested a ZnAl-LDH for diclofenac sodium removal in water and doped the structure with Bi<sub>2</sub>O<sub>3</sub> to increase size. In these conditions, ibuprofen adsorption was significantly increased, although adsorption occurred apparently on the outer surface.

In the specific case of the mixed solutions of phosphate and ibuprofen, it can be seen that in both cases, LDH shows a greater adsorption capacity for ibuprofen than for phosphate (Table 3). Compared to the behavior shown by each LDH composite when there is only one contaminant in the water, the amount of phosphate adsorbed decreases while that of ibuprofen increases, especially in the case of LDH<sub>D</sub> (10 percentage points less of phosphate and almost 20 percentage points more of ibuprofen). As it happens in the previous cases, LDH<sub>C</sub> shows the highest adsorption of both compounds.

**Table 3.** Results for adsorption of mixed solutions containing phosphate and ibuprofen varying from 2.5 to 20 mg/L. Variation coefficients (%) of triplicates were under 10% in all cases.

LDH <sub>D</sub> (Oven-Dried)					LDH <sub>C</sub> (Calcined)			
Phosphate			Ibuprofen		Phosphate		Ibuprofen	
$C_0$ (mg/L)	$C_t$ (mg/L)	Adsorption (%)	$C_t$ (mg/L)	Adsorption (%)	$C_t$ (mg/L)	Adsorption (%)	$C_t$ (mg/L)	Adsorption (%)
2.5	1.0	38.0	1.5	58.0	1.2	48.0	1.8	72.0
5	2.3	46.8	3.2	64.0	3.4	68.0	2.4	48.0
10	4.9	48.9	4.5	45.0	6.9	69.0	6.7	67.0
20	7.0	35.0	10.1	50.5	14.3	71.5	14.1	70.5

### 3.2. Evaluation of the Adsorption of Phosphates and Ibuprofen in the Composite: Kinetic Study

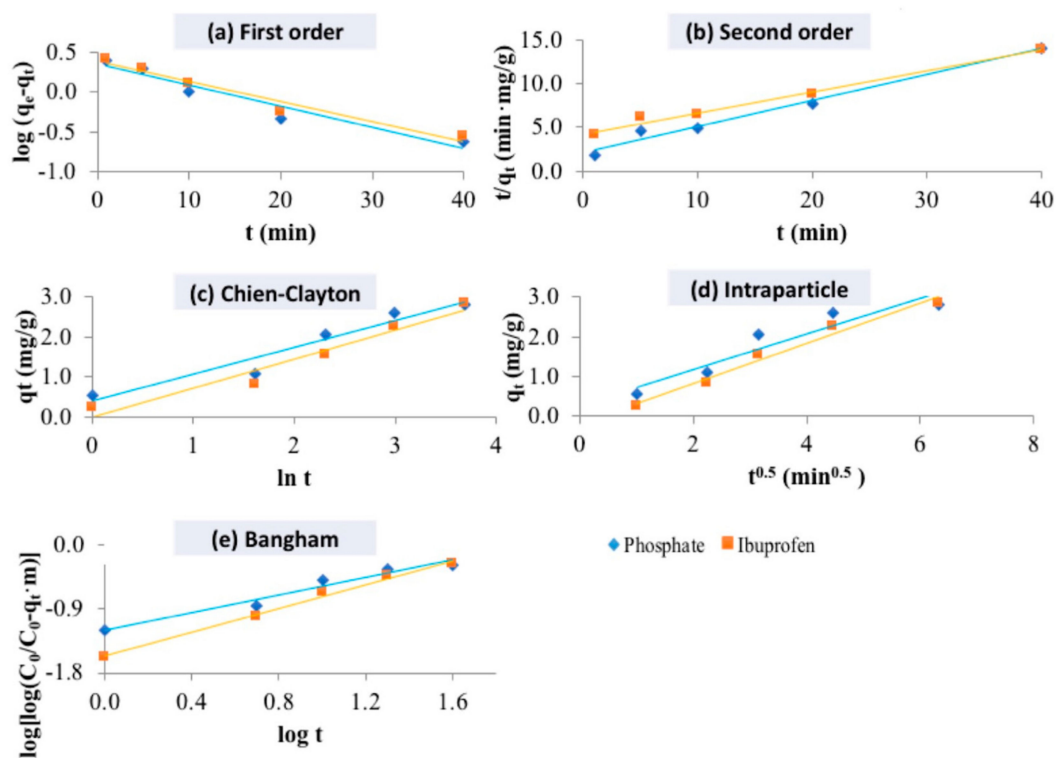
The adsorption of phosphate or ibuprofen onto calcined LDH was conveniently represented by kinetic models, which were helpful to predict the adsorption behavior of these compounds. Thus, in the experiments carried out with an initial concentration of 20 mg/L, the 52% of phosphate was adsorbed in the first 10 min of experiments, whereas ibuprofen needed 20 min to reach the 57% of adsorption onto LDH<sub>C</sub>. After 40 min of treatment, phosphate and ibuprofen removed from solution exceed 70% of the initial concentration.

