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3 1 **Phosphate Recovery from Treated Municipal Wastewater using Hybrid Anion Exchangers**
4
5 2 **containing Hydrated Ferric Oxide nanoparticles**

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36 17 **Abstract**

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38 18 **BACKGROUND:** This study presents the evaluation of two ion exchangers (granular and
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40 **fibrous) impregnated with nanoparticles of hydrated ferric oxide (HFO) as selective**
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43 20 sorbents for phosphate recovery from aqueous solutions. The hybrid impregnated anion
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45 21 exchangers combine the durability and mechanical strength of a polymeric weak base
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47 22 anion exchange resin with the high sorption affinity of HFO towards phosphate species.
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49 23 Dynamic experiments were carried out and data obtained were fitted to a well-known
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51 24 fixed-bed sorption model.

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54 25 **RESULTS:** The theoretical sorption capacities reported by the Thomas model were in
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56 26 good agreement to the breakthrough experimental capacities determined from the
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3 27 sorption data. The sorption capacity decreased when using wastewater treatment plant
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5 28 secondary effluents in comparison with synthetic water mainly due to the presence of
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7 29 organic matter and suspended solids. The phosphate sorbed on the impregnated ion
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9 30 exchangers were efficiently desorbed by using a 0.5 mol/L sodium hydroxide solution,
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11 31 reporting up to 90% of recovery.

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14 32 CONCLUSION: The reusability of sorbents was evaluated through five sorption-
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16 33 desorption working cycles. Fiban-As was able to operate up to three consecutive cycles
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18 34 with good sorption performance whilst a significant decrease of sorption capacity after the
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20 35 first cycle was observed for FO36 resin.

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25 37 **Keywords:** phosphate recovery; fibrous ion exchanger; hybrid exchanger; hydrated ferric oxide
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27 38 (HFO); FO36; Fiban-As.

28 29 30 31 32 40 **1. Introduction**

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34 41 Phosphorous is a non-renewable resource for which there is no substitute¹ and human
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36 42 activities have heavily altered the phosphorus global cycle by consuming in years what the nature
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38 43 takes millions of years to create without closing the natural cycle of the element ¹. It is an
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40 44 essential element of the current agricultural system and it is a very valued resource due to its
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42 45 main role in fertilizer production in order to supply the increasing world food demand ².

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44 46 Traditionally, rock phosphate is the raw material used in the production of phosphate fertilizer.
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46 47 However, phosphorus is mined at just a handful of locations worldwide, primarily the United
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48 48 States, China, Morocco and the Western Sahara ³. An evaluation of the supply chain reveals that
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50 49 only 20% of mined phosphorus is consumed with the balance lost in the process ². Excreted
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52 50 phosphate is a recoverable resource, however when it permeates into surface water it can trigger
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3 51 eutrophication. Excessive nutrient loading on receiving waterways has been identified both in the
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5 52 USA and in Europe as the largest contributor to the degradation of water quality ⁴.

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7 53 Secondary sources such as municipal wastewater have long been thought to act as mineral
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9 54 deposits, and the recovery of phosphorus from them is valued and has increasingly been
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11 55 recognized as being a part of a more sustainable wastewater treatment process. Many methods
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13 56 have been investigated for phosphate removal from wastewater namely physical and coagulation
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15 57 methods ⁴, chemical precipitation by using ferric, calcium or aluminium salts ⁵, biological
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17 58 treatment ⁶ and adsorption ⁷⁻¹⁰.

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20 59 However, chemical or biological processes currently being practiced are no longer deemed
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22 60 adequate in meeting new discharge limits. For example, in the UK under the Water Framework
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24 61 Directive (WFD) phosphorus discharge limits are at 0.1 mg/L making conventional
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26 62 chemical/biological processes insufficient and thus creating the need for more efficient treatment
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28 63 methods. Phosphorus recovery through adsorption has proven to be a more cost efficient
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30 64 technique. The main advantage of using adsorption is that no excess sludge is produced and it
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32 65 offers reversibility and therefore directs recovery of phosphorus. Development in the area of
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34 66 phosphorus recovery via adsorption has led to the use of a wide range of adsorbents. To
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36 67 maintain economic feasibility of the process the adsorbents should be: i) abundance and low-cost
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38 68 to ensure constant supply, ii) display high selectivity, and iii) recover phosphorus in a suitable
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40 69 form. Adsorbents that could be used are classified into natural and synthetic materials.

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43 70 Natural adsorbent materials are often locally abundant, easy to dispose and include
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45 71 environmental friendly by-products such as orange peel, biochar, calcinated shellfish shells ^{11,12},
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47 72 fly ash ¹³ and slag ^{10,14,15}. These adsorbents can be used as agricultural amendments, because
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49 73 they contain both P and other useful contents (either organic carbon or minerals such as calcium)
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51 74 ¹⁶.

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3 75 Alternatively, adsorption onto various chemicals (e.g., nanoscale zero-valent iron), minerals
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5 76 (zeolites, lanthanum), mineral wastes (concrete, iron slag) are not useable as agricultural
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7 77 amendments, but the objective is to desorb the nutrient to obtain a clean P solution from which a
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9 78 useful phosphate product can be precipitated. Unlike natural absorbents, synthetic media can be
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11 79 optimized to have specific properties that will increase adsorptive capacity and be adjusted to
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13 80 withstand operational conditions.

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16 81 In recent years, new alternatives have been developed as more selective sorbents. Adsorption
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18 82 is the most suitable technique particularly for low phosphate concentrations and is easy to
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20 83 operate, fast and inexpensive ¹⁷.

