Synthesis of hydrated ferric oxide on cation exchange resin for phosphate and hardness removal in water

Le Ba Tran\textsuperscript{1,2,3,4}, Trung Thanh Nguyen\textsuperscript{1,2,*}, Tri Thich Le\textsuperscript{1,2}, Quynh Anh Nguyen Thi\textsuperscript{1,2}, Phuoc Toan Phan\textsuperscript{2,3,4}, Surapol Padungthon\textsuperscript{5} and Nhat Huy Nguyen\textsuperscript{2,4,*}

\textsuperscript{1} Nanomaterial Laboratory, An Giang University, 18 Ung Van Khiem St., Dong Xuyen Dist., Long Xuyen City, An Giang Province, Vietnam
\textsuperscript{2} Vietnam National University Ho Chi Minh City, Linh Trung Ward, Thu Duc City, Ho Chi Minh City, Vietnam
\textsuperscript{3} Faculty of Engineering - Technology - Environment, An Giang University, 18 Ung Van Khiem St., Dong Xuyen Dist., Long Xuyen City, An Giang Province, Vietnam
\textsuperscript{4} Faculty of Environment and Natural Resources, Ho Chi Minh City University of Technology (HCMUT), 268 Ly Thuong Kiet St., Dist. 10, Ho Chi Minh City, Vietnam, Vietnam
\textsuperscript{5} Department of Environmental Engineering, Khon Kaen University, 123 Moo 16 Mittraphap Rd., Nai-Muang, Muang District, Khon Kaen 40002, Thailand

*Email: ntthanh@agu.edu.vn, nnhuy@hcmut.edu.vn

Abstract. In this study, a potential adsorbent was synthesized from iron salt and cation exchange resin (FeOOH@CR) and applied for phosphate adsorption in batch experiments. The characteristics of FeOOH@CR materials before and after phosphate adsorption were determined by FTIR, XRD, and SEM. The factors affecting the adsorption process such as reaction time, solution pH, material dosage, concentration, temperature, and competing ions were tested. Kinetic, thermodynamic and isothermal models of the adsorption process were applied to study the nature of the adsorption process. The properties of phosphate adsorption, effect of competitive ions and material reusability were also examined. Results showed that the adsorption time reached equilibrium after 48 h and the suitable adsorption condition was found at solution pH of 6.5, material dosage of 5 g/L. In addition, the durability of the material after 5 times of regeneration was investigated with the remained adsorption ability of about 55% as compared to the original one.

Keywords: phosphate adsorption; ion exchange resins; hydrated iron oxide, hardness

1. Introduction
The anthropogenic nutrients in the aquatic environment should be reduced to protect the water sources for human uses and reduce eutrophication (e.g., algae growth) in the water environment, which decreases the oxygen content in the water and damages aquatic life conditions[1, 2]. The concentration of phosphorus have been significantly increased in water due to excess fertilizer use and also from the discharge of municipal wastewater. Therefore, controlling phosphorus is necessary for the country's ecological survival [3, 4]. Phosphate concentration limit in domestic wastewater in Vietnam is less than or equal to 6 mgP-PO_{4}^{3-}/L (Column A, QCVN 14:2008/BTNMT). Nevertheless, to meet increasingly stringent requirements, methods such as chemical precipitation, biologic processes, and adsorption by functionalized materials are
all common methods for phosphorus removal [5]. Chemical precipitation has been shown to be an uneconomically process due to the high cost of key chemicals and feeding systems in some circumstances, as well as the massive amount of metal salts produced [5, 6]. Because of its cost-effectiveness, biologic treatment has become a popular method for removing phosphorus from wastewater [5]. Nonetheless, advanced biological methods can remove more than 95% of total phosphorus. However, the operational problems in the process can be difficult to control to achieve stability [7]. Besides, this process are unable to meet the mandated level or lower phosphate concentration to near zero or below 10 mg/L [8, 9]. In addition, large reactor volumes, energy, and sludge disposal need result in significant capital and operational costs, ineffective at low phosphate concentrations of less than 10 mg/L. Physical and chemical techniques such as electrodialysis and chemical denitrification have also been reported for nutrient removal [10]. Both methods are successful, but they are non-selective, making them costly and with limited application potential [10].

