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Powdered Ca-activated zeolite for phosphate removal from treated wastewater

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Abstract

BACKGROUND: A powdered zeolitic material synthesised from fly ash (FA) (NaP1-FA) and its Calcium modified form (CaP1-NA) were studied as sorbent materials for the recovery of phosphate from treated wastewater effluents. Phosphate-sorption equilibrium experiments were performed by varying the experimental conditions, including the solution pH, phosphate concentration, and the presence of competing ions.

RESULTS: The maximum phosphate-sorption capacities were 57 ± 5 and 203 ± 11 mgP-PO₄/g for NaP1-FA and CaP1-NA, respectively. The sorption capacities of both zeolites in the pH range expected for wastewater effluents (pH from 7 to 9) were slightly dependent on pH, exhibiting maxima at pH 8. Phosphate removal proceeds through two main mechanisms: a) surface

complexation with $\equiv\text{AlOH}$ and $\equiv\text{FeOH}$ groups of the zeolitic structure or unreacted minerals from the FA, and b) the formation of Ca-phosphate phases, mainly brushite.

CONCLUSIONS: The removal mechanisms were confirmed by XRD analyses and P speciation. The stabilities of the phosphate-loaded zeolite samples evaluated by the extraction experiments confirmed their potential availabilities in soil applications. Finally, the higher solubility of brushite compared with that of Hap makes this zeolitic material promising as a novel inorganic zeolite/CaP1-NA/brushite fertiliser.

Keywords: phosphate recovery; powder synthetic zeolite; calcium modification; waste valorisation; brushite; fertilizer

1. Introduction

Increasing energy demands worldwide have led to increased utilisation of coal and the production of large quantities of fly ash (FA) as a waste product. The global production of FA in 2010 exceeded 750 million tons/year, with 38 million tons produced in Europe alone.^{1,2} FA is enriched with SiO_2 and Al_2O_3 , and thus, it can be transformed by chemical treatment into zeolite-like crystalline materials. The synthesis of zeolites is attracting attention as an effective use for coal fly ash CFA, possibly because of its similar composition to the volcanic material that serves as the precursor of natural zeolites.

Zeolites are microporous aluminosilicate minerals that could be used as ion exchangers in domestic and industrial water purification and softening applications³. The substitution of silicon (Si) by aluminium (Al) atoms in the crystal framework leads to extra negative charges that must be balanced by surrounding counter ions (such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+}); these counter ions can be easily exchanged for other surrounding cations in contact with aqueous solutions. Therefore, several studies on the use of zeolites for the removal of hazardous cations^{4,5} and

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anions and organic compounds with modified zeolites ⁶ have been reported. By applying several synthesis methods, different families of zeolites have been synthesised from FA; ⁶⁻⁸ however, few have been successfully converted into pure-phase zeolites.^{9,10}

The removal of phosphate from wastewaters has been linked to the need for their reuse and valorisation, both of which could be achieved using a reactive material capable of achieving high phosphate-removal ratios in solution and suitable for use as a fertiliser in soil and agricultural applications.¹¹ This process could be developed if low-cost sorbents are available.¹² Querol et al.¹³ demonstrated the economic and technical viability of synthesising NaP1-FA under mild hydrothermal conditions without using templates. NaP1-FA was evaluated for the removal of toxic metals from acid mine drainage and brines¹⁴ because of its unique ion-exchange and water-sorption properties, which are attributable to its high porosity, surface area, and cation exchange capacity (CEC) and its unusual framework flexibility.¹⁵ NaP1-FA also has a high capacity to adsorb ammonium and potassium K, and it has been evaluated as a slow-release fertiliser; however, the sorption of oxyanions as phosphate is not favoured by the zeolite structure.¹⁶ The use of mixtures of synthetic apatites and natural zeolites as solid media for growing plants and as a fertiliser has been postulated.^{17,18} However, because of the low solubility and availability of P from hydroxyapatite (Hap) in soils, efforts have been directed towards the preparation of relatively soluble Hap ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) by growing crystals on the surface of Ca-containing minerals. These materials include Ca silicates, such as wollastonite;¹⁹ Ca-Al layered double hydroxide; and Hap.^{20,21} However, little work has been done to prepare a reactive material to a) efficiently remove phosphate from wastewater effluents in the form of relatively soluble phosphates (e.g., brushite ($\log K_{\text{so}}=6.59$))²² compared to Hap ($\text{Ca}_5(\text{PO}_4)_3\text{OH}(\text{s})$, $\log K_{\text{so}}=116.8$)²³ and b) to achieve suitable properties for use as a synthetic fertiliser.

