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# Modifying the resin type of hybrid anion exchange nanotechnology (HAIX-Nano) to improve its regeneration and phosphate recovery efficiency

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In order to avoid eutrophication of freshwater systems, regulations all around the world have become increasingly stringent toward the maximum phosphate concentration allowed in wastewater discharges. Traditional phosphate removal methods such as chemical precipitation and enhanced biological phosphorus removal struggle to lower phosphate levels to the new requirements. Hybrid anion exchange nanotechnology (HAIX-Nano) is composed of a selective adsorption material able to remove phosphate down to levels close to zero. Moreover, HAIX-Nano is not affected by intermittent flow and does not produce sludge making it an interesting alternative. The regeneration process of HAIX-Nano typically requires a chemical solution with a high concentration of sodium hydroxide (NaOH) and sodium chloride (NaCl) (2–5% w/w of each). To lower the environmental impact and the operational cost of the technology, this study aims to enhance the HAIX-Nano regeneration efficiency. Therefore, the backbone of HAIX-Nano, which is normally a strong base anionic (SBA) resin, was changed for a weak base anionic (WBA) resin. The resulting material (WBA-2) exhibited a higher adsorption capacity than the traditional version of HAIX-Nano (SBA-1) under the tested conditions, while also showing a much higher regeneration efficiency. For a desorption solution of only 0.4% NaOH and no NaCl, WBA-2 showed an average regeneration efficiency of  $78 \pm 1\%$  compared to SBA-1 with  $24 \pm 1\%$ .

npj Clean Water (2021)4:53; https://doi.org/10.1038/s41545-021-00142-1

#### INTRODUCTION

Before wastewaters can be discharged in the environment, they need to go through a nutrient removal step where excess nitrogen and phosphates are reduced to acceptable levels<sup>1</sup>. If this step is skipped, freshwater systems receiving the wastewater can become overly enriched in nutrients leading eventually to eutrophication. Eutrophication leads to adverse effects for the ecology and greatly reduces the water quality<sup>2,3</sup>. The estimated cost of eutrophication has reached billions of dollars in the United States<sup>4</sup>. What is defined as "too much phosphates" in wastewaters depends on many items including the location and water body in which the water is discharged. Nevertheless, regulations across the globe are generally becoming more stringent towards maximal phosphate levels allowed to be discharged. For example:

- Florida Everglades: 0.01 mg/L as P<sup>5</sup>
- Guideline England: 0.1 mg/L as P<sup>6</sup>,
- Industrial effluents in China: 0.5 mg/L as P<sup>7</sup>
- WWTPs discharging effluent to the Lake Simcoe Watershed in Ontario: 0.1 mg/L as P<sup>8</sup>.

While traditional phosphate removal methods such as chemical precipitation are good at removing most of the phosphate contained in wastewater, they struggle to remove it down to levels as low as  $0.1 \text{ mg/L}^9$  (P-PO<sub>4</sub>). For example, about 3 to 5 times more aluminum or iron salts are needed to remove phosphate down to  $0.1 \text{ mg/L}^{6,10}$ . Hybrid ion exchange nanotechnology (HAIX-Nano) is a regenerable adsorption technology able to remove phosphate to a nearzero level<sup>5</sup>. Thus, it could be used as a complementary method to remove phosphate, or in certain cases like decentralized

wastewater treatment plants (WWTPs), as a substitute for traditional removal methods.

To regenerate a saturated HAIX-Nano media, typically high amounts of NaOH and NaCl are required. Although one study in literature has succeeded to partially regenerate HAIX-Nano using only one bed volume (BV) of 2% NaOH<sup>11</sup>, most studies use between 10 and 15 BVs and between 2 and 5% w/w of both NaCl and NaOH<sup>5,7,12–15</sup>. This makes the operational costs for HAIX-Nano slightly too expensive to compete with current phosphate removal technologies on the market<sup>6</sup>. To lower the environmental impact and operational cost of HAIX-Nano, this study investigated a way to reduce its chemical needs.