The kinetic coefficients obtained when fitting to a pseudo-first-order equation showed similarities between phosphate and ibuprofen adsorption onto LDH<sub>C</sub> (Table 4). Thus, phosphate adsorption gave a theoretical capacity of 2.238 mg/g, whereas ibuprofen slightly increased the capacity to 2.882 mg/g. Figure 2 shows the correlation between the experi-

mental data and the theoretical data when they were described by using the pseudo-first-order kinetic model.

**Table 4.** Comparison of kinetic parameters for pseudo-first-order, pseudo-second-order, Chien–Clayton, intraparticle diffusion, and Bangham kinetic models.

Kinetic Model	Kinetic Parameters	LHD <sub>C</sub>	
		Phosphate	Ibuprofen
Pseudo-first-order	$q_e \text{ exp (mg/g)}$	2.822	2.860
	$q_e \text{ calc (mg/g)}$	2.238	2.882
	$k_1 \text{ (1/min)}$	0.061	0.082
	$r^2$	0.928	0.998
Pseudo-second-order	$q_e \text{ exp (mg/g)}$	2.822	2.860
	$q_e \text{ calc (mg/g)}$	3.347	4.137
	$k_2 \text{ (1/min)}$	0.043	0.014
	$r^2$	0.982	0.989
Chien–Clayton model	$\alpha$	1.219	0.734
	$\beta$	1.489	1.375
	$r^2$	0.940	0.948
Intraparticle diffusion model	$k_p$	0.453	0.509
	$C$	0.268	−0.202
	$r^2$	0.898	0.978
Bangham model	$\alpha$	0.620	0.838
	$k_0$	0.003	0.002
	$r^2$	0.963	0.994



**Figure 2.** Kinetic plots for the adsorption of phosphate and ibuprofen onto calcined layered double hydroxide (LHD<sub>C</sub>) applying different kinetic models: (a) pseudo-first-order, (b) pseudo-second-order, (c) Chien–Clayton model, (d) intraparticle diffusion model, and (e) Bangham model.



Table 4 includes the kinetic parameters obtained after modeling the experimental data following the pseudo-second-order kinetic model and Figure 2 shows the variation of the experimental data when they were adjusted to this pseudo-second-order kinetic model, revealing that there was a close agreement between the experimental and theoretical capacities predicted by the model. The best capacities predicted by the model (4.137 mg/g) were achieved when adsorbing ibuprofen.

Regarding the kinetic parameters obtained after applying the Chien–Clayton kinetic model (Table 4), it was observed that the  $\alpha$  value predicted by this model to the evaluation of phosphate was higher (1.219) than that obtained for ibuprofen (0.734).

Moreover, in order to evaluate the possibility of other factors affecting the adsorption process, such as surface adsorption, ion exchange, complexation, complexation–chelation, or microprecipitation, experimental data were analyzed by an intraparticle diffusion model. The slope of the linear part of the curve of  $q_t$  vs.  $t^{0.5}$  indicates the rate of adsorption controlled by intraparticle diffusion (see Figure 2). When the intercept— $C$ —equals zero, then the intraparticle diffusion is the only controlling step. However, if  $C$  does not pass through the origin, it indicates that there are other processes involved in the rate of adsorption. In this case, the intraparticle diffusion model gave  $C$  values higher than 0 for phosphate, which indicates that there are other processes, apart from the intraparticle diffusion, involved in the rate of adsorption. Instead, when analyzing the behavior of ibuprofen, it can be concluded that intraparticle diffusion is the only mechanism involved in its adsorption. The higher  $k_p$  showed by ibuprofen indicates that there is greater intraparticle diffusion for this compound than for phosphate. This suggests that mixtures of both compounds will decrease the phosphate diffusion rate to a greater extent. This is in agreement with what was observed experimentally in this study.