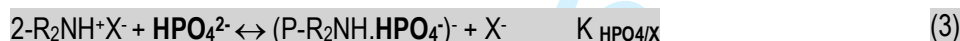
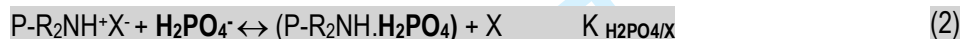
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23 84 Polymeric ion exchangers became a very suitable alternative as they combine high
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25 85 mechanical and hydraulic properties with the selectivity of hydrated metal oxides (HMO) toward
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27 86 oxyanions as phosphate ^{18,19}. Among the variety of hydrated metal oxides, hydrated ferric oxide
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29 87 (HFO) is characterized to be innocuous, inexpensive, readily available, chemically stable over a
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31 88 wide pH range and provides sizes of freshly precipitated amorphous HFO particles between 10 to
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33 89 100 nm ²⁰.

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36 90 Several attempts have been made to disperse HFO nanoparticles within various support
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38 91 materials such as alginate, zeolite, cation exchange resin or activated carbon, with not expected
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40 92 improvement in material sorption capacity ²⁰⁻²³. In the last years, it was shown that the ligand
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42 93 sorption capacity can be greatly increased by dispersing HFO nanoparticles within polymeric
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44 94 anion exchangers ²⁴.

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47 95 The aim of this study was to explore the phosphate sorption capacity, the regeneration and
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49 96 the reusability of two hybrid inorganic/polymeric sorbents impregnated with amorphous iron
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51 97 hydroxide particles in bead and fibrous forms as well as to quantify their capacity to recover
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53 98 phosphate from treated domestic wastewater as tertiary treatment.

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3 99 Previous studies revealed that equilibrium experimental data were well described by Langmuir
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5 100 isotherm model and reported sorption capacities of 89 and 163 mg PO₄/g for FO36 and Fiban-As,
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7 101 respectively. The effect of interfering anions on sorption capacity was evaluated through fractional
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10 102 factorial experiments concluding that both sorbents are highly selective to phosphate compared
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12 103 with bicarbonate, sulfate, nitrate and chloride. Furthermore, kinetic experiments showed that
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14 104 sorption kinetic for both sorbents is controlled by the particle diffusion step ^{25,26}.

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16 105 Sorption mechanism for FO36 could be described by the combination of the exchange of P(V)
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18 106 anions (H₂PO₄⁻/ HPO₄²⁻) with tertiary amine groups of the resin (Eqs. 1-3) and the sorption/ion-
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20 107 exchange of P(V) anions (H₂PO₄⁻/ HPO₄²⁻) with ≡FeOH groups of supported HFO particles (Eq. 4
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22 - 5) ²⁷. In the case of Fiban-As, the sorption can be described by only the interaction of phosphate
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24 108 ions with ≡FeOH groups present on the fiber surface.
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42 111 where P-R₂N represents P-CH₂-NH⁺(CH₃)₂ and the counter anion for FO36 (X⁻) is SO₄²⁻
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46 113 The purpose is to assess the overall sorption performance of both sorbents in fixed bed
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48 114 column experiments and to use a well-established fixed-bed sorption approach (Thomas model)
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50 115 in order to describe the experimental data and to determine the sorption capacity. Finally, the
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52 116 regeneration and reuse capacity of the sorbents were also evaluated through five working cycles
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55 117 by carrying out elution and sorption-desorption experiments, respectively.
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119 2. Material and Methods

120 2.1 Materials

121 Lewatit FO36 resin was provided by the Lanxess Company (Germany) and the fibrous ion
 122 exchanger Fiban-As was synthesized at the Institute of Physical Organic Chemistry, National
 123 Academy of Sciences (Belarus). FO36 resin is commercialized by Lanxess with a cost around
 124 USD 25/ L of bed. In the case of Fiban-As, the ion exchanger was developed by the Belarus
 125 National Academy of Sciences and has not yet been commercialized. Typical characteristics of
 126 both sorbents are summarized in Table 1 ^{25,26}. Both ion exchangers were used in the sorption
 127 experiments as supplied.

128 Table 1. Physicochemical properties of Lewatit FO36 and Fiban-As.

	Lewatit FO36	Fiban-As
Matrix	PS-DVB	Acrylic
Structure	Macroporous	
Functional groups	Tertiary amine groups P-CH ₂ -N- (CH ₂ -CH ₃) ₂	Secondary amine groups N- (CH ₃) ₂
Iron oxide content (%)	18-23 (%)	1.07 (mmol/g)
Physical form	Brown, round beds 0.35 (±0.06)	Staple fiber
pH range	4.5-8.5	4.5-8.5

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130 2.2 Dynamic sorption experiments

131 All column experiments were conducted in duplicate using glass columns of 100 mm length and
 132 15 mm internal diameter (Omnifit), uniformly packed with 9.5 g and 3.5 g of FO36 and Fiban-As,
 133 respectively. A synthetic phosphate aqueous solution (10 mgPO₄³⁻/L) containing chloride (300
 134 mg/L), hydrogen carbonate (300 mg/L), sulfate (150 mg/L) and nitrate (50 mg/L) was used for
 135 experiments with multicomponent composition. These concentrations were selected accordingly

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3 136 to the average background composition of a secondary effluent in a wastewater treatment plant
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5 137 (WWTP). Moreover, the secondary effluent was also used (characteristics are summarized in
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7 138 Table 2) in dynamic experiments. It is worth to mention that the used secondary effluent showed
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9 139 brown colour and high quantity of suspended solids.