HAIX-Nano is typically composed of a strong base anionic (SBA) resin skeleton impregnated with hydrated ferric oxide (HFO) nanoparticles<sup>5,16</sup>. Both the SBA resin and HFO particles provide sorption sites for phosphate ions. The quaternary ammonium functional groups  $(R_4N^+)$  from the ion exchange resin have coulombic interactions with orthophosphates, but also with any other anions. For example, sulfate ions have an even stronger affinity for the functional groups than phosphates and generate an important competition<sup>5,7,17</sup>. The positively charged functional groups also indirectly increase the adsorption capacity through the Donnan membrane effect<sup>5,16</sup>. On the other hand, HFO nanoparticles have a much stronger affinity towards phosphate ions than any other common ions found in wastewater (Cl<sup>-</sup>, SO<sub>4</sub><sup>2</sup>, NO<sub>3</sub><sup>-</sup>, etc.). HFO adsorption sites form ligand exchange interactions with the orthophosphates making the sorption process strongly selective<sup>18,19</sup>. OH<sup>-</sup> ions also form ligand exchange interactions with the HFO surface, but they can not compete with the phosphate in the wastewater because the pH is too low<sup>20</sup>. For the desorption process, a high concentration of

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Fig. 1 Comparison of phosphate behavior during the adsorption and desorption process for SBA and WBA resins. During the adsorption process, at near neutral pH, both SBA and WBA resins are able to bind with phosphate ions. During the desorption process, at high pH, phosphate ions can still bind with the SBA resin, but are unable to bind with the WBA resin.

hydroxide ions is introduced in the system, thereby raising the pH. Hydroxide ions can then displace phosphate ions from the HFO sorption sites, effectively desorbing them. Above the point of zero charge of iron oxide, which is between 8 and 9.5<sup>21</sup>, the ability of phosphate to maintain its binding with the HFO greatly decreases<sup>20</sup>.

Although a higher pH will help desorbing phosphate from the HFO surface, it also increases its affinity for the quaternary ammonium groups. A higher pH increases the charge of orthophosphate species as can be seen in Eqs. 1 and 2. Equation 3 shows an affinity sequence of an SBA resin for different anions<sup>17</sup>. As we can see, higher charged phosphate species have an increased affinity for the functional groups of the resin. Since the phosphate anions desorbed from the HFO are highly concentrated and have an increased affinity for the guaternary ammonium groups, they can readily bind to the functional groups during the desorption process<sup>22</sup>. This phenomenon renders the phosphate desorption process inefficient. The only way to avoid this, is by using both high concentrations of NaOH and NaCl in the desorption solution. Chloride (Cl<sup>-</sup>) ions provide a competition for quaternary ammonium sorption sites and prevent PO<sub>4</sub><sup>3-</sup> from binding with those groups<sup>22</sup>.

$$H_2 PO_4^- + OH^- \leftrightarrow HPO_4^{2-} \qquad pK_a = 7.2 \tag{1}$$

 $HPO_4^{2-} + OH^- \leftrightarrow PO_4^{3-} \qquad pK_a = 12.31 \tag{2}$ 

$$PO_4^{3-} > SO_4^{2-} > HPO_4^{2-} > CI^- > H_2PO_4^- > OH^-$$
(3)

The aim of this study is to improve the desorption efficiency of HAIX-Nano by modifying its parent resin. The idea is to use a weak base anionic (WBA) resin instead of an SBA resin as the support for the HFO nanoparticles. WBA resins have positively charged tertiary ammonium groups ( $R_3NH^+$ ) at near neutral pH. Consequently, they contribute to the adsorption process in the same way as quaternary ammonium groups would in an SBA resin. However, tertiary ammonium groups lose their charge at higher pH, thereby losing their adsorption potential<sup>17,19</sup>. During the desorption process, the pH of the solution is raised and the functional groups are deprotonated, making it very unfavorable for the phosphate ions to bind with them. Figure 1 presents both kinds of functional groups either during the process of adsorption or during the process of desorption. As we can see, both the SBA and WBA resin can bind with phosphate during the adsorption process. During the desorption process, the SBA resin retains the phosphate by binding with it as explained above. On the other hand, the WBA resin does not interact with the phosphate. Therefore, it is hypothesized that for a HAIX-Nano material made from a WBA resin, phosphate ions should be able to diffuse out of the pores even at low NaOH concentrations and with no NaCl present.