Among these methods, adsorption is a low-cost, small-footprint, and effective technique for phosphate at low (or trace) quantities [10]. Adsorption techniques have been extensively studied in recent years due to the advantages of simplicity of design, ease of operation, and minimal sludge generation [11, 12]. Adsorbents such as fly ash, sludge, zeolite, aluminum, iron oxides, and even waste items have been used to remove phosphate [5]. The adsorbents' performance in terms of phosphate removal has been described in the literature with varied degrees of success [13]. Some materials have been the focus of recent phosphate adsorption experiments such as anion exchange resin [14, 15], aluminum/iron oxide-hydroxide [16], magnetic chitosan composites [17], fly ash and activated carbon [18] and inorganic adsorbent [19, 20]. Furthermore, prior studies of ferric oxyhydroxide (FeOOH) adsorption onto cation exchange resin have demonstrated good phosphate adsorption activity [5, 13]. Some studies show that hydrated iron(III) oxide is innocuous, inexpensive, readily available, and chemically stable over a wide pH range [21]. As a result, ferric oxyhydroxide nanomaterials can be applied to phosphate treatment and it gives good effect. Co-precipitation was a method applied to synthesize this material onto anion exchange resin by NH₃ solution to treat phosphate, Cr(VI), arsenate, chromate, Pb²⁺, and Zn²⁺ [5, 22, 23]. Hydrous iron oxide onto anion exchange resin (Purolite FerrIX A33E) was also used to treat phosphate in batch and the reaction time reached equilibrium was 48h [24]. In addition, material hydrated Fe(III) oxide onto anion exchange resin had been successfully synthesized by co-precipitation method with NaOH solution for phosphate treatment and the batch reaction time to reach equilibrium was 72h [10].

On the other hand, the presence of divalent ions like iron, manganese, calcium, and magnesium in water is referred to as hardness. The most common species for water hardness are calcium and magnesium [25]. Water hardness can be a nuisance in some situations. It is an important aesthetic parameter to assess water quality. However, it also depends on the local conditions that can accept different hardness [26]. Consumers can tolerate water supplies with total hardness greater than 200 mg/L, but they are regarded poor resources and values greater than 500 mg/L are not appropriate for most home consumptions [25, 26]. Hard water causes deposits in boilers and domestic appliances, as well as having a variety of effects on detergent cleaning performance [27]. Several human investigations have linked magnesium and calcium to cardiovascular disease and cancer [28-30]. Besides, lime and soda ash are used to remove hardness from water in water purification and treatment plants. The significant volume of liquid sludge produced, as well as the requirement to re-carbonate the softened water, are two major downsides of this procedure [31, 32]. Furthermore, the use of extra chemicals to minimize sludge creation is prohibited, therefore water hardness species cannot be completely removed in most circumstances [26]. Various methods have recently been studied for the removal of a wide variety of ionic and molecular species from various water streams, including electro-deionization [32], electro-membrane processes [33], capacitive deionization [34], membrane and fluidized pellet reactor [35], ion exchange process [36, 37] and adsorption [38, 39], including those responsible for hardness (e.g. Ca²⁺ and Mg²⁺ cationic species). Ion exchange methods have been
proposed as an alternate option that is currently in commercial usage around the world [26]. The fact demonstrates that ion exchange resins are frequently used in the treatment of water hardness, lowering costs and improving treatment efficiency.

Recent research have revealed that hardness and phosphate treatment can be done separately, making treatment systems more complex, with a larger footprint and higher costs. In this study, iron oxyhydroxide on cation exchange resins was used to create a new FeOOH@CR material for simultaneous removal of phosphate and cations such as Ca$^{2+}$ and Mg$^{2+}$ in this study. This research demonstrates a vision for the material’s practical use in the treatment of phosphate at low concentrations and water with significant hardness.