In this study, both the Na⁺-zeolite (NaP1-FA), synthesised from coal fly ash (CFA), and its Ca-modified form (CaP1-NA) were evaluated as sorbents for phosphate recovery from aqueous

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3 76 solution. The phosphate-sorption performance was studied by varying the experimental
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5 77 conditions, such as the solution pH, coexisting ions, and initial phosphate concentration. The
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7 78 results are presented in terms of equilibrium isotherms in non-competitive and competitive
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9 79 experiments with other common anions present in wastewater effluents. Furthermore, the
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11 80 phosphate-sorption removal mechanisms were evaluated using a speciation methodology.
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13 81 Finally, the stability of the phosphate-loaded zeolite samples was evaluated by extraction
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15 82 experiments using bicarbonate solutions to determine their potential availability in soil
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17 83 applications.
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23 85 2. Materials and methods

26 86 2.1. Synthesis of NaP1-FA and CaP1-NA

27 87 Na⁺-zeolite (NaP1-FA) was synthesised from Narcea CFA with 3 mol/L NaOH at 125°C for 8 h
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29 88 using a hydrothermal method, as described elsewhere ¹³. Ca-zeolite (Ca²⁺-zeolite CaP1-NA) was
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31 89 prepared by a cation-exchange process. First, 250 g of NaP1-FA was immersed in 1000 mL of a
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33 90 0.5-mol/L CaCl₂ solution for 1 h at room temperature, which was then filtered through a 0.2-μm
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35 91 membrane filter and rinsed with distilled water to remove the CaCl₂ solution ¹⁶. The cation-
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37 92 exchange and washing cycle was repeated five times. The sample obtained was dried for 72 h at
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39 93 50–60°C.
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46 95 2.2. Phosphate-removal equilibrium experiments

47 96 Phosphate test solutions were prepared by dissolving a weighed amount of Na₂HPO₄·2H₂O in
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49 97 water obtained from a Milli-Q-Academic-A10 apparatus (Millipore Co. France). Batch experiments
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51 98 were performed at room temperature (21±1°C). Samples of zeolites (0.2 g) were mechanically
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53 99 mixed in special polyethylene stoppered tubes with an aqueous phosphate solution (12 mL) at
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56 100 different initial concentrations of phosphate (100–16,000 mg L⁻¹) until equilibrium was achieved
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(24 h). The influence of pH on the phosphate sorption was evaluated by using 0.1-mol/L HCl or NaOH solution to adjust the initial pH. After phase separation with a 0.2- μ m syringe filter, the equilibrium pH was measured using a pH electrode (Crison GLP22), and the total phosphate concentration was measured using spectrophotometric colourimetry ²⁴. The phosphate equilibrium sorption capacity determined using Eq. 1.

$$q_e = (C_0 - C_e) \frac{v}{m_s} \quad (1)$$

where C_0 (mg/L) and C_e (mg/L) represent the initial and equilibrium total phosphate concentrations, respectively; v (L) is the aqueous solution volume; and m_s (g) is the mass of zeolite.

2.3. Phosphate-removal equilibrium experiments in the presence of competing ions

The effect of common coexisting ions in wastewater, such as chloride, sulfate, nitrate, and bicarbonate, on the sorption of phosphate was investigated by adding 300 mg HCO_3^-/L , 300 mg Cl^-/L , 250 $\text{SO}_4^{2-}/\text{L}$, and 50 mg NO_3^-/L to 100-15,000 mg $\text{P-PO}_4^{3-}/\text{L}$. A given mass of CaP1-NA (0.2 g) was added, and the solution was agitated at 400 rpm for 24 h at $21 \pm 2^\circ\text{C}$. After filtration with a 0.2- μ m membrane filter, the residual phosphate concentration was analysed using spectrophotometric colourimetry. The typical values of the effluent streams from secondary treatment at the El Prat wastewater treatment plant (WWTP) (Barcelona, Spain) were used to determine the feed composition.