## RESULTS AND DISCUSSION SEM and EDS tests

Figure 2 shows scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) analysis from beads of each HAIX-Nano version that were cut in half. Consequently, the interior of each adsorbent can be observed. Figure 2a, c, e represent the SEM images of SBA-1, WBA-1, and WBA-2, respectively. Figure 2b, d, f represent the close-up images for the EDS analysis of SBA-1, WBA-1, and WBA-2, respectively. The zones selected for the EDS analysis go from the interior of the beads to the exterior allowing to assess the quality of the iron dispersion.

A few disparities can be observed between those images. First, there is an apparent difference in the pore size. Indeed, SBA-1 seems to have much larger pores than the two WBA versions of HAIX-Nano. The SBA resin has a higher degree of crosslinking than its weak base counterpart used in the study. A higher degree of crosslinking enables a more rigid network and thus bigger pores<sup>19</sup>.

Table 1 represents the iron content in % w/w for the different zones identified in the images of Fig. 2b, d, f. It is important to note that the EDS analyses did not consider hydrogen and nitrogen in the mass balance, so iron content values may be slightly inflated, though they still reflect important trends. We can see in the close-up image of Fig. 2c that WBA-1 seems to have an iron oxide crust on its surface. The corresponding zone 4 shows an iron content of 52.7%, which suggests the presence of almost pure iron oxide. This iron oxide crust indicates a segregation of the iron oxide on the exterior of the resin beads and may cause additional boundary layer resistance for the mass transfer during the adsorption process of phosphates.

Further EDS analysis done on the interior of WBA-1 shows that zones 1 and 2 have respectively 2.6% and 3.3% of iron, which supports the idea that the WBA-1 synthesis method produces a poor dispersion of HFO throughout the resin bead. On the other hand, the WBA-2 synthesis procedure seems to produce a great dispersion of HFO with interior zones 1 and 2 at 24.3% and 23.5% of iron, while the exterior zones 3 and 4 have 30.6% and 31.3% of iron content. For SBA-1, the dispersion of iron is good with zones 1, 2 and 3 having similar iron contents of 34.7%, 32.8%, and 31.3%, respectively. Since SBA-1 seems to have much larger pores and the best dispersion of iron oxide, one might expect that it has the fastest initial adsorption rate because of an easier diffusion of phosphate. Since WBA-2 also has a good dispersion of iron, the adsorption process should also be favorable. While WBA-1 might have a good adsorption capacity for phosphate, it was decided that further tests would not be pursued on it. The important segregation of iron oxide on the surface of the resin bead suggests a poor synthesis method and the lifespan of the resulting



Fig. 2 SEM and EDS images of HAIX-Nano samples. a, b SBA-1 (SEM, EDS), c, d WBA-1 (SEM, EDS), e, f WBA-2 (SEM, EDS).

Table 1.         EDS analysis of SBA-1, WBA-1, and WBA-2: % Fe for the four selected zones.							
	% Fe						
	SBA-1	WBA-1	WBA-2				
Zone 1	34.7	2.6	24.3				
Zone 2	32.8	3.3	23.5				
Zone 3	31.3	24.5	30.6				
Zone 4	N/A	52.7	31.3				

material is expected to suffer because of the brittleness of the iron crust that can easily desintegrate over time.

#### **Fixed-bed column experiments**

Figure 3 presents adsorption uptake curves for both WBA-2 and SBA-1 in a fixed-bed setup. The initial adsorption rate of both

versions of HAIX-Nano is similar over the first hour. Then, SBA-1's adsorption rate starts to slow down more rapidly than WBA-2. Both curves seem to be close to a plateau near their end, suggesting that a certain equilibrium is reached. However, it is important to remember that the phosphorus concentration of the influent is quite high at 48 mg  $P-PO_4/L$ , while having an empty bed contact time (EBCT) of 2.1 min. Consequently, it is plausible that both adsorbents are further away from their equilibrium than it might seem, since they may be limited by intra-particle diffusion (IPD).