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11 140 During the column sorption operation, the both types of water were pumped upwards through the
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13 141 column at a constant flow rate (2 mL/min). Samples from the outlet of the column were collected
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15 142 using a fraction collector (Gilson FC204) at given time intervals.
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21 144 Table 2. Chemical parameters of wastewater treatment plant secondary effluent

pH	8.34	Chloride (mg Cl ⁻ /L)	395.8
Conductivity (μS/cm)	218	Nitrate (mg NO ₃ ⁻ /L)	0.13
TOC (mg C/L)	14	Sulfate (mg SO ₄ ²⁻ /L)	233.52
Phosphate (mg PO ₄ ³⁻ /L)	10.36		

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38 148 Sorbents were considered saturated when column outlet effluent concentration reached the 95%
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40 149 of inlet concentration. Saturated columns (loaded sorbents) were washed in close loop with
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42 150 deionized water for 30 minutes and then were regenerated using NaOH solution (20 g/L) at the
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44 151 same flow rate than sorption experiments (2 mL/min). Later on, 0.1 M HCl (500 mL) was pumped
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46 152 into the column in order to regenerate the functional groups of the sorbent bed and finally it was
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48 153 conditioned with deionized water (1 L) before reusing. Regeneration capacity was evaluated
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50 154 through five sorption-desorption cycles.
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157 2.4 Analytical methods

158 Samples obtained from the multicomponent (synthetic and secondary effluent) experiments were
159 filtered with 0.20 μm filters and were analysed spectrophotometrically to determine total
160 phosphate content (Hewlett Packard, Model HP-8453) using the colorimetric stannous chloride
161 protocol ASTM 4500-P²⁸. Ionic chromatography (Dionex ICS1000 CS-16 (Vertex, Molins de Rei,
162 Spain)) was used to determine Cl^- , SO_4^{2-} and NO_3^- concentrations in samples. Solid samples
163 were analysed using a JEOL 3400® field emission scanning electron microscope with energy
164 dispersive system (FE-SEM-EDS) (JEOL Europe SAS, Croissy Sur Seine (France)).

166 2.5 Breakthrough capacity

167 The breakthrough point is chosen arbitrarily at 5% of initial concentration of phosphate, C_b (mg/L);
168 and the sorbent is considered to be exhausted when the effluent concentration, C_x (mg/L),
169 reaches the 90% of C_0 (initial concentration of PO_4^{3-} , mg/L). The capacity at exhaustion q_{column}
170 (mg/g) is determined by calculating the total area below the breakthrough curve (amount of PO_4^{3-}
171 sorbed by mass of sorbent in the sorption zone from the breakpoint to exhaustion)^{29,30}.

$$172 \quad q_{\text{column}} = \frac{\int_{V_b}^{V_x} (C_0 - C) dv}{m_s} \quad (6)$$

173 Where C is the outlet PO_4^{3-} concentration (mg/L) and m_s is the mass of the particle/fiber (g) in the
174 column (the sorbent loss to the water phase during the experiment can be considered negligible).

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176 A well-known model was used to describe the phosphate sorption on both sorbents under flow
177 dynamic conditions. The Thomas Model assumes Langmuir sorption isotherm, no axial dispersion
178 and that the driving force obeys second-order reversible reaction kinetics³¹ was used to fit the
179 experimental data as expressed by Eq. 7.

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{K_T q_0 m}{Q} - K_T C_0 t$$

(7)

180 where K_T is the Thomas rate of constant (mL/min·mg), q_0 the PO_4^{3-} sorption capacity (mg/g), Q
181 the flow rate (mL/min) and m the mass of fibre (g).

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183 3. Results and Discussion

184 3.1. Physico-chemical characterization of sorbents

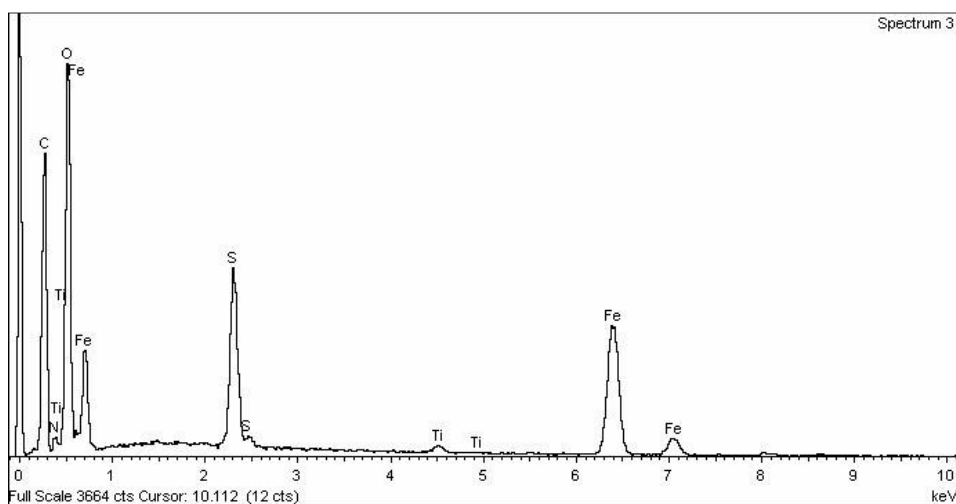
185 The characterization of raw sorbents was performed by Scanning Electron Microscope and
186 Energy Dispersive X-Ray Spectrometer (SEM/EDS). The FO36 shows a perfect spherical form of
187 the beads with an average diameter of 220 – 250 μm according to the SEM analysis. For Fiban-
188 As, irregular filament forms were visualized with an average section size of 40 – 50 μm ^{25,26}.

189 The spectra for EDS for both raw FO36 and Fiban-As are shown in Figure 1. Both sorbents
190 revealed the presence of iron, despite in the case of FO36, the content of iron is significantly
191 higher than for Fiban-As, which could be an indicative of an improved selectivity.