Finally, experimental data were fitted to the Bangham model [34], and  $\log[\log(C_0/(C_0 - q_t m))]$  values were plotted against  $\log(t)$  in Figure 2. The linearity of these plots confirms the applicability of the Bangham equation and indicates that diffusion of phosphate into pores of the adsorbent controls the adsorption process [34] although according to the intraparticle diffusion model, other processes were also involved. Results were poorer for ibuprofen, which confirms the fact that only intraparticle diffusion models its behavior.

Overall, for all the kinetic fittings, high correlation coefficients ( $r^2$ ) were obtained with values between 0.898 and 0.998 (see Table 4), although the best  $r^2$  were obtained using the first-order kinetic model for ibuprofen and pseudo-second-order kinetic model for phosphate. Several authors observed a pseudo-second-order in similar LDH [47,48] for nutrients in water, whereas ibuprofen kinetics have received less attention.

### 3.3. Evaluation of the Recovery of Phosphates from the Composite

Desorption was carried out in this study to adsorbed phosphate in LDH<sub>C</sub> with water. The initial phosphate concentration was 20 mg/L, and the treatment was able to recover up to 11.77 mg/L after 10 min of treatment, which supposes the 59% of the phosphate in the initial solution. The interest in the recovery of phosphate relies on the fact that it is a material that could be revalorized as a fertilizer. Phosphate recovery is a matter of great concern due to the depletion of natural sources of phosphorus [49]. In fact, the European Commission has included phosphate rock in the list of 20 critical raw materials, being considered an irreplaceable raw material with great economic impact. Thus, other authors have also paid attention to its recovery in water. Nuryadin et al. [47] also found promising results in its desorption using 1 N NaOH in ZrO<sub>2</sub>/Mg-Fe LDH. In addition, Onishi et al. [50] tested the potential of these materials to act as phosphorus fertilizer analyzing the release sorption.

## 4. Conclusions

The adsorption performance of phosphate and ibuprofen in a layered double hydroxide (LDH) clay doped with magnesium and aluminum was investigated in this study. This work demonstrates that LDH composites are capable of removing both contaminants from

wastewater, although the calcination of the LDH is recommended instead of oven-dried LDH, as it significantly increased the adsorption capacity. Phosphate was more efficiently removed when analyzing single solutions, reaching adsorptions up to 70% after 20 min. Instead, ibuprofen seems to diffuse better in mixed solutions, reaching adsorptions up to 64%, on average. Different kinetic models explain their behavior, with ibuprofen fitting to a pseudo-first model and phosphate to a pseudo-second-order model. Finally, phosphate could be efficiently recovered from wastewater, with recoveries up to 59% in 10 min.

**Author Contributions:** Methodology, J.F. and L.G.-G.; investigation, G.C.; writing—original draft preparation, R.D.-R.; writing—review and editing, J.d.V., J.F., L.G.-G., and J.P.G.-C.; project administration, R.D.-R.; funding acquisition, R.D.-R. All authors have read and agreed to the published version of the manuscript.

**Funding:** The authors thank the Defense University Center at the Spanish Naval Academy (CUD-ENM) for all the support provided for this research (Project PICUD-2020-03).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