It is important to recall that the sulfate ions concentration in the influent was quite high (1160 ppm  $SO_4^{2-}$ ), meaning that the competition for ion exchange sites was strong. The experimental conditions thus reflect well the performance of an adsorbent for environments where a strong selectivity towards phosphate is needed. For example, wastewaters containing a low concentration of phosphate but high concentration of other anions such as sulfate or chloride will present an important competition for the ion exchange sites provided by either the quaternary ammonium groups or the tertiary ammonium groups. In those cases, HFO



Fig. 3 Adsorption uptake of phosphate over time. Adsorption uptake (mg P-PO<sub>4</sub>/mL of HAIX-Nano) vs time (minutes) for WBA-2 and SBA-1.



Fig. 4 Intra-particle diffusion plots. Adsorption uptake (mg P/mL of HAIX-Nano) vs time<sup>1/2</sup> (min<sup>1/2</sup>) for WBA-2 and SBA-1.

adsorption sites are expected to do most of the phosphate removal. This kind of situation can be encountered, for example, if HAIX-Nano is used as a polishing technology following a chemical precipitation process using a sulfate salt<sup>5,23</sup>.

The performance of every version of HAIX-Nano was tested for up to six adsorption/desorption cycles (in batch experiments) and showed stable adsorption capacities throughout the cycles. Moreover, the SBA version was also proven to last over 2 years of continuous use in a previous work done by Blaney et al.<sup>3</sup>.

#### **Adsorption kinetics**

Figure 4 shows the kinetic plots for the intra-particle diffusion (IPD) model. This model consists of plotting the adsorption uptake in function of the square root of time. Note that for this kinetic model and the following ones (Avrami and pseudo-second order (PSO) models), adsorption uptake was measured on a volume basis (mg P/mL of HAIX-Nano). It is more convenient to measure the wet volume of the adsorbent than to dry it and measure the mass. Moreover, HAIX-Nano is normally sold on a volume basis.

The IPD model is good for assessing if diffusion is a rate-limiting step. As can be seen, the first part of the curve is linear, meaning that IPD is a rate-limiting step<sup>24,25</sup>. However, since the intercepts of the curves are not zero, it means that IPD is not the sole rate-limiting step. A negative intercept normally means a combination of film diffusion and surface reaction control<sup>24,26,27</sup>. These results are in agreement with what has been observed previously with HAIX-Nano (SBA version), meaning that IPD is the main limiting step<sup>11,16,18</sup>.

Both HAIX-Nano versions are limited by IPD. To improve the phosphorus removal efficiency, the contact time needs to be increased. In the second part of the plot, the slopes of the curves become less steep, meaning that the adsorption is slowing down and saturation of the materials is approaching. In this part, the boundary layer is increasing which is due to an increase in internal mass transfer<sup>28</sup>. Note that the inflexion point of the SBA-1 plot is at 9.26 min<sup>1/2</sup> (86 min), while for WBA-2, it is at 11.95 min<sup>1/2</sup> (143 min). Since the SBA-1 inflexion point is so much earlier, it suggests that SBA-1 is probably much closer to its saturation point than WBA-2.

Table 2.	2. Kinetic parameters for Avrami and pseudo-second order models.								
	Experiment	Avrami			Pseudo-second order				
	Final $q_{t}$ (mg P/mL)	$K_{\rm A}$ (10 <sup>-3</sup> min <sup>-1</sup> )	q <sub>e</sub> (mg/mL)	R <sup>2</sup>	$K_2$ (10 <sup>-3</sup> mg*mL <sup>-1</sup> *min <sup>-1</sup> )	q <sub>e</sub> (mg/mL)	R <sup>2</sup>		
WBA-2	2.66	5.88	3.07	0.9998	1.05	4.98	0.9986		
SBA-1	2.02	11.95	2.14	0.9997	2.94	3.06	0.9979		

Kinetic parameters from two different models (PSO and Avrami) were extracted from the adsorption uptake curves<sup>24,29–31</sup>. Although those models are normally used for batch data, they can also be used for fixed-bed setups as long as the data comes from an adsorption uptake curve and is properly fitted<sup>30–32</sup>. Both models were fitted using least square minimization and further validated with the coefficient of determination ( $R^2$ ) and the average relative error (ARE). The fits with both the PSO model and the Avrami model were good with ARE values ranging from 1.2 to 3.2% and  $R^2$  values higher than 0.99.