2. Materials and Methods

2.1. Chemicals

Lab-grade chemicals used in the study such as FeCl$_3$·6H$_2$O, NH$_4$Cl, NH$_3$ (28-34 vol.%), and NaCl were from China, and HCl, KH$_2$PO$_4$, KCl, K$_2$SO$_4$, MgCl$_2$, KNO$_3$, and CaCl$_2$ were from Merck. Cation exchange resin H$^+$ (225H) was from India and deionized water was taken from the laboratory. The solutions contain phosphate (the concentration of mgPO$_4$$^{3-}$ in the solution of the experiments is calculated by the concentration of mgP in PO$_4$$^{3-}$ in the solution), calcium, magnesium were prepared by dissolving KH$_2$PO$_4$, CaCl$_2$, MgCl$_2$ salts into deionized water.

2.2. Material synthesis and characterizations

FeOOH@CR material was prepared according to a process in the previous publications [5, 22, 23]. The cation-exchange resin hybrid adsorbent was dispersed with ferric oxyhydroxide particles prepared by the following procedure. At first, 2 mL of HCl solution was added into 0.2 L of 12.5% w/w FeCl$_3$·6H$_2$O solution and the mixture was stirred for 5 min with a stirrer. After the mixture was completely dissolved, the solution had a low pH of 3. Next, 10 g of dry H$^+$ ion exchange resins (225H of India) was added to the solution and the solution was stirred at 500 rpm for 20 min. The solids were then separated from the mixture and washed with deionized water 3 times, followed by agitating for 10 min at 500 rpm in 200 mL of deionized water containing 1 g of NH$_4$Cl and 2 mL of NH$_3$ solution (28-34 vol. %). Subsequently, the material was separated from the solution and washed with deionized water 3 times. Finally, the material was dried in the open air until it turns red.

Scanning electron microscopy - SEM (JCM-7000, JEOL Ltd, Japan) was used to examine the morphology of the material. Energy dispersive X-ray analysis EDX (JCM-7000, JEOL Ltd, Japan) was used to determine various elemental compositions. Fourier-transform infrared spectroscopy - FTIR (Alpha, Bruker, Germany) was used to determine the surface chemistry. X-ray diffraction –XRD (D2 Phaser Benchtop X-ray Powder Diffraction, AERIS, Malvern Panalytical Ltd, Netherlands) was used to evaluate the crystal phase and crystalline structure of the materials.

2.3. Adsorption tests

Batch adsorption studies were used to investigate the adsorption of phosphate and cations (i.e. Mg and Ca). In the first test, 0.25 g of material was added to 50 mL of phosphate solution (20 mgPO$_4$$^{3-}$/L) and allowed to adsorb for up to 80 h. The material was then removed from the solution, and a sample of the solution was collected for UV-Visible spectroscopy analysis of the phosphate concentration (V-730 UV, JASCO International Co.Ltd, Japan). The investigated influencing parameters include: contact time (0 - 80 h), adsorbent dosage (2 - 30 g/L), solution pH (2 - 12), competing ions in solution (sulfate, bicarbonate, chloride, and nitrate), initial phosphate concentration (10 - 50 mg/L) and temperature (5 - 40 °C). The phosphate adsorption capacity (in terms of phosphorous, (mgPO$_4$$^{3-}$/g or mgP/g) was calculated as the following equation [5, 22].

$$Q_e = \frac{c_0-c_1}{m} \times V \quad (2.1)$$
Where \( C_0 \) and \( C_e \) are initial and equilibrium concentrations of phosphate in terms of phosphorous (mgPO\(_4^3-\)/L). \( V \) is the volume of solution (L) and \( m \) was the mass of the material (g).

The simultaneous adsorption of phosphate and cations (Mg and Ca) was achieved by adding 0.25 g of resin into 50 mL of a solution containing 20, 100, and 100 mg/L of phosphate, calcium, and magnesium, respectively. The other steps of the experiment were similar to the previous phosphate adsorption experiment. The solution was then taken for measurement of phosphate content using UV-Visible spectroscopy and calcium and magnesium content using atomic absorption spectroscopy (AAS, PerkinElmer Aanalyst 400, PerkinElmer, Inc., USA).