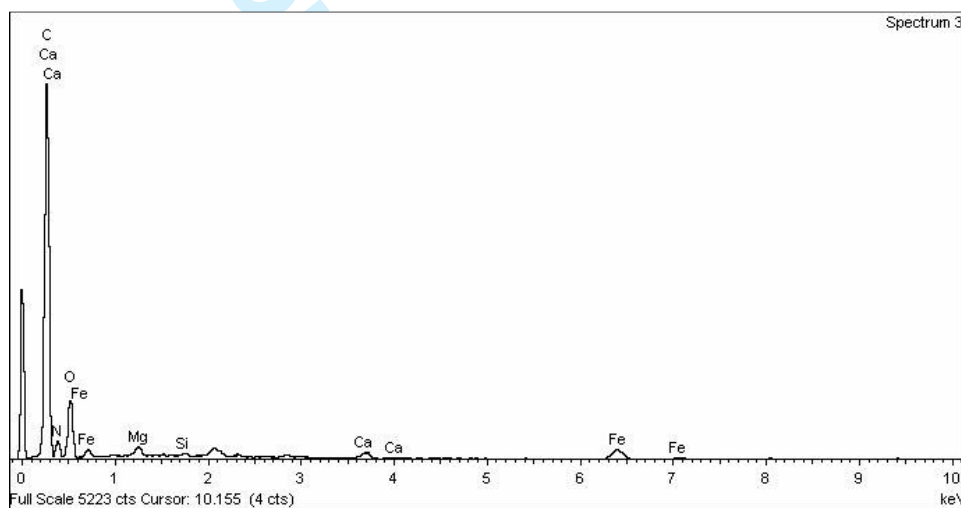
192 It also could be identified the constituents of the polymeric matrix; carbon, oxygen, titanium and
193 sulphide in the case of FO36 and carbon, nitrogen and oxygen in the case of Fiban-As.

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a



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195 Figure 1. EDS spectra of a) resin FO36 and b) fiber Fiban-As

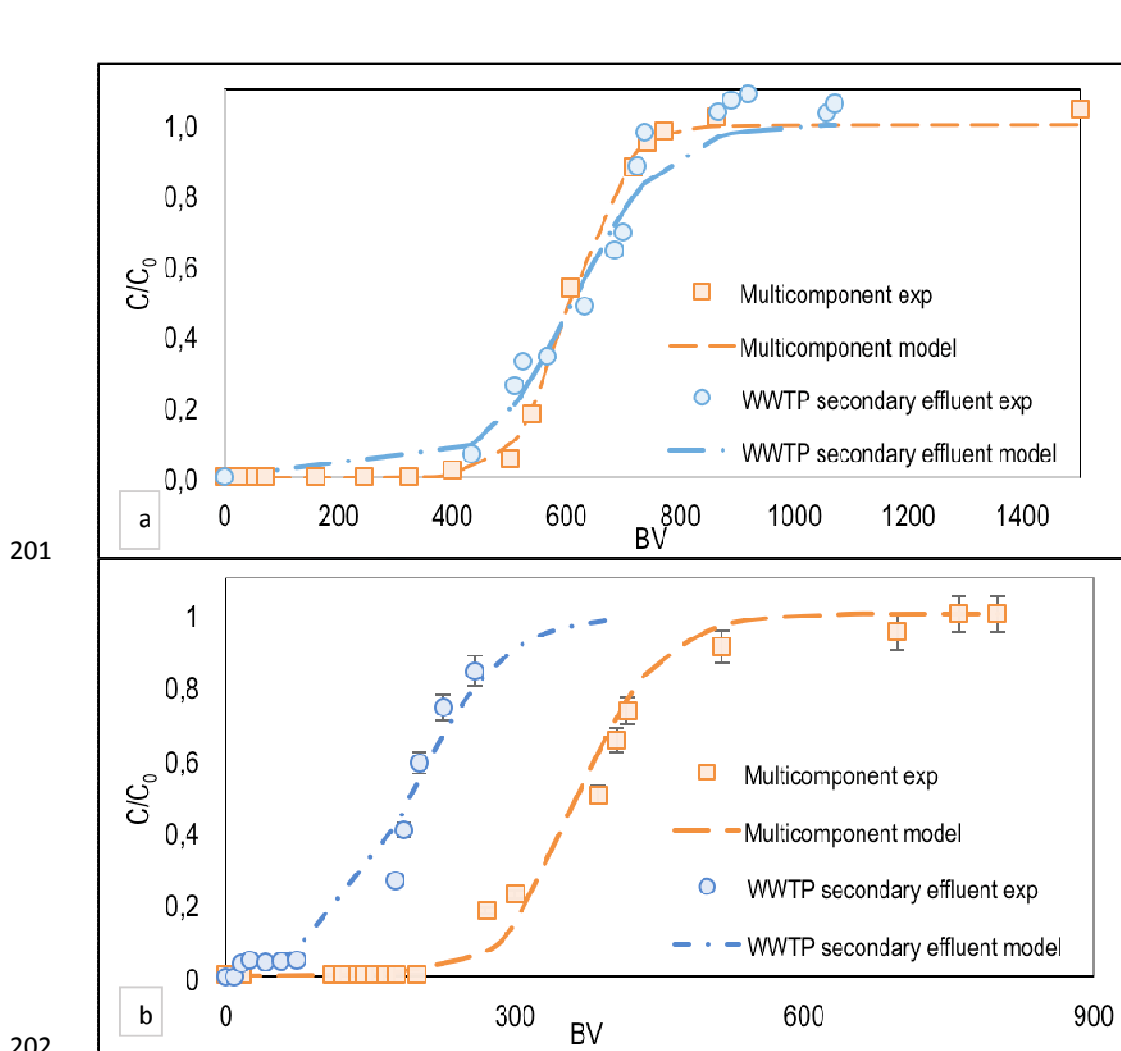
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197 3.2. Sorption experiments

198 The results of dynamic experiments were used to obtain the breakthrough curves for phosphate

199 sorption in multicomponent (synthetic and secondary effluent) aqueous solution systems onto

200 FO36 and Fiban-As sorbents. The experimental breakthrough curves are shown in Figure 2.



203 Figure 2. Flow dynamic experiments data for multicomponent and WWTP secondary effluent
 204 systems and the theoretical breakthrough curves obtained by Thomas model for a) FO36 and b)
 205 Fiban-As.