The kinetic parameters from the two models can be seen in Table 2.  $K_A$  and  $K_2$  are the adsorption rate constants for the Avrami equation and for the PSO model.  $q_e$  is the adsorption uptake at equilibrium predicted for each model. In other words, it corresponds to the adsorption capacity estimated for the experimental conditions. The final experimental adsorption uptake is also written for each HAIX-Nano version.

We can see that the projected adsorption capacity  $q_e$  is different depending on the model. This is normal as the Avrami kinetic model is closely derived from the Pseudo-first order model (PFO). PFO and PSO kinetic models often give different predictions. PSO is normally thought to be mathematically superior for representing adsorption processes and is generally better for estimating adsorption capacity<sup>24</sup>. Even with their differences, it is possible to observe similar trends in both models. For example, in both models the predicted adsorption capacity is much higher for WBA-2 while the adsorption rate constants ( $K_A$  and  $K_2$ ) are higher for SBA-1. This is in line with what was observed in the previously presented SEM analyses. As seen on the SEM images, SBA-1 shows much larger pores, allowing for a faster initial adsorption rate proportional to its lower adsorption capacity. The final adsorption uptake is 32% higher for WBA-2 than SBA-1, while the predicted adsorption capacities are 44% higher for WBA-2 with the Avrami equation and 63% higher with the PSO model. Over time, the gap between the adsorption uptake of WBA-2 and SBA-1 is expected to widen as the adsorption uptake curves suggest. This is coherent considering that SBA-1 has a fast initial adsorption rate that rapidly decreases over the adsorption process.

#### Acid digestion of HAIX-Nano

The digestion tests showed that the iron content for SBA-1 is 26.4% (w/w) while the iron content for WBA-2 is 21.4% (w/w). Note that while the iron content is higher for SBA-1, WBA-2 still has a higher adsorption capacity on a volume basis. This is coherent with what was observed previously by Pan et al.<sup>7</sup>, who compared two versions of HAIX-Nano (both SBA). One of them had 19.8% Fe (ArsenX), while the other had only 10.2% (HFO-201). Interestingly, HFO-201 had a slightly higher removal efficiency of phosphate, event though its iron content was two times lower. Higher loadings of iron can cause blockage of pores or even favor agglomeration of HFO particles which decreases available adsorption sites.

In the original patent for HAIX-Nano (SBA version)<sup>33</sup>, the authors obtained an iron content of 16.1% with 3 cycles of synthesis, while the synthesis for WBA-2 in this study uses 4 cycles to impregnate an iron content of 21.4%. This means that the impregnation efficiency for each synthesis procedure is similar. It is interesting to

Table 3.	able 3. Removal and desorption efficiency for SBA-1 and WBA-2.					
HAIX ver	sion	Removal efficiency	Desorption efficiency			
WBA-2		62%±1%	78%±1%			
SBA-1		43% ± 1%	24% ± 1%			

note that the patented version of SBA-1 uses potassium permanganate, ferrous sulfate and acetone as the main chemicals for the synthesis procedure<sup>33</sup>. On the other hand, the synthesis for WBA-2 in this study only uses ferric chloride, sodium hydroxide and ethanol. Therefore, the synthesis proposed in this study has the advantage of not using a strong oxidizer such as permanganate.

#### **Desorption efficiency tests**

The removal and desorption efficiencies in batch tests for both versions of HAIX-nano are presented in Table 3. The removal efficiencies obtained in batch confirm what was predicted during the kinetic modeling tests. WBA-2 was able to remove over 44% more phosphate than SBA-1 for an adsorption period of 20 h. As we can see, the average desorption efficiency for WBA-2, 78%, is three times higher than the average desorption efficiency for SBA-1, 24%. This desorption process was done using a solution of 25 BV at 0.4% NaOH, and no NaCl. This data is very interesting as it shows that WBA-2 can be desorbed with much weaker solutions of NaOH and without NaCl. In the elution curve produced by Pan et al.<sup>7</sup>, it took roughly 3.5 BV of a solution with 5% NaOH and 5% NaCl to recover about 80% of the phosphorus for an SBA version of HAIX-Nano. This is 75% more NaOH than what was used in this experiment and an important amount of NaCl was also used in the latter study.