3. Results and discussion

3.1. Characterizations of materials

The morphology and surface elemental composition of the materials were examined by SEM and EDX-mapping, respectively (Figure S1, S2, and S3 of Supplementary Data). Accordingly, the composition of the elements on the surface of the materials is summarized in Table 1 with the main components of C, O, Fe, Ca, Mg, and Al. Phosphate was only detected in the structure of the FeOOH@CR material after phosphate adsorption (Figure S2), but not in those of the resin (Figure S1) and fresh FeOOH@CR material (Figure S3). This result showed that the process was successful when iron was present on the surface of the material. Besides, phosphate was also adsorbed on the surface of the material after the experimental process.

| Material/ Elements | Resin       | Fresh FeOOH@CR | FeOOH@CR after adsorption |
|--------------------|-------------|----------------|--------------------------|
| C                  | 42.37 ± 0.12 | 42.45 ± 0.14   | 52.41±0.11               |
| O                  | 57.63 ± 0.16 | 38.48 ± 0.19   | 18.83±0.15               |
| Fe                 | 19± 0.35    | 18.83±0.15     | 20.44±0.28               |
| Ca                 | 0.01 ± 0.01 | 0.01 ± 0.01    | 0.01 ± 0.01              |
| Mg                 | 0.07 ± 0.01 | 0.06 ± 0.01    | 0.06 ± 0.01              |
| P                  | 0.92 ± 0.02 |                |                          |

Surface functional groups of the nanomaterials are usually determined by FTIR [40, 41]. In this study, the surface chemical structure of FeOOH@CR before and after adsorption was examined to clarify the adsorption mechanism occurring on the surface of the material. The FTIR spectra of FeOOH (i.e., goethite and lepidocrocite) were also provided for reference purposes. As can be observed in Figure 1, all samples have a peak at wavenumber of 3390 cm\(^{-1}\), which is assigned to the H-O-H vibration of the hydrated group. The peaks at the region of 789 and 880 cm\(^{-1}\) characterize for Fe-OH-Fe vibration [41-43] while the peaks at 466 and 746 cm\(^{-1}\) are attributed to the Fe-OH vibrations [42, 43]. The absorption bands at 3133 and 3384 cm\(^{-1}\) are related to the stretching vibrations of the OH groups. The peak of phosphate ranges from 1000-1100 cm\(^{-1}\) [44-46]. In this study, the dose of phosphate was much smaller than iron and the peak of phosphate was also located at the same position as the peak of iron (lepidocrocite and goethite reference [42, 43]). These results are similar to those reported in the previous studies [42, 43].
Figure 1. FTIR spectra of (1) FeOOH@CR after phosphate adsorption, (2) fresh FeOOH@CR, and (3) lepidocrocite and goethite reference [42, 43].

Figure 2 shows the XRD patterns of the materials in the 2θ range of 10 - 70°, indicating that the substance is hydrated ferric oxide nanomaterial (FeOOH). The orthorhombic iron oxide-hydroxide structure of the FeOOH@CR material is shown by the distinctive peaks at 2θ of 31.06, 33.10, 38.99, 41.93, 46.19, 48.21, 54.66, and 57.55° (JCPDS card no 18-0639). However, the material is usually considered as amorphous phase because the intensities of these peaks are quite low and sometimes interfered with background noise. This could be attributed to the material's low-temperature production without calcination for the crystallization of iron oxide-hydroxide.

Figure 2. XRD patterns of (1) FeOOH@CR after phosphate adsorption, (2) fresh FeOOH@CR, and (3) iron oxide-hydroxide reference (JCPDS card no. 18-0639) [47].
3.2. Adsorption of phosphate onto FeOOH@CR

During the 80-h experiment, Figure 3 demonstrates that the adsorption capacity of FeOOH@CR increased with increasing adsorption time. With an adsorption capacity of 3.10 mgPO₄³⁻/g, it reached equilibrium after about 48 h, which is similar to that described in the literature. Using FeOOH@CR material, there are three primary stages in phosphate adsorption, including the first stage of quick adsorption in the first 24 h, the second stage of slow adsorption in the next 24 h, and the last stage of equilibrium after 48 h of adsorption.