- Nash, D.M.; Halliwell, D.J. Tracing phosphorous transferred from grazing land to water. *Water Res.* **2000**, *34*, 1975–1985. [\[CrossRef\]](#)
- Devesa-Rey, R.; Iglesias, M.L.; Díaz-Fierros, F.; Barral, M.T. Total phosphorous distribution and bioavailability in the bed sediments of an Atlantic basin (Galicia, NW Spain): Spatial distribution and vertical profiles. *Water Air Soil Pollut.* **2009**, *200*, 341–352. [\[CrossRef\]](#)
- Li, J.; Zheng, B.; Chen, X.; Li, Z.; Xia, Q.; Wang, H.; Yang, Y.; Zhou, Y.; Yang, H. The use of constructed wetland for mitigating nitrogen and phosphorus from agricultural runoff: A review. *Water* **2021**, *13*, 476. [\[CrossRef\]](#)
- Álvarez-Vázquez, L.; Fernández, F.J. Optimal control of a bioreactor. *Appl. Math. Comput.* **2010**, *216*, 2559–2575. [\[CrossRef\]](#)
- Chaturvedi, P.; Shukla, P.; Giri, B.S.; Chowdhary, P.; Chandra, R.; Gupta, P.; Pandey, A. Prevalence and hazardous impact of pharmaceutical and personal care products and antibiotics in environment: A review on emerging contaminants. *Environ. Res.* **2021**, *194*, 110664. [\[CrossRef\]](#) [\[PubMed\]](#)
- Pironti, C.; Ricciardi, M.; Proto, A.; Bianco, P.M.; Montano, L.; Motta, O. Endocrine-disrupting compounds: An overview on their occurrence in the aquatic environment and human exposure. *Water* **2021**, *13*, 1347. [\[CrossRef\]](#)
- Reyes, N.J.D.G.; Geronimo, F.K.F.; Yano, K.A.V.; Guerra, H.B.; Kim, L.-H. Pharmaceutical and personal care products in different matrices: Occurrence, pathways, and treatment processes. *Water* **2021**, *13*, 1159. [\[CrossRef\]](#)
- Kannan, K.; Reiner, J.L.; Se, H.Y.; Perrotta, E.E.; Tao, L.; Johnson-Restrepo, B.; Rodan, B.D. Polycyclic musk compounds in higher trophic level aquatic organisms and humans from the United States. *Chemosphere* **2005**, *61*, 693–700. [\[CrossRef\]](#)
- Gonzalez-Gil, L.; Mauricio-Iglesias, M.; Carballa, M.; Lema, J.M. Why are organic micropollutants not fully biotransformed? A mechanistic modelling approach to anaerobic systems. *Water Res.* **2018**, *142*, 115–128. [\[CrossRef\]](#)
- Gonzalez-Gil, L.; Krah, D.; Ghattas, A.-K.; Carballa, M.; Wick, A.; Helmholtz, L.; Lema, J.M.; Ternes, T.A. Biotransformation of organic micropollutants by anaerobic sludge enzymes. *Water Res.* **2019**, *152*, 202–214. [\[CrossRef\]](#)
- Jurado, A.; Vázquez-Suñé, E.; Pujades, E. Urban groundwater contamination by non-steroidal anti-inflammatory drugs. *Water* **2021**, *13*, 720. [\[CrossRef\]](#)
- Acosta-Herrera, A.A.; Hernández-Montoya, V.; Castillo-Borja, F.; Pérez-Cruz, M.A.; Montes-Morán, M.A.; Cervantes, F.J. Competitive adsorption of pollutants from anodizing wastewaters to promote water reuse. *J. Environ. Manag.* **2021**, *293*, 112877. [\[CrossRef\]](#) [\[PubMed\]](#)
- Das, T.K.; Scott, Q.; Bezbaruah, A.N. Montmorillonite-iron crosslinked alginate beads for aqueous phosphate removal. *Chemosphere* **2021**, *281*, 130837. [\[CrossRef\]](#) [\[PubMed\]](#)
- Vecino, X.; Devesa-Rey, R.; Moldes, A.B.; Cruz, J.M. Formulation of an alginate-vineyard pruning waste composite as a new eco-friendly adsorbent to remove micronutrients from agroindustrial effluents. *Chemosphere* **2014**, *111*, 24–31. [\[CrossRef\]](#)
- Vecino, X.; Devesa-Rey, R.; de Lima Stebbins, D.M.; Moldes, A.B.; Cruz, J.M.; Alcantar, N.A. Evaluation of a cactus mucilage biocomposite to remove total arsenic from water. *Environ. Technol. Innov.* **2016**, *6*, 69–79. [\[CrossRef\]](#)
- Jawad, A.; Peng, L.; Liao, Z.; Zhou, Z.; Shahzad, A.; Ifthikar, J.; Zhao, M.; Chen, Z.; Chen, Z. Selective removal of heavy metals by hydrotalcites as adsorbents in diverse wastewater: Different intercalated anions with different mechanisms. *J. Clean. Prod.* **2019**, *211*, 1112–1126. [\[CrossRef\]](#)
- Zubair, M.; Daud, M.; McKay, G.; Shehzad, F.; Al-Harathi, M.A. Recent progress in layered double hydroxides (LDH)-containing hybrids as adsorbents for water remediation. *Appl. Clay Sci.* **2017**, *143*, 279–292. [\[CrossRef\]](#)