2.4. Speciation of phosphate-loaded zeolite samples using a sequential extraction protocol

The speciation of phosphorus (P) adsorbed in loaded zeolites (NaP1-FA and CaP1-NA) was achieved using a modified four-step sequential extraction ²⁵⁻²⁷. First, 30-mL aliquots of 1000 mg $\text{P-PO}_4^{3-}/\text{L}$ at pH 7 were equilibrated with pre-weighed tubes containing 3 g of each type of zeolite:

NaP1-FA and CaP1-NA. After shaking for 24 h at room temperature, the suspensions were centrifuged, and the powders were collected and dried in an oven at 50–60°C. The adsorbed phosphate was sequentially extracted. One gram of each sample was weighed into a 50-mL centrifuge tube and then treated as described in Table 1.

Table 1.

2.5. Desorption of phosphate from loaded zeolites samples using bicarbonate solutions.

First, 0.5-g samples of phosphate-loaded zeolites (NaP1-FA and CaP1-NA) with phosphate contents ranging from 11 to 173 mmol/L were mixed with 20-mL solutions containing a mixture of NaHCO₃ (0.1 M) and Na₂CO₃ (0.1 M) in 50-mL plastic bottles. The bottles were mechanically shaken (Heidolph) at 21±1°C for 24 h at a constant agitation speed of 200 rpm. At the end of the experiment, the samples were withdrawn from the test bottles and filtered through a 0.45-µm membrane filter; the residual phosphate concentration was analysed using spectrophotometric colourimetry.

2.6. Physicochemical characterisation of zeolites

At the end of the sorption and desorption experiments, the zeolite samples were washed with water to remove the interstitial water and then oven-dried at 60°C for structural and textural analysis. The mineralogical composition was analysed by a Bruker D8 A25 Advance X-Ray Diffractometer θ - θ with CuK α 1 radiation, Bragg-Brentano geometry, and a linear LynxEyeXE detector. The diffractograms were obtained from 4° to 60° of 2 θ with a step size of 0.015° and a counting time of 0.1 s as the sample rotated. The solids in powder form were identified by standard Joint Committee on Powder Diffraction Standards (JCPDS) files and were matched with Powder Diffraction Files (PDFs) no. 009-0077 for (brushite), no. 039-1374 (garronite), 039-0219 (NaP1), 046-1045 (quartz), and 015-0776 (mullite).

The samples' morphologies were examined by JEOL 3400 Field Emission Scanning Electron Microscopy with Energy Dispersive System FE-SEM-EDS prior gold metallisation.

The point of zero charge (PZC) values of NaP1-FA and CaP1-NA were determined, and the common intersection point (CIP) method was applied to the potentiometric titration curves obtained at four ionic strengths ^{28–30}. First, 0.1 g of zeolite was equilibrated with 25 mL of solutions with different ionic strengths (0.01-, 0.05-, 0.1-, and 0.5-M KNO₃) for 24 h at 200 rpm and 21±1°C. Following equilibration, a small quantity of 0.1-M KOH was added to the suspension to increase the pH beyond 10 (pH_{in}). The suspension was then titrated with 0.0454-M HNO₃ to pH≈3 using an automatic titrator (Mettler Toledo). The net surface charge was correlated with the PZC determined from the titration data for the adsorbed amounts of [H⁺] and [OH⁻] ions. Therefore, the titration curves of different ionic strength intersect at pH=pH_{PZC}. The surface charge was calculated according to Eq. 2 ³¹.

$$b = C_b - C_a + [H^+] - [OH^-] \quad (2)$$

where b (mol/g) is the net amount of hydroxide ions consumed; C_b and C_a (mol/L) are the base and acid concentrations, respectively; and [H⁺] and [OH⁻] denote the proton and hydroxide concentrations, respectively, calculated from the measured pH for a given mass of zeolite (g) and a given volume of solution (L). All measurements were performed in triplicate, and the average values are reported.

3. Results and discussion

3.1. Characterisation of the CaP1-NA modified zeolites.

The conversion of FA into zeolitic materials through the batch hydrothermal synthesis process involves three stages: i) the dissolution of Al and Si from FA, ii) the deposition of aluminosilicate gel on the FA surface, and iii) the crystallisation of zeolite from aluminosilicate gel ³². The three Al- and Si-containing phases of the FA are i) amorphous aluminosilicate glass, ii) quartz, and iii) mullite. Aluminosilicate glass is the largest component and is the most unstable in the

hydrothermal environment, and therefore, it exhibits the highest rate of dissolution^{33,34} makes the largest contribution to the produced zeolites.