![Figure 3](image-url)

**Figure 3.** Phosphate adsorption capacity and concentration during 80 h of adsorption.

(Condition: 5 gFeOOH@CR/L, 20 mgPO₄³⁻/L, pH 6.0, room temperature of ~ 27 °C)

As shown in Table 2, the kinetics of phosphate adsorption onto FeOOH@CR were investigated using three kinetic models of pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. All three models can be utilized to describe phosphate adsorption based on the correlation coefficient (R² > 0.9). However, because it has the greatest R² value of 0.9848 (Figure S4) with similar predicted and tested adsorption capacities, the pseudo-first-order model is the best suitable adsorption model for phosphate adsorption utilizing FeOOH@CR. At a phosphate concentration of 20 mg/L, the K adsorption rate constant was calculated to be 0.0641 (g.mg⁻¹.h⁻¹).

**Table 2.** Equations and parameters of kinetic models for phosphate adsorption using FeOOH@CR.

| Kinetic model      | Linear equation | R²   | Capacity (Qₑ,cal) mg·g⁻¹ |
|--------------------|-----------------|------|-------------------------|
|                    |                 |      | Modeling | Experimental |
| Pseudo-first-order | y = -0.0641x + 1,237 | 0.9848 | 3.45       | 3.07         |
| Pseudo-second-order| y = 0.2599x + 4.268  | 0.9701 | 3.85       |              |
The adsorption capacity of materials is affected by solution pH, which is an important parameter. Figure 4 shows the phosphate adsorption capability of the materials from pH 2 to 12. It was also shown that the adsorption capacity increased steadily from pH 2 to pH 6.5, peaking at 2.78 mgPO₄³⁻/g. In addition, the point of zero charge (pHpzc) of the material was determined to be 6.5 (Figure S5). When the pH is less than 6.5, the material surface has a positive charge, which increases the adsorption of negatively charged phosphates in the forms of HPO₄²⁻ and H₂PO₄⁻ (Reactions 1, 2, and 3), and are retained by iron oxyhydroxide by forming a complex inside the sphere. Because HPO₄²⁻ forms stronger amphoteric complexes than H₂PO₄⁻ (Reactions 6 and 7), reducing the pH causes more phosphate to stay in the form of H₂PO₄⁻, which has a lower negative charge, making the adsorption process more difficult. Furthermore, the solution with low pH reduces the electrostatic attraction between the positively charged iron oxyhydroxide groups and the phosphate ions by reducing the negative charge of phosphate from divalent to monovalent. When the pH was higher than 6.5, the adsorption capacity gradually dropped until it was just 2.12 mgPO₄³⁻/g at pH 12. FeOOH is deionized and negatively charged at these high pH levels (Reaction 4 and 5). As a result, phosphate adsorption is inhibited by electrostatic repulsion and Donnan co-ion exclusion [48, 49].

\[
\begin{align*}
    \text{H}_3\text{PO}_4 & \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^- & \text{pKa}_1 = 2.15 \\
    \text{H}_2\text{PO}_4^- & \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} & \text{pKa}_2 = 7.20 \\
    \text{HPO}_4^{2-} & \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-} & \text{pKa}_3 = 12.35 \\
    \text{FeOH}^+ & \rightleftharpoons \text{FeO}^- + \text{H}^+ & \text{pKa}_1 = 6.5 \\
    \text{FeOH}^- & \rightleftharpoons \text{FeO}^- + \text{H}^+ & \text{pKa}_2 = 8.5 \\
    \text{FeOH}_2^+(\text{Cl}^-) + \text{H}_2\text{PO}_4^- & \rightleftharpoons \text{FeOH}_2^+:\text{H}_3\text{PO}_4^- + \text{Cl}^- & \text{(3.6)} \\
    \text{FeOH}_2^+(\text{Cl}^-) + \text{HPO}_4^{2-} & \rightleftharpoons 2(\text{FeOH}_2^+:\text{HPO}_4^{2-} + 2\text{Cl}^-) & \text{(3.7)}
\end{align*}
\]
Figure 4. Effect of solution pH on phosphate adsorption.