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 207 In the case of FO36, the shape of breakthrough curves approximately follows the same trend for
 208 multicomponent and WWTP secondary effluent systems as can be seen in Figure 2, where a
 209 common s-shaped breakthrough curve was observed with a breakthrough volume at 500 BV. A
 210 different behaviour was observed in the case of Fiban-As, where more significant differences
 211 were observed with faster breakthrough volumes for WWTP secondary effluent (75 BV) than
 212 synthetic water (236 BV). The suspended solids and natural organic matter present in secondary

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3 213 effluent sample can cause the differences in treated bed volumes, since phosphate initial and
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5 214 competing ions concentrations are similar.

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7 215 The experimental and the sorption parameters obtained by fitting the experimental breakthrough
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9 216 data to Thomas model for PO_4^{3-} sorption onto FO36 and Fiban-As are summarized in Table 3.
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11 217 Experimental data revealed that the resin FO36 reported better sorption performance than Fiban-
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13 218 As regarding sorption of phosphate in all studied experimental conditions, most probably due to
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15 219 the dual sorption mechanism in the case of FO36 as is was explained in introduction section.
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21 220
22 221 Table 3. Thomas model parameters for phosphate sorption in multicomponent synthetic water
23 222 containing competing anions and WWTP secondary effluent.

	FO36		Fiban-As	
	q_0 (mg PO_4 /g)	r^2	q_0 (mg PO_4 /g)	r^2
Multicomponent synthetic water with competing anions	11.4	0.98	9.8	0.91
WWTP secondary effluent	10.3	0.93	5.0	0.95

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39 224 Martin et al.³² evaluated a hybrid anion exchange resin (PhosX^{np}) in fixed bed mini column
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41 225 experiments with real final effluent from two UK sewage treatment works, one with treatment
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43 226 based on chemical precipitation with Fe(III) chloride salts into an activated sludge process and
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45 227 one based on trickling filter treatment with no specific phosphorus removal process.

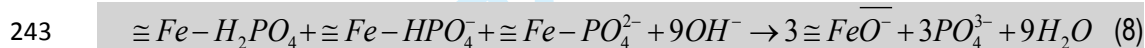
46
47 228 Results show that the hybrid sorbent has high capacity for removing phosphate with performance
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49 229 greatly exceeding that of a standard anion exchanger Amberlite IRA-410. Sorption capacities
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51 230 were reached at 4000 and 1000 bed volumes for the chemical precipitation (treated 0.4 mg P-
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53 231 PO_4 /L) and trickling filter works (treating 15 mg P- PO_4 /L), respectively. PhosX^{np} resins reached
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55 232 saturation after treating 1000 BV with a resin capacity of 23.6 mg PO_4 /g from a starting
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3 233 concentration of 15.2 mg P-PO₄/L. In contrast, the standard anion-exchange resin Amberlite
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5 234 IRA400 saturated after 170 BV with a resin capacity of 1 mgP-PO₄/g. This was due to the resin
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7 235 preference for sulfate, which results in early breakthrough and chromatographic elution of
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9 236 phosphate. In comparison with the wastewater effluent in this study, sulfate and chloride
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11 237 concentrations were smaller, and additionally the treated effluent contains 10 mg P-PO₄/L. Then,
12
13 238 in terms of resin capacity, measured values are comparable to those reported by Martin et al. ³².

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240 3.2 Desorption experiments

241 Resin was regenerated with sodium hydroxide solutions to revert the extraction reaction as
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23 242 described by Eq. 8:



244 The experimental data from desorption experiments is summarized in Table 4. The recovery ratio
245 was estimated taking into account the experimental sorption uptake during the sorption step as a
246 reference in calculations. The phosphate concentrations recovered using a regeneration volume
247 of 5 BV were 1382±12 mg/L and 707±10 mg/L for FO36 and Fiban-As, in synthetic solutions and
248 1080±11 mg/L and 1141±12 mg/L for FO36 and Fiban-As in WWTP secondary effluent system,
249 respectively. It should be pointing out that concentration factors higher than 400 were obtained
250 after the desorption step for both sorbents.

251 Similar studies performed with hybrid resin (PhosX^{np}) reported a total of 80% elution of P in the
252 first bed volume, generating a P concentrated of 1.3 g P-PO₄/L and a recommendation of losing a
253 20% reduction on resin capacity to achieve high concentration factors to simplify the subsequent
254 P recovery processes ³².