The X-Ray Diffraction (XRD) patterns of the Na zeolite (NaP1-FA) and the synthesised Ca zeolite (CaP1-NA) are shown in Figure 1a. NaP1 ($\text{Na}_6(\text{Al}_6\text{Si}_{10}\text{O}_{32}) \cdot 12\text{H}_2\text{O}$), mullite ($\text{Al}_2\text{Si}_2\text{O}_{13}$), and a trace of quartz (SiO_2) were the main phases identified in NaP1-FA. The XRD patterns of CaP1-NA indicated the presence of mullite, quartz, calcite (CaCO_3), and garronite ($\text{NaCa}_{2.5}(\text{Si}_{10}\text{Al}_6)\text{O}_{32} \cdot 14\text{H}_2\text{O}$) as the predominant phases. The SEM observation (Figure 1b) showed that NaP1-FA and CaP1-NA coat the FA. As shown in Figure 1b, the coating of NaP1-FA is not complete, as reported by Cama et al.¹⁵.

Fig. 1.

The chemical compositions of both zeolitic materials are listed in Table 2 and indicate that NaP1-FA and CaP1-NA contained mainly Al_2O_3 and SiO_2 , which accounted for a total of 74%. The synthesis of CaP1-NA considerably increased the Ca^{2+} content (from 1.4 to 7.4% (82.5 mg/g)). Accordingly, the Na^+ content decreased significantly (from 7.6 to less than 1%) because of treatment with CaCl_2 and the partial exchange of sodium and calcium ions in the zeolite structure.

Table 2.

The acid-base characterisation revealed pH_{PZC} values of 6.1 ± 0.2 for CaP1-NA and 5.4 ± 0.2 for NaP1-FA (Figure 2), which are in agreement with values reported for natural zeolites (clinoptilolite) (5.2 ± 0.2)³⁵. The increased pH_{PZC} of CaP1-NA suggests a decrease in the acidity of the metal-hydroxide groups ($\equiv\text{MOH}$) of the zeolite structure after modification with calcium-salts resulting from complexation with Ca(II) ions. The determined pH_{PZC} value is in agreement with values reported for $\alpha\text{-Al(OH)}_3(\text{s})$ ($\text{pH}_{\text{PZC}}=5.0$) and Fe(OH)_3 ($\text{pH}_{\text{PZC}}=5-7$).

Fig. 2.

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3 199 Indeed, some studies ^{36–38} have reported that Fe- and Al-based surface groups on zeolites
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5 200 become positively charged and that their anion-sorption capacity (e.g., $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$) via ligand
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7 201 exchange increase because of chemical interactions and electrostatic forces. The latter give rise
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9 202 to Columbic attraction or repulsion between binding sites and sorbing ions ³⁹.

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14 204 **3.2. Phosphate-sorption capacities of CaP1-NA and NaP1-FA: Dependence on pH and** 15 16 17 205 **phosphate concentration**

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19 206 The effects of the initial phosphate concentration on phosphate sorption and the equilibrium pH
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21 207 for both zeolites are shown in Figure 3a. The phosphate-sorption capacity increased as the initial
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23 208 phosphate concentration increased. Additionally, the equilibrium pH exceeds the initial pH (8),
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25 209 reaching values as high as 9.5 for CaP1-NA and 9 for NaP1-FA, at lower initial phosphate
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27 210 concentrations (up to 20 mmol/L) and then decreases back to the initial value for NaP1-FA and
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29 211 7.5 for CaP1-NA. Moreover, the shape of the phosphate-sorption isotherm indicates that CaP1-
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31 212 NA has a higher affinity for phosphate than NaP1-FA, as shown by the higher slope of the
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33 213 isotherm. This high affinity results in the nearly quantitative removal of phosphate by CaP1-NA
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35 214 (98%) at low residual phosphate concentrations in solution. In contrast, for NaP1-FA, the removal
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37 215 ratios achieved were below 25% (data not shown). As the initial phosphate concentration was
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39 216 increased, the sorption capacities of the zeolites increased, reaching maxima of 207 mg/g and 50
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41 217 mg/g for CaP1-NA and NaP1-FA, respectively (Figure .4).