The desorption solution needed to efficiently desorb WBA-2 requires much less chemicals than SBA-1 and thus is much cheaper. Moreover, the resulting desorbed solution is much easier to handle. When the phosphate is desorbed out of HAIX-Nano, it needs to be precipitated to recover it, normally using a calcium salt. As mentioned before, for a typical desorption protocol, a solution with 2-5% NaOH and NaCl would be used. Since there is so much NaOH, the addition of Ca<sup>2+</sup> can coprecipitate calcium hydroxide. The solution resulting from the precipitation step is also more difficult to handle<sup>5,7,12</sup>, since it has a high pH and a high salinity content. In other words, the desorption procedure of a typical HAIX-Nano (SBA) technology produces waste solutions. However, when a low concentration of NaOH is used to desorb the phosphate in WBA-2, the resulting solution is much easier to handle since the pH is lower. The salinity of the solution is also drastically reduced. For example, the dissolved solids are 10 times less concentrated for a solution using only 0.4% NaOH than for a solution using 2% NaOH and 2% NaCl. Therefore, the regeneration protocol for WBA-2 is more sustainable since it facilitates nutrient recovery, produces less waste while also requiring less chemicals. Finally, being able to desorb phosphate at low concentrations of regenerant opens up the possibility of efficiently regenerating HAIX-Nano with very low energy requirements<sup>34</sup>.

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#### Qualitative comparison

Two key anecdotes are worth discussing about the regeneration of SBA-1 specifically: odor emission and iron oxide leaching. During the desorption step, when SBA-1 is exposed to high pH values, a fishy odor was emitted. This is normally caused by the presence of trimethylamine, which is typically released when anion exchange resin functional groups break up<sup>19</sup>. Also, if the desorption solution for SBA-1 was switched from a high ionic concentration (2% w/w) to a very diluted one such as distilled water, iron oxide nanoparticles were released from the resin as the water became brown. This could be attributed to osmotic pressure pushing out the water inside HAIX-Nano pores because of the concentration gradient. The concentration of iron oxide leaching out was low, but might be problematic for long term use. It is worth noting that even though iron leaching was observed in previous studies, Blaney et al.3 did prove that with proper regeneration, HAIX-Nano (SBA) could be used for 2 years of lifetime<sup>5</sup>. Interestingly, no odor was associated with the regeneration of WBA-2 and no leaching of iron oxide was observed.

Overall, HAIX-Nano is a promising phosphorus removal technology for decentralized WWTPs or for cases where the final P concentration in the effluent must be very low. However, to date, HAIX-Nano technology used high amounts of chemicals in the form of NaOH and NaCl for its regeneration. Therefor, the technology is expensive and produces waste in the form of a high salinity and high pH solution. In order to increase the desorption efficiency of HAIX-Nano, this study changed its parent resin from an SBA to a WBA type. Because a WBA resin gets deprotonated at high pH, the desorption efficiency is higher and the amount of NaOH and NaCl can be reduced. The conclusions derived from this research are:

- The WBA-2 synthesis procedure used a basic rinse, followed by the iron impregnation. This synthesis procedure produced a good dispersion of HFO through the resin pores that is similar to the commercial version of HAIX-Nano FerrIX A33E (SBA-1).
- Because of its larger pores, SBA-1 has a higher adsorption rate constant. However, kinetic models predicted that WBA-2 has an overall adsorption capacity of 44–63% higher for the tested conditions.
- For a low NaOH concentration of 0.4% w/w and no NaCl, WBA-2 showed a desorption efficiency (78%) three times higher than SBA-1 (24%).
- The higher desorption efficiency of WBA-2 means that the regeneration process associated with HAIX-Nano will be both less expensive and more sustainable.

#### METHODS

#### **Resin materials**

The commercially available weak base anion exchange resin A111 from Purolite (Philadelphia, PA) was used as the parent resin for the weak base versions of HAIX-Nano made in this study. FerrIX A33E was also provided by Purolite, which is an already synthesized version of HAIX-Nano made with an SBA resin. The FerrIX version of HAIX-Nano is called SBA-1 for simplicity.