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257 Table 4. Summary of the results of sorption-desorption of phosphate onto FO36 and Fiban-As in
 258 multicomponent synthetic water containing competing anions and WWTP secondary effluent

Water type	Eluent	pH	Flow rate (mL/min)	Feed (mL)	Adsorbed (mg PO ₄)	Eluted (mg PO ₄)	Recovery (%)
FO36							
Multicomponent synthetic water with competing anions	NaOH 20 g/L	13.2	2	500	108	84	78
WWTP secondary effluent					60	45	75
Fiban-As							
Multicomponent synthetic water with competing anions	NaOH 20 g/L	13.2	2	500	35	33	93
WWTP secondary effluent					18	17	94

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260 The results are in agreement with those reported by Sperlich³³ using granular ferric oxide (GFH)
 261 to sorb phosphate and desorption was performed using 1 M NaOH (40 g/L) solution with
 262 approximately 80% of the initially bound phosphorus desorbed in the first regeneration step.
 263 Partial elution of phosphate from FO36 resin could be associated to a side co-removal
 264 mechanism of phosphate ions with Ca(II) ions involving the formation of calcium phosphates
 265 (hydroxyapatite or brushite)³⁴. The increase of phosphate concentration on the ion-exchange
 266 sites at high conversion ratios justifies reaching the saturation of both minerals on the resin

267 phase. Both minerals are highly insoluble in strong alkaline media, as the used for the
 268 regeneration, and it could explain the partial resin regeneration. The formation of calcium
 269 phosphate minerals on the sorbent structure has been described on the removal of phosphate by
 270 using calcium rich sorbents ³⁴. FSEM-EDAX and XRD analysis did not identified both minerals on
 271 the resin structure. Consequently, the differences on regeneration behaviour of FO36 in
 272 comparison with Fiban-As is not fully understood.

273 Those rich concentrated solutions could be used to obtain phosphate secondary resources for the
 274 production of fertilizers or to in-plant production of slow-release fertilizers by using Mg(II) and K(I)
 275 to produce struvite or Ca(II) to produce brushite (CaHPO₄(s)) ³⁵. According to Sperlich, the
 276 recovery of phosphate by precipitation of calcium phosphate resulted in more than 90%
 277 phosphorus removal and the precipitate was postulated as a potential fertilizer ³³.

279 3.3 Sorption-desorption working cycles

280 Results of modelling experimental of five sorption-desorption cycles for FO36 and Fiban-As are
 281 collected in Table 5.

283 Table 5. Column experiments results for five consecutive sorption regeneration cycles using
 284 multicomponent synthetic water as test sample and NaOH 20g/L as desorption solution for FO36
 285 and Fiban-As.

		1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle
FO36	K _T	0.20	0.35	0.28	0.26	0.09
	q ₀	6.67	1.71	0.48	0.42	0.33
			(<76%)	(<93%)	(<94%)	(<95%)
	r ²	0.93	0.93	0.79	0.86	0.81
Fiban-As	K _T	0.23	0.23	0.26	0.51	0.20

	q_0	9.81	8.81 (<10%)	7.04 (<28%)	3.87 (<61%)	1.81 (<82%)
	r^2	0.91	0.95	0.94	0.87	0.95

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287 Data shown that resin FO36 sorbent capacity is significantly decreased from the first regeneration
288 until the third cycle, when these characteristics became almost stable with low sorption capacity.

289 In view of these results, the reuse of the sorbent lacks of interest due to the sorption capacity
290 decreases up to 70%. The measured resin capacities after 5 cycles of operation approaches
291 those for standard anion exchange resins ^{32,36,37} and then the application of FO36 on phosphate
292 removal is questionable.

293 The high reduction of the phosphate capacity of the FO36 resin is postulated to be related to the
294 dissolution or losses of iron hydroxide nanoparticles or the reduction of the phosphate capacity
295 due to the organic matter content. Blaney et al. ³⁷ reported that hydrated iron hydroxide
296 nanoparticles are expected to remain fixed within the exchanger for many operation cycles
297 however all the work done was carried out with synthetic solutions of phosphate ions. Moreover,
298 other studies described a small decrease of iron from the surface of the resin beads by
299 comparing new, used and regenerated beads through EDAX analysis ³².

300 Measured values of major elements present on the surface of the beads (C, O, N) during the
301 different usage cycles were in accordance with ion-exchange polymer bed composition. The
302 visual inspection of the hybrid beads shown to be smoother after use, hinting that nanoparticles
303 on the surface were being lost as it was confirmed by EDAX. In the present study, similar
304 behaviour was reported when the surface of FO36 resin was analysed by SEM-EDAX. Taking
305 into account the macroporous structure of the polymer beads a more detailed study on the
306 mesopores structure is needed.

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3 307 In the case of Fiban-As, it can be observed that sorbent capacity decreases after each
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5 308 regeneration cycle but not at the same level than resin FO36 and could be potentially reused for
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7 309 at least three cycles.

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10 310 It worth to point out that during regeneration of FO36 resin was observed a brown colour in the
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12 311 elution samples due to iron oxides presence in solution and in consequence a decrease in the
13
14 312 sorbent mass available for next cycle. The loss of iron oxides content could explain the quick
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16 313 decrease of phosphate sorption capacity.

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18 314 Sperlich³³ reported similar results when performing column test using GFH as sorbent. Due to
19
20 315 the incomplete desorption, the capacities of regenerated GFH were lower compared to the raw
21
22 316 sorbent samples and decreased with each additional use. In differential column-batch reactor
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24 317 tests, 85 % and 70 % of the initial capacity were reached after the first and second regeneration
25
26 318 cycle, respectively. When using rapid small-scale column test, the calculated capacity decreased
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28 319 to 99% after the first and 80% of the initial capacity after the second regeneration. Although
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30 320 regeneration of the material is clearly limited, up to 3 operation cycles appear feasible

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34 321 For hybrid ion-exchange resins containing iron hydroxide nanoparticles (PhosX^{np}), the only
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36 322 reported cycles of regeneration and elution experiments, indicates a non-deterioration of resin
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38 323 capacity after 10 partial regenerations³². However, the reported shapes of the breakthrough
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40 324 curves shown a reduction on the resin capacity with the initial reported values by a factor of 10
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42 325 and a displacement with cycles to lower resin capacities.

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45 326 The contactor scale on the performance of an iron hydroxide nanoparticle impregnated sorbent
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47 327 has been shown to impact both the operational sequence and the total capacity of phosphate
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49 328 uptake³². Increasing contactor size results in logarithmic increases in the observed P removal
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51 329 capacity of the hybrid sorbents and bed life is significantly extended in larger columns.