42 43 44 45 46 218 **Fig. 3.**

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48 219 According to the removal patterns exhibited by NaP1-FA and CaP1-NA zeolitic materials, the
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50 220 sorption of phosphate ions, mainly H_2PO_4^- and HPO_4^{2-} , that occurs in the expected pH range (7 to
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52 221 9) may follow two postulated mechanisms:

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55 222 a) Surface complexation with $\equiv\text{AlOH}$ and $\equiv\text{FeOH}$ functional groups originally present as Al and
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57 223 Fe oxides or in the zeolitic structure via two main reactions:

224 a1) Outer-sphere complexes with $\equiv\text{MOH}_2^+$ surface groups

226 a2) Inner-sphere complexes with $\equiv\text{MOH}$ surface groups

228 where M represents Al or Fe.

229 b) Formation of Ca-phosphate minerals with Ca(II) ions present on the zeolite through two main
230 reactions:

231 b1) Ca-phosphate minerals with Ca(II) present on the zeolitic material as CaO(s) and
232 $\text{CaCO}_3(\text{s})$:

235 Both mineral phases can be formed in the expected pH range, as shown in Figure 5.4.

236 b2) Formation of Ca-phosphate minerals with Ca(II) ions occupying the ion-exchange groups
237 of the zeolitic structure

240 where $\equiv\text{ZO}^-$ represents the anionic groups of the zeolite structure.

241 The phosphate sorption that occurs via the formation of surface complexes (Eqs. 3–4) is
242 consistent with the observed results at low phosphate concentrations (Figure 3b), which involved
243 the removal of H_2PO_4^- (Eq. 3) and the formation of inner-sphere complexes (Eq. 4). For high initial
244 phosphate concentrations (50–200 mmol/L), the most favoured reaction is the formation of Ca-
245 phosphate (e.g., brushite or Hap) (Eqs. 6–7) with the release of H^+ ions and the resulting

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3 246 decrease in the pH to 7.5 for CaP1-NA. For NaP1-FA, the lower Ca(II) content results in a lower
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5 247 sorption capacity, and thus, the recovery of phosphate ions should be conceived of as a
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7 248 combination of Eqs. 3–6. XRD analysis of the samples after the sorption experiments revealed
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9 249 the presence of brushite in most of the analysed CaP1-NA samples, while for NaPa1-NA, the
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11 250 presence of Ca-phosphate minerals was not observed. This could be attributable to the contents
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13 251 of these minerals on the samples being below the limit of detection or the formation of the
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15 252 minerals within the small channels of the zeolite as undetectable nanocrystals.
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18 253 The formation of Ca-phosphate (brushite and Hap) is thermodynamically favoured in the
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20 254 expected pH range, as shown in Figure S1 (Supplementary material). Hap is more stable than
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22 255 brushite, which is considered its precursor phase. However, as the reaction proceeds on the
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24 256 microporous zeolite structure, brushite is formed and then stabilised, thereby stopping the
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26 257 conversion to Hap.
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29 258 The phosphate-sorption isotherms of CaP1-NA and NaP1-FA at different pH values (7, 8, and 9)
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31 259 are shown in Figure 4. The phosphate-loading capacity of CaP1-NA is higher than that of NaP1-
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33 260 FA; e.g., 203 ± 11 mg/g compared with 57 ± 5 mg/g at pH 8. The larger sorption capacity of CaP1-
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35 261 NA is associated with its Ca content and high availability for reaction, mainly at the ion-exchange
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37 262 sites, while the lower sorption capacity of NaP1-FA is related to unreacted Ca in the form of CaO.
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39 263 It should be mentioned that the initial S_{BET} increased during zeolite modification from 6.3 to 13.6
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41 264 m²/g. Thus, the higher Ca content and larger surface area enhance the phosphate sorption, as
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43 265 previously reported ⁴⁰. The surface charge properties of the active sites (Fe and Al sites) of both
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45 266 zeolites were 8% Al and 2.5% Fe (Table 2). The larger amount of Al in NaP1-FA plays an
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47 267 important role in phosphate removal at neutral pH, and the magnitude of the Columbic attractive
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49 268 force decreases as the active sites become neutral.
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55 269 The sorption isotherm data were fitted using Langmuir (Eq. 7) and Freundlich isotherm models
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57 270 (Eq. 8):
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$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (7)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (8)$$

where C_e (mg/L) and q_e (mg/g) are the equilibrium total phosphate concentrations in the aqueous and solid phases, respectively; q_m (mg/g) is the maximum sorption capacity; K_L (L/mg) is the Langmuir sorption equilibrium constant; n is a constant indicating the Freundlich isotherm curvature; and $K_f ((\text{mg/g})/(\text{mg/L})^n)$ is the Freundlich equilibrium constant. The sorption parameters and regression coefficients (R^2) obtained from the linear regression of Eqs. 7 and 8 are listed in Table 3.