#### Synthesis of WBA-1

For making the first version of HAIX-Nano with a WBA resin (WBA-1), 5.3 g of virgin A111 resin is first rinsed with ethanol. Then, a solution is made by adding 15 g of anhydrous ferric chloride to 25 mL of distilled water, 20 mL of ethanol and 5 mL of HCI (35%; W/W). The solution is added to the resin and agitated for an hour. The solution is then separated from the resin, after which the resin is rinsed for 20 s with distilled water and ethanol (20 mL; 50/50 V/V). The solution is then decanted and the resin is agitated in 100 mL of 3% NaOH (W/W) and 3% NaCl in water for 10 min<sup>7</sup>. This last step is repeated with a fresh solution and with 15 min of agitation. The solution is decanted and the resin is rinsed thoroughly with distilled water until the water is clear. The synthesis for WBA-1 only requires one cycle and is very fast.

#### Synthesis of WBA-2

For making the second version of HAIX-Nano with a WBA resin (WBA-2), a sample of 5.3 g of virgin resin is first rinsed with ethanol, then with distilled water. For one hour, the resin is agitated in 100 mL of 5% (w/w) sodium hydroxide solution and then rinsed for 20 s with 100 mL of distilled water. The goal here is to remove the leftover NaOH outside of the resin beads to avoid iron precipitation on the outer layer. For three hours, the resin is agitated at 240 rpm in a solution of 5% (w/w) ferric chloride dissolved in ethanol and distilled water (50/50; V/V). The solution is then separated from the resin and the resin is agitated in 200 mL of distilled water for 90 s. The solution is decanted and the resin is put in 200 mL of ethanol and water (50/50; V/V) where it is agitated for 90 s. The solution is decanted and the resin is put in 100 mL of ethanol where it is agitated for 120 s. The solution is decanted again and the resin is left to air dry overnight. This procedure is repeated for three new cycles. This second synthesis procedure should promote a better dispersion of iron throughout the resin beads. By letting the beads soak in the sodium hydroxide first, we are transforming all the functional groups into their base form, which has no charge ( $R_3NH^+ \rightarrow R_3N$ :). Since the functional groups are uncharged at first, the Fe<sup>3+</sup> can freely enter the pores without being repelled by the Donnan exclusion effect<sup>19</sup>. As the Fe<sup>3+</sup> ions diffuse through the pores, they are precipitated into HFO nanoparticles by either reacting with the tertiary ammonium groups or the OH- ions still present in the pores.

#### SEM and EDS tests

SEM analyses coupled with EDS were executed to look at the dispersion of iron inside the different versions of HAIX-Nano. Dry beads from each of the HAIX-Nano versions were cut in half before the analysis, allowing to see the interior of the spheres.

#### **Fixed-bed column experiments**

Continuous mini-column experiments (9 mm diameter) were done to obtain breakthrough curves. HAIX-Nano samples were freshly conditioned before each test. The samples were immersed in a sodium hydroxide and sodium chloride solution. A neutralization step consisting mainly of a weak HCI solution with NaCl followed. Finally, the HAIX-Nano samples were rinsed in distilled water. 1.5 mL of each HAIX-Nano version (in chloride form) was put in a mini-column. A synthetic phosphate solution was pumped through the column at a flow rate of 0.7 mL/min, making the empty bed contact time (EBCT) 2.1 min. The solution had a concentration of 48 ppm P-PO<sub>4</sub>, 2100 ppm K<sub>2</sub>SO<sub>4</sub>, and a pH of 7.5. Sulfate ions were added in large quantity so that the main adsorption mechanism under study would be the one associated with the HFO nanoparticles<sup>5,7</sup>.

The effluent was collected and analyzed for phosphates at 10 mL, 20 mL, and then for every other 20 mL until 160 mL. The concentration was taken for the cumulative volume for each aliquot. For example, the concentration analyzed for the aliquot at 40 mL is equivalent to the average concentration between 20 mL and 40 mL. This allowed to plot the adsorption uptake vs time, but for a continuous setup. The advantage of producing an adsorption uptake curve in a fixed bed setup instead of a batch one is that it stabilizes the pH of the influent to treat. Indeed, the ion exchange resin contained in HAIX-Nano can release hydroxide ions during the adsorption process, which modifies the initial pH of the solution to treat. This is extremely difficult to control in a batch setup. Indeed, it is even advised to adapt tests that are normally done in batch (such as an isotherm analysis) in a fixed-bed setup<sup>19</sup>. A Hach DR3900 spectrophotometer was used to analyze phosphorus (using Hach TNT-843 and TNT-846).