18. Azimzadeh, Y.; Najafi, N.; Reyhanitabar, A.; Oustan, S.; Khataee, A.R. Modeling of phosphate removal by Mg-Al layered double hydroxide functionalized biochar and hydrochar from aqueous solutions. *Iran. J. Chem. Chem. Eng.* **2020**, *40*, 565–579. [\[CrossRef\]](#)
19. Zhu, R.; Yan, L.; Song, W.; Ma, Z.; Jia, R.; Sun, S. Mechanochemical synthesis of Ca-Al-Fe layered double hydroxide for efficient phosphate removal from aqueous solution. *Mater. Express* **2021**, *11*, 524–532. [\[CrossRef\]](#)
20. Kim, T.-H.; Lundehøj, L.; Nielsen, U.G. An investigation of the phosphate removal mechanism by MgFe layered double hydroxides. *Appl. Clay Sci.* **2020**, *189*, 105521. [\[CrossRef\]](#)
21. Maia, M.A.; Dotto, G.L.; Perez-Lopez, O.W.; Gutterres, M. Phosphate removal from industrial wastewaters using layered double hydroxides. *Environ. Technol.* **2020**, *6*, 1–11. [\[CrossRef\]](#)
22. Nava-Andrade, K.; Carbajal-Arízaga, G.G.; Obregón, S.; Rodríguez-González, V. Layered double hydroxides and related hybrid materials for removal of pharmaceutical pollutants from water. *J. Environ. Manag.* **2021**, *288*, 112399. [\[CrossRef\]](#)
23. Santamaría, L.; Vicente, M.A.; Korili, S.A.; Gil, A. Progress in the removal of pharmaceutical compounds from aqueous solution using layered double hydroxides as adsorbents: A review. *J. Environ. Chem. Eng.* **2020**, *8*, 104577. [\[CrossRef\]](#)
24. Rosset, M.; Sfreddo, L.W.; Perez-Lopez, O.W.; Féris, L.A. Effect of concentration in the equilibrium and kinetics of adsorption of acetylsalicylic acid on ZnAl layered double hydroxide. *J. Environ. Chem. Eng.* **2020**, *8*, 103991. [\[CrossRef\]](#)
25. Rudzinski, W.; Plazinski, W. Theoretical description of the kinetics of solute adsorption at heterogeneous solid/solution interfaces. On the possibility of distinguishing between the diffusional and the surface reaction kinetics models. *Appl. Surf. Sci.* **2007**, *253*, 5827–5840. [\[CrossRef\]](#)
26. Lagergren, S. About the theory of so-called adsorption of soluble substances. *Sven. Vetenskapsakad. Handlingar* **1898**, *24*, 1–39.
27. Plazinski, W.; Rudzinski, W.; Plazinska, A. Theoretical models of sorption kinetics including a surface reaction mechanism: A review. *Adv. Colloid Interface Sci.* **2009**, *152*, 2–13. [\[CrossRef\]](#)
28. Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. *Process. Biochem.* **1999**, *34*, 451–465. [\[CrossRef\]](#)
29. Azizian, S. Kinetic models of sorption: A theoretical analysis. *J. Colloid Interface Sci.* **2004**, *276*, 47–52. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Chien, S.H.; Clayton, W.R. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Sci. Soc. Am. J.* **1980**, *44*, 265–268. [\[CrossRef\]](#)
31. Weber, W.J.; Morris, J.C. Kinetic of adsorption on carbon from solutions. *J. Sanit Eng. Div. ASCE* **1963**, *89*, 31–60. [\[CrossRef\]](#)
32. Islam, M.; Mishra, S.; Swain, S.K.; Patel, R.; Dey, R.K.; Naushad, M. Evaluation of Phosphate Removal Efficiency from Aqueous Solution by Polypyrrole/BOF Slag Nanocomposite. *Separat. Sci. Technol.* **2014**, *49*, 2668–2680. [\[CrossRef\]](#)
33. Acelas, N.Y.; Martin, B.D.; López, D.; Jefferson, B. Selective removal of phosphate from wastewater using hydrated metal oxides dispersed within anionic exchange media. *Chemosphere* **2015**, *119*, 1353–1360. [\[CrossRef\]](#)
34. Aharoni, C.; Ungarish, M. Kinetics of activated chemisorption Part 2-Theoretical models. *J. Chem. Soc. Faraday Trans. 1* **1977**, *73*, 456–464. [\[CrossRef\]](#)
35. Sahin, O.I.; Saygi-Yalcin, B.; Saloglu, D. Adsorption of ibuprofen from wastewater using activated carbon and graphene oxide embedded chitosan-pva: Equilibrium, kinetics, and thermodynamics and optimization with central composite design. *Desalin. Water Treat.* **2020**, *179*, 396–417. [\[CrossRef\]](#)