The experimental and predicted sorption isotherm data by the Langmuir model at different pH values for the CaP1-NA and NaP1-FA zeolites are shown in Figure 4.

Fig. 4.

Table 3.

The phosphate-removal data for CaP1-NA were well described by the Langmuir isotherm, while for NaP1-FA, the Freundlich isotherm was more suitable. This behaviour was explained by Pengthamkeerati et al. ⁴¹, who reported that the phosphate-adsorption processes of zeolite derived from FA using different treatment methods can be described using different isotherm models. Langmuir isotherm is more suitable for the adsorption pattern of phosphate on the alkaline-treated and Ca-rich zeolite CaP1-NA. In contrast, the Freundlich isotherm better describes physical adsorption, and as a result, this model is suitable for the phosphate-adsorption pattern of NaP1-FA.

The XRD patterns of phosphate-loaded CaP1-NA samples with initial phosphate concentrations ranging from 8 to 15 g/L at pH values of 7, 8, and 9 are shown in Figure 5. These patterns revealed the formation of Ca-phosphate in the form of brushite ($\text{CaPO}_3(\text{OH}) \cdot 2\text{H}_2\text{O}(\text{s})$) as the

major phase at pH 7 and 8 and as a minor phase at pH 9. Similar phosphate-removal and brushite-formation results were reported by Pengthamkeerati et al.⁴¹ with Ca-zeolites and by other researchers (e.g. Lu et al., and Xu et al)^{42,43} with FA. The formation of brushite instead of Hap is associated with the prevalence of kinetic control. In fact, the reactive crystallisation of brushite has been described to occur^{44,45} through five successive stages: (i) spontaneous Hap precipitation, (ii) complete dissolution of Ca and Hap growth, (iii) initial appearance of brushite nuclei, (iv) coexistence of Hap and brushite, and (v) transformation of Hap into brushite and subsequent brushite growth.

Fig. 5.

The transformation of Hap into brushite would not be expected because Hap is the most thermodynamically stable species. Nevertheless, under the conditions, Hap appears to be in a low-crystallinity state and in metastable equilibrium with brushite, whose faster crystal growth drives the transformation.

Both zeolites exhibit maximum sorption capacities at pH 8, which slightly decrease as the pH increases to 9 or decreases to 7. This pH-dependent sorption behaviour is in agreement with the brushite formation observed in most of the samples analysed by XRD (Figure 5). The logarithmic solubility dependence of brushite and the phosphate-loading capacity as a function of pH are plotted in Figure 6. The minimum solubility corresponding the highest brushite stability occurs at pH 8 (maximum loading capacity) and decreases slightly as the pH is decreased to pH 7 or increased to 9.

Fig. 6.

Similar behaviour was observed for NaP1-FA, the maximum sorption capacities were observed at pH 8 and 7 and were slightly reduced when the pH increased to 9, which could be in agreement

with the potential involvement of the CaO(s) present on the zeolite in brushite formation and the acid-base properties of the $\equiv\text{AlOH}$ and $\equiv\text{FeOH}$ surface groups, which exhibit pH_{pcz} of approximately 6 for hydrated Al oxides ⁴⁶ and 7 for hydrated Fe oxides. As a result, at basic pH values exceeding the pH_{pcz} , the formation of outer-sphere complexes will be negligible. Additionally, in alkaline conditions, the formation of inner-sphere complexes is not favoured, and thus, the removal ratio decreases.

The phosphate-sorption capacities of zeolites and FA as reactive materials for phosphate removal are compared in Table 4, which shows that the phosphate-sorption capacities of CaP1-NA exceed previously reported values.

Table 4.