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332 Conclusions

333 Column studies on the evaluation of composite fibres and polymeric beads obtained by
334 incorporation of HFO for selective removal of oxyanions have been conducted. The advantage of
335 these hybrid ion exchangers is the higher selectivity toward oxyanions and its lower affinity for
336 nitrate, chloride and sulfate ions. Thus, these sorbents can be also used for selective recovery of
337 phosphate ions.

338 Moreover, the regenerability, reuse and the high mechanical strength and therefore easy to
339 backwash or to pump in suspension of Fiban-As represent significant advantages compared to
340 other sorbents.

341 Dynamic experiments reported a maximum loading of 48 ± 4 and 28 ± 2 mg PO₄/g sorbent on
342 FO36 and Fiban-As, respectively. Regeneration studies showed that the sorbent can be eluted
343 efficiently with NaOH solutions achieving pre-concentration factors up to 360 allowing the
344 valorisation of these rich PO₄³⁻ solutions as calcium and magnesium mineral phosphates.

345 Despite FO36 showed the best sorption performance in terms of sorption capacity, this is not the
346 best option for being used as sorbent for phosphate recovery from WWTP effluents as it is not
347 available for being reused. In desorption process, it was observed that iron was released during
348 regeneration step and it was confirmed by the sorbent mass losses, which in the end represented
349 a significant sorption capacity reduction.

350 The small scale column trials described in this study are very useful for an initial assessment of
351 efficiency of the process, but operation parameters (e.g., linear velocities and pressures) involved
352 in full scale operation could be much higher. Then, until such validation is completed on a pilot
353 scale, the life cycle of the hybrid impregnated resin will not be adequately quantifiable.

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12 360 **References**

- 13
14 361 1. Bennett, E. M. & Schipanski, M. E. in *Fundam. Ecosyst. Sci.* (Elsevier, 2013).
15
16 362 2. Schröder, J. J., Cordell, S., Smit, A. L. & Rosemarin, A. Sustainable use of phosphorus,
17
18 363 Report 357. (2010).
19
20 364 3. Jasinski, S. M. *Phosphate Rock Statistics and Information*. (2015).
21
22 365 4. Peleka, E. N., Mavros, P. P., Zamboulis, D. & Matis, K. A. Removal of phosphates from
23
24 366 water by a hybrid flotation–membrane filtration cell. *Desalination* 198, 198–207 (2006).
25
26 367 5. Seida, Y. & Nakano, Y. Removal of phosphate by layered double hydroxides containing
27
28 368 iron. *Water Res.* 36, 1306–1312 (2002).
29
30 369 6. Razali, M., Zhao, Y. & Bruen, M. Effectiveness of a drinking-water treatment sludge in
31
32 370 removing different phosphorus species from aqueous solution. *Sep. Purif. Technol.* 55, 300–306
33
34 371 (2007).
35
36 372 7. Awual, R. & Jyo, A. Rapid column-mode removal of arsenate from water by crosslinked
37
38 373 poly(allylamine) resin. *Water Res.* 43, 1229–1236 (2009).
39
40 374 8. Awual, M. R. & Jyo, A. Assessing of phosphorus removal by polymeric anion exchangers.
41
42 375 *Desalination* 281, 111–117 (2011).
43
44 376 9. Jellali, S., Wahab, M. A., Hassine, R. Ben, Hamzaoui, A. H. & Bouselmi, L. Adsorption
45
46 377 characteristics of phosphorus from aqueous solutions onto phosphate mine wastes. *Chem. Eng.*
47
48 378 *J.* 169, 157–165 (2011).
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 379 10. Haddad, K. et al. Raw and treated marble wastes reuse as a low cost material for
4
5 380 phosphorus removal from aqueous solutions: efficiencies and mechanisms. *Comptes rendus*
6
7 381 *Chim.* 18, 75–87 (2015).
- 8
9 382 11. Xiong, J., Qin, Y., Islam, E., Yue, M. & Wang, W. Phosphate removal from solution using
10
11 383 powdered freshwater mussel shells. *Desalination* 276, 317–321 (2011).
- 12
13 384 12. Abeynaike, A., Wang, L., Jones, M. I. & Patterson, D. A. Pyrolysed powdered mussel
14
15 385 shells for eutrophication control: effect of particle size and powder concentration on the
16
17 386 mechanism and extent of phosphate removal. *Asia-Pacific J. Chem. Eng.* 6, 231–243 (2011).
- 18
19 387 13. He, X., Xu, W., Sun, W. & Ni, J. Phosphate removal using compounds prepared from
20
21 388 paper sludge and fly ash. *Environ. Earth Sci.* 70, 615–623 (2012).
- 22
23 389 14. Barca, C., Gérente, C., Meyer, D., Chazarenc, F. & Andrès, Y. Phosphate removal from
24
25 390 synthetic and real wastewater using steel slags produced in Europe. *Water Res.* 46, 2376–84
26
27 391 (2012).
- 28
29 392 15. Jaouadi, S., Wahab, M. A., Anane, M., Bousselmi, L. & Jellali, S. Powdered marble
30
31 393 wastes reuse as a low-cost material for phosphorus removal from aqueous solutions under
32
33 394 dynamic conditions. *Desalin. water Treat.* 52, 7–9 (2014).
- 34
35 395 16. Scholz, R. W., Ulrich, A. E., Eilittä, M. & Roy, A. Sustainable use of phosphorus: a finite
36
37 396 resource. *Sci. Total Environ.* 461–462, 799–803 (2013).
- 38
39 397 17. Baliarsingh, N., Parida, K. M. & Pradhan, G. C. Influence of the nature and concentration
40
41 398 of precursor metal ions in the brucite layer of LDHs for phosphate adsorption –a review. *RSC*
42
43 399 *Adv.* 3, 23865–23878 (2013).
- 44
45 400 18. Zhu, X. & Jyo, A. Column-mode phosphate removal by a novel highly selective
46
47 401 adsorbent. *Water Res.* 39, 2301–2308 (2005).
- 48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 402 19. Awual, M. R., Jyo, A., El-Safty, S. a, Tamada, M. & Seko, N. A weak-base fibrous anion
4
5 403 exchanger effective for rapid phosphate removal from water. *J. Hazard. Mater.* 188, 164–71
6
7 404 (2011).
8
9
10 405 20. DeMarco, M. J., SenGupta, A. K. & Greenleaf, J. E. Arsenic removal using a
11
12 406 polymeric/inorganic hybrid sorbent. *Water Res.* 37, 164–176 (2003).
13
14 407 21. Huang, C. C. & Vane, L. M. Enhancing Removal by a Activated Carbon. *Res. J. Water*
15
16 408 *Pollut. Control Fed.* 61, 1596–1603 (1989).
17
18 409 22. Katsoyiannis, I. & Zouboulis, A. Removal of arsenic from contaminated water sources by
19
20 410 sorption onto iron-oxide-coated polymeric materials. *Water Res.* 36, 5141–5155 (2002).
21
22
23 411 23. Onyango, M. S., Kojima, Y., Matsuda, H. & Ochieng, A. Adsorption Kinetics of Arsenic
24
25 412 Removal from Groundwater by Iron-Modified Zeolite. *J. Chem. Eng. Japan* 36, 1516–1522
26
27 413 (2003).
28
29 414 24. Nie, G., Wang, J., Pan, B. & Lv, L. Surface chemistry of polymer-supported nano-
30
31 415 hydrated ferric oxide for arsenic removal: effect of host pore structure. *Sci. China Chem.* 58, 722–
32
33 416 730 (2015).
34
35
36 417 25. You, X., Guaya, D., Farran, A., Valderrama, C. & Cortina, J. L. Phosphate removal from
37
38 418 aqueous solution using a hybrid impregnated polymeric sorbent containing hydrated ferric oxide
39
40 419 (HFO). *J. Chem. Technol. Biotechnol.* 91 (3) 693-704 (2016).
41
42
43 420 26. You, X., Farran, A., Guaya, D., Valderrama, C., Soldatov, V. & Cortina J.L. Phosphate
44
45 421 removal from aqueous solutions using a hybrid fibrous exchanger containing hydrated ferric oxide
46
47 422 nanoparticles. *J. Environ. Chem. Eng.* 4, 388–397 (2016).
48
49 423 27. Dzombak, D. A. & Morel, F. M. M. *Surface Complexation Modeling: Hydrous Ferric*
50
51 424 *Oxide.* (John Wiley & Sons, Inc., 1990).
52
53
54 425 28. American Public Health Association. in *Stand. Methods Exam. Water Wastewater* 108–
55
56 426 117 (American Public Health Association, 1992).
57
58
59
60