#### **Adsorption kinetics**

The results from the adsorption uptake curves were fitted to three adsorption kinetic models. The intraparticle diffusion (IPD) model follows the adsorption uptake  $q_t$  (mg P-PO<sub>4</sub>/mL of HAIX-Nano) evolution with the square root of time,  $t^{1/2}$ . When the relation is linear, it shows that the adsorption process is mostly controlled by IPD<sup>24–27,31</sup>. The Avrami equation is derived from the pseudo-first order model with the difference that a constant *n* is added to address the time dependency of the adsorption process<sup>24,29–31</sup>. The PSO model is also used as it is one of the best models to mathematically represent adsorption processes<sup>24,25,29–31</sup>. The IPD model (4), the Avrami Eq. (5) and the PSO model (6) are written here below as equations. Note that each *k* represents the theoretical

adsorption uptake at equilibrium.

$$q_t = k \cdot t^{1/2} \tag{4}$$

$$q_t = q_e - q_e \cdot \exp(-k \cdot t^n) \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k \cdot q_e^2} + \frac{t}{q_e} \tag{6}$$

The Avrami model and the PSO model were fitted with a least squares minimization, followed by a validation with the coefficient of determination  $(R^2)$  and the ARE<sup>32,35</sup>.

#### Acid digestion of HAIX-Nano

Fresh HAIX-Nano samples were analyzed for their total iron content. All samples were rinsed in ethanol and allowed to dry at room temperature over a week. Then, about 0.3 g of each dry sample was weighted and then put in 25 mL of 10% (w/w)  $H_2SO_4$  for 4 h at 70 °C. The final solution was diluted and then analyzed for the iron concentration. A Hach DR3900 spectrophotometer was used to analyze iron (using Hach TNT-858) concentrations.

#### Removal and desorption efficiency tests

To test the desorption efficiency of HAIX-Nano, batch tests were performed in Erlenmeyer flasks. 1 mL of each HAIX-Nano version was introduced in 100 mL of the same solution used for the fixed-bed experiments explained above. The flasks were agitated for 20 h. The final phosphate concentration was analyzed, and the solution was separated from the beads. 25 mL of a solution with 0.4% (w/w) of NaOH was added to each flask. They were agitated at 250 rpm for 4 h and 30 min. Then, the desorption solutions were analyzed for their phosphate concentration. The removal and desorption efficiency were calculated as follows:

$$Removal efficiency = \frac{m_{adsorbed phosphate}}{m_{total initial phosphate}}$$
(7)

 $Desorption \ efficiency = \frac{m_{desorbed \ phosphate}}{m_{adsorbed \ phosphate}} \tag{8}$ 

#### DATA AVAILABILITY

All treated data that support the findings of this study are included in the present article. Raw datasets can be obtained from the corresponding author upon request.

#### CODE AVAILABILITY

No codes were produced during the study.

Received: 27 July 2021; Accepted: 1 November 2021; Published online: 15 December 2021

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#### ACKNOWLEDGEMENTS

This work was financially supported by the Fonds de Recherche du Québec Nature et Technologies through a PhD scholarship awarded to the first author (291344). Céline Vaneeckhaute is financially supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) through the award of an NSERC Discovery grant (RGPIN-2017-04838). Céline Vaneeckhaute holds the Canada Research Chair in Resource Recovery and Bioproducts Engineering.

#### **AUTHOR CONTRIBUTIONS**

C.V. and X.F. conceptualized and planned the experiments. X.F. did the experimental work and performed data analysis. X.F. drafted the initial version of the manuscript. C. V. substantially revised the manuscript. All authors contributed to and approved the final version of the manuscript. All authors are accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work were appropriately investigated and resolved.

#### **COMPETING INTERESTS**

The authors declare no competing interests.

#### ADDITIONAL INFORMATION

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