3.3. P speciation of the phosphate in loaded CaP1-NA/NaP1-FA

The speciation results of CaP1-NA and NaP1-FA zeolitic materials are shown in Figure 7. The easily exchangeable speciation (KCl-P) associated with exchange reactions as defined by Eq. 3 accounts for up to 20% for NaP1-FA and less than 10% for CaP1-NA. The dissolved species obtained using NaOH solutions (NaOH-P) reveal that the P bound to the hydrated metal oxides (the inner-sphere and outer-sphere complexes described by Eqs. 3–4) makes only a small contribution for NaP1-FA (less than 5%) and no contribution for CaP1-NA. In NaOH solutions, the $\equiv\text{MOH}^{2+}$ and $\equiv\text{MOH}$ groups are deprotonated, and the excess OH ions disrupt the $\equiv\text{MH}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ complexes. The HCl-P speciation (was in line with laboratory experiments reported by other researchers (e.g. Wang et al. And Meis et al., ^{47,48})) associated with Ca-phosphate mineral phases (brushite and Hap) accounts for up to 80% for NaP1-FA and more than 90% for CaP1-NA. The species produced by the residual speciation contributed less than 1% for both zeolites.

Fig. 7.

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346 3.4. Effect of competing ions on phosphate sorption

347 Coexisting ions, such as chloride, sulfate, nitrate, and carbonate, that are generally present in
348 treated wastewater do not interfere with phosphate uptake through competitive sorption, as
349 shown in Figure 8. Differences between the samples containing individual species, mixtures of
350 species, and no coexisting ions are not statistically significant. Given that the main phosphate-
351 removal mechanism is based on the formation of insoluble Ca-phosphate minerals and weak
352 complexes with MOH surface groups, none of the evaluated anions could form insoluble forms
353 with Ca anions, and their complexation with Fe and Al oxides was also less favoured than that
354 with phosphate anions. According to Zhang et al. ⁴⁹, this can be attributed to the specific sorption
355 of phosphate on the adsorbent because the phosphate ions adsorbed on the strongly specific
356 sites were rarely exchangeable, even in solutions containing excessive amounts of coexisting
357 ions. This suggests that CaP1-NA has high sorption selectivity for phosphate anions and great
358 potential for use in treated wastewater expected to contain high concentrations of these anions.

359 Fig. 8.

361 3.5. Desorption of phosphate from loaded zeolite samples

362 The phosphate desorption achieved using 0.1 mol/L NaHCO₃/Na₂CO₃ solutions increased as the
363 amount of phosphate on the zeolitic material decreased (Figure 9a-b). Partial desorption (30 to
364 70%) was reported for CaP1-NA, whereas values of 10 to 70% were observed for NaP1-FA in a
365 single-extraction trial. These results are in agreement with the speciation results obtained in using
366 excess bicarbonate ions. Indeed, during labile speciation (P-KCl), phosphate anions will be
367 displaced by bicarbonate ions, and partial brushite dissolution will be achieved, as indicated in
368 Figure 6, which shows that increasing the pH increases the solubility of brushite by up to one
369 order of magnitude. It can be concluded that phosphate sorption on CaP1-NA is relatively

irreversible and that the bonding between the active sites and the adsorbed phosphate is quite strong.

Fig. 9.

4. Conclusions

NaP1-FA zeolitic material synthesised from Narcea FA and its Ca-modified form (CaP1-NA) are capable of high phosphate sorption in neutral to slightly basic conditions. The maximum phosphate-sorption capacities determined at pH 8 were 65 ± 7 and 203 ± 11 mgP-PO₄/g zeolite for NaP1-FA and CaP1-NA, respectively. The sorption capacity in the expected pH range of wastewater effluents (e.g., from 7 to 9) was slightly dependent on the pH and was maximised at pH 8 for CaP1-NA and pH 9 for NaP1-FA. Phosphate removal by NaP1-FA occurred via a surface complexation mechanism involving the AlOH and FeOH surface groups of the unreacted Fe and Al oxides originally present on the FA or the potential formation of Ca-phosphate phases using the original CaO present on the FA. In contrast, for CaP1-NA, the main removal mechanism included the formation of a Ca-phosphate, brushite, as confirmed by XRD analyses. The higher solubility of brushite compared with that of Hap makes this zeolitic material promising as a novel inorganic zeolite/CaP1-NA/brushite fertiliser.

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Table 1. Chemical extraction scheme for phosphate speciation of loaded zeolites

Reagent conditions	Speciation name	Speciation (associated phosphate forms)	Step
40-mL 2 M KCl for 2h	KCl-P	Soluble and exchangeable P	1
40-mL 0.1 M NaOH for 17h	NaOH-P	Fe- and Al-bound P	2
40-mL 0.5 M HCl for 24h	HCl-P	Ca-bound P	3
40 ml 8 M HNO ₃ /5 M HClO ₄	Res-P	Residual P	4

Table 2. Average chemical composition of zeolitic adsorbents NaP1-FA and CaP1-NA by using FSEM-EDX

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	CaO	K ₂ O	P ₂ O ₅	MgO
NaP1-FA (%)	48.3	22.5	6.1	15.2	3.0	3.3	1.3	1.2
CaP1-NA (%)	47.8	23.3	5.7	2.0	15.8	3.0	1.53	1.4

¹. Composition values have been expressed as oxide forms.