- 1
2
3 427 29. Florido, A., Valderrama, C., Arévalo, J., Casas, I., Martínez, M. & Miralles, N. Application
4
5 428 of two sites non-equilibrium sorption model for the removal of Cu(II) onto grape stalk wastes in a
6
7 429 fixed-bed column. *Chem. Eng. J.* 156, 298–304 (2010).
- 8
9 430 30. Gupta, V. K., Srivastava, S. K. & Tyagi, R. Design parameters for the treatment of
10
11 431 phenolic wastes by carbon columns (obtained from fertilizer waste material). *Water Res.* 34,
12
13 432 1543–1550 (2000).
- 14
15 433 31. Yılmaz İpek, İ., Kabay, N. & Yüksel, M. Modeling of fixed bed column studies for removal
16
17 434 of boron from geothermal water by selective chelating ion exchange resins. *Desalination* 310,
18
19 435 151–157 (2013).
- 20
21 436 32. Martin, B. D., Parsons, S. A. & Jefferson, B. Removal and recovery of phosphate from
22
23 437 municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide
24
25 438 nanoparticles. *Water Sci. Technol.* 60, 2637–2645 (2009).
- 26
27 439 33. Sperlich, A. Phosphate adsorption onto granular ferric hydroxide (GFH) for wastewater
28
29 440 reuse. (2010).
- 30
31 441 34. Hermassi, M., Valderrama, C., Moreno, N., Font, O., Querol, X., Batis, N.H., Cortina, J.L.,
32
33 442 Powdered Ca-activated zeolite for phosphate removal from treated waste-water. *J. Chem.*
34
35 443 *Technol. Biotechnol.* 91 (7), 1962-1971 (2016).
- 36
37 444 35. Hermassi, M., Valderrama, C., Dosta, J., Cortina, J. L. & Batis, N. H. Evaluation of
38
39 445 hydroxyapatite crystallization in a batch reactor for the valorization of alkaline phosphate
40
41 446 concentrates from wastewater treatment plants using calcium chloride. *Chem. Eng. J.* 267, 142–
42
43 447 152 (2015).
- 44
45 448 36. Zhao, D. & Sengupta, A. K. Ultimate removal of phosphate from wastewater using a new
46
47 449 class of polymeric ion exchangers. *Water Res.* 32, 1613–1625 (1998).
- 48
49 450 37. Blaney, L. M., Cinar, S. & SenGupta, A. K. Hybrid anion exchanger for trace phosphate
50
51 451 removal from water and wastewater. *Water Res.* 41, 1603–13 (2007).
- 52
53
54
55
56
57
58
59
60