36. Vargues, F.; Brion, M.A.; Rosa da Costa, A.M.; Moreira, J.A.; Ribau Teixeira, M. Development of a magnetic activated carbon adsorbent for the removal of common pharmaceuticals in wastewater treatment. *Int. J. Environ. Sci. Technol.* **2021**, *18*, 2805–2818. [\[CrossRef\]](#)
37. Wang, X.-J.; Zhu, X.-P.; Lan, L.-M.; Zuo, H.-B. Removal of chromium from laboratory wastewater using preparation-adsorption technology with a Mg/Al/Cr layered compound. *RSC Adv.* **2016**, *6*, 85595–85602. [\[CrossRef\]](#)
38. Zhu, J.; Zeng, B.; Mo, L.; Jin, F.; Deng, M.; Zhang, Q. One-pot synthesis of Mg[Al] layered double hydroxide (LDH) using MgO and metakaolin (MK) as precursors. *Appl. Clay Sci.* **2021**, *206*, 106070. [\[CrossRef\]](#)
39. Moustafa, D.; Mahmoud, R.; El-Salam, H.M.A.; Shehata, N. Utilization of residual zinc-iron-layered double hydroxide after methyl orange management as a new sorbent for wastewater treatment. *Appl. Nanosci.* **2021**, *11*, 709–723. [\[CrossRef\]](#)
40. Cheng, F.; Nie, F.; Zhao, C.; Wu, X.; Lu, J.; Jiang, D.; Pan, J. Phosphorus adsorption characteristics and mechanism of biochar loaded Mg/Al-LDHs composites. *Nongye Gongcheng Xuebao/Trans. Chin. Soc. Agric. Eng.* **2021**, *37*, 226–234. [\[CrossRef\]](#)
41. Gao, Z.; Sasaki, K.; Qiu, S. Structural Memory Effect of Mg–Al and Zn–Al layered Double Hydroxides in the Presence of Different Natural Humic Acids: Process and Mechanism. *Langmuir* **2018**, *34*, 5386–5395. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Zhong, P.; Ping, K.; Qiu, X.; Chen, F. Sorption of humic acid to layered double hydroxides prepared through ion thermal method. *Desalin. Water Treat.* **2017**, *93*, 109–119. [\[CrossRef\]](#)
43. Lu, H.; Liu, S.; Zhang, H.; Qiu, Y.; Zhao, J.; Zhu, Z. Decontamination of arsenic in actual water samples by calcium containing layered double hydroxides from a convenient synthesis method. *Water* **2018**, *10*, 1150. [\[CrossRef\]](#)
44. Kostić, M.; Radović, M.; Velinov, N.; Najdanović, S.; Bojić, D.; Hurt, A.; Bojić, A. Synthesis of mesoporous triple-metal nanosorbent from layered double hydroxide as an efficient new sorbent for removal of dye from water and wastewater. *Ecotox. Environ. Saf.* **2018**, *159*, 332–341. [\[CrossRef\]](#)
45. Dasgupta, S. Controlled release of ibuprofen using Mg Al LDH nano carrier. *IOP Conf. Ser. Mater. Sci.* **2017**, *225*, 012005. [\[CrossRef\]](#)
46. Kumari, P.; Pal, B.; Das, R.K. Superior adsorptive removal of eco-toxic drug diclofenac sodium by Zn–Al LDH-xBi<sub>2</sub>O<sub>3</sub> layer double hydroxide composites. *Appl. Clay Sci.* **2021**, *208*, 106119. [\[CrossRef\]](#)
47. Nuryadin, A.; Imai, T.; Kanno, A.; Yamamoto, K.; Sekine, M.; Higuchi, T. Phosphate adsorption and desorption on two-stage synthesized amorphous-ZrO<sub>2</sub>/Mg–Fe layered double hydroxide composite. *Mater. Chem. Phys.* **2021**, *266*, 124559. [\[CrossRef\]](#)

- 
48. Zhang, J.; Xia, Q.; Hong, X.; Chen, J.; Liu, D. Synthesis of layered double hydroxides with nitrate and its adsorption properties of phosphate. *Water Sci. Technol.* **2021**, *83*, 100–110. [[CrossRef](#)]
  49. Sena, M.; Seib, M.; Noguera, D.R.; Hicks, A. Environmental impacts of phosphorus recovery through struvite precipitation in wastewater treatment. *J. Clean. Prod.* **2021**, *280*, 124222. [[CrossRef](#)]
  50. Onishi, B.S.D.; dos Reis Ferreira, C.S.; Urbano, A.; Santos, M.J. Modified hydrotalcite for phosphorus slow-release: Kinetic and sorption-desorption processes in clayey and sandy soils from North of Paraná state (Brazil). *Appl. Clay Sci.* **2020**, *197*, 105759. [[CrossRef](#)]