Table 3. Langmuir and Freundlich isotherm parameters for CaP1-NA and NaP1-FA at different pH.

Adsorbent		CaP1-NA			NaP1-FA		
		pH 7	pH 8	pH 9	pH 7	pH 8	pH 9
Adsorption isotherm models							
Langmuir equation	q_m	192	203.6	153	55.9	57.3	43.3
	K_L	0,004	0.004	0.006	0.0006	0.00035	0.0004
	R^2	0,86	0.99	0.96	0.82	0.90	0.91
Freundlich equation	K_f	1.45	14.8	17.6	2.23	0.0065	0.81
	n	1.36	3.4	2.9	3.01	1.17	2.48
	R^2	0.96	0.78	0.93	0.88	0.93	0.98

Table 4. Comparison of phosphate sorption capacity for different materials based Zeolite and FA

Material	q_m (mg/g)	pH	Reference
Zeolite NaP1-FA	57.33	8	This study
Calcium modified Zeolite NaP1-FA (CaP1-NA)	203.6	8	This study
Zeolite/Lanthanum hydroxide (La-ZFA)	71.94	>9.24	50
Zeolite/hydrate iron oxide (ZFA/Fe ₂ O ₃)	18.2	6.6	51
Zeolite synthesized from fly ash by alkaline fusion	132, 157, 184.	7	52
NaOH treated fly ash (TFA-NaOH)	57.14	8-12	41
Calcium modified Zeolite NaP1/hydroxyapatite	24.1	9	16
Fly ashes from three coal-burning power plants	90, 91, 108	11, 11, 12	42
Synthesis zeolite –Ca	30.46	6.78	53
Natural zeolite (Clinoptilolite)	13.8	n.a	54

n.a = not available

Figure captions:

Fig. 1. (a) XRD patterns of NaP1-NA and its modified zeolite CaP1-NA and (b) SEM: NaP1-NA and CaP1-NA.

Fig. 2. Potentiometric titration curve, at 0.01, 0.05, 0.1, and 0.5 M KNO_3 for Zeolite: a) CaP1-NA and b) NaP1-NA.

Fig. 3. (a) The equilibrium pH evolution as a function of initial phosphate concentration (initial pH 8) for CaP1-NA and NaP1-NA zeolitic material and (b) the uptake concentration as a function of equilibrium adsorbed concentration.

Fig. 4. Phosphate sorption isotherms at different pH and predicted uptake by the Langmuir (left) and Freundlich (right) isotherms for (a-b) CaP1-NA and (c-d) NaP1-NA modified zeolitic material.

Fig. 5. XRD pattern after phosphate sorption by CaP1-NA zeolitic material modified and brushite formation at different pH.

Fig. 6. The experimental P(V) sorption capacity at different pH and the estimated curve of brushite solubility for the CaP1-NA isotherm.

Fig. 7. Phosphate speciation of the NaP1-NA and CaP1-NA with initial amount of phosphate in equilibrium ($q_e = 12 \pm 1$ mg/g).

Fig. 8. Effect of coexisting anions on phosphate recovery at different initial phosphate concentration with fixed and mixed anions ($\text{Cl}^- = 300$ mg/L; $\text{SO}_4^{2-} = 250$ mg/L; $\text{NO}_3^- = 50$ mg/L; $\text{HCO}_3^- = 300$ mg/L).

Fig. 9. Phosphate desorption using mixture of NaHCO_3 (0.1M) and Na_2CO_3 (0.1 M) from loaded zeolite (a) CaP1-NA and (b) NaP1-NA.

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Fig. 6.

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Supplementary material

Fig. S1. Species distribution diagram and solubility as a function of pH for the system calcium and phosphate using the HYDRA-Medusa data base ⁵⁵ for both phases: (a-b) CaHPO₄·2H₂O (Brushite) and (c-d) Ca₅(PO₄)₃OH (Hydroxyapatite). In the box is indicating the pH range evaluated (maximum and minimum values).