(Condition: 48 h, 5 g FeOOH@CR/L, 20 mg PO₄³⁻/L, and room temperature of ~ 27 °C)

The adsorption capacity of phosphate is influenced by the dose of FeOOH@CR adsorbent, as shown in Figure 5. The adsorption capacity declines as the adsorbent dose increases, whereas the adsorption efficiency and the output water quality gradually improves. The phosphate adsorption must meet the QCVN 14:2008/BTNMT (Column A) standard with an output phosphate content of less than 6 mgP/L. When the adsorbent dose was raised in the range of 2 - 10 g/L, the phosphate adsorption capacity declines drastically, then slowly in the range of 10 - 30 g/L. For the following studies, the optimum adsorbent dosage was chosen at 5 g/L.
Figure 5. Effect of dosage on the adsorption of phosphate.

(Condition: 48 h, 20 mgPO$_4^{3-}$/L, pH 6.5, and room temperature of ~ 27 °C)

Figure 6 describes the effect of phosphate concentration and temperature on the adsorption capacity, which gradually increases as the concentration rises. This is due to the high phosphate concentration in the solution increasing the density of phosphate ions in the solution, making the adsorption occurs easier. Similarly, as the temperature rises, the mobility of phosphate ions increases, favoring adsorption. This is readily visible in solutions with starting concentrations ranging from 10 to 50 mgPO$_4^{3-}$/L at temperatures of 5, 20, 30, and 40 °C.
Figure 6. Effect of initial phosphate concentration and temperature on the adsorption of phosphate. 
(Condition: 48 h, 5 gFeOOH@CR/L, pH 6.5)

The link between the phosphate on the materials surface and its equilibrium concentration in the solution at constant temperature was described using the Langmuir and Freundlich isotherm models [50, 51]. Table 3 shows the adsorption isotherm parameters. Although both the Langmuir and Freundlich models are suitable for describing phosphate adsorption at 30 and 40 °C, the Langmuir model has a better correlation coefficient with R² of 0.9974 at 30 °C, making it more favorable. The K_L value, which is the Langmuir constant that represents the adsorbent's affinity for its surface [52-54], was estimated from the equation to be 0.26552 and 0.3705 L/mg at 30 °C and 40 °C, respectively.

Table 3. The isotherm parameters of phosphate adsorption onto FeOOH@CR material.

| Isotherm model | Parameter       | Temperature (°C) |
|---------------|----------------|------------------|
|               |                | 5                | 25               | 30               | 40               |
| Langmuir      | Q_max (mg/g)   | 20.534           | 7.5245           | 6.51466          | 7.5245           |
|               | K_L (L/mg)     | 0.0035           | 0.1002           | 0.26552          | 0.3705           |
|               | R²             | 0.2013           | 0.8818           | 0.9974           | 0.9903           |
| Freundlich    | K_f((mg/g)(L/mg)ⁿ) | 13.37           | 0.95             | 0.61             | 0.45             |
|               | n              | 1.04             | 1.90             | 2.29             | 2.41             |
|               | R²             | 0.9802           | 0.9288           | 0.9249           | 0.9664           |
The thermodynamic process of adsorption, on the other hand, is stated using equilibrium constants at different temperatures (such as 278, 293, 303, and 313 °K) utilizing factors such as Gibbs free energy (ΔG), entropy (ΔS), and enthalpy (ΔH). The Gibbs free energy (ΔG) is a measure of whether a substance is physically or chemically adsorbed. The ΔG values between -20 and 0 kJ/mol indicate a physical adsorption process while those between -80 and -400 kJ/mol indicate chemisorption [55]. At 278, 293, 303, and 313 °K, the ΔG was estimated to be -0.845, -4.389, -6.751, and -9.114 kJ/mol, showing that the adsorption process was spontaneous at all investigated temperatures [53]. Van der Waals forces, hydrogen bonds, ionic pairs, and other polar and nonpolar interactions should all play a part in the interaction between phosphate ions and the FeOOH@CR surface during the adsorption process [53, 55, 56]. The positive value of ΔH indicates that this is an endothermic adsorption process with 64.84 (kJ/mol). The value of ΔS is higher than 0, indicating that the affinity and contact between the adsorbate and the adsorbent of the adsorption process are increasing [56]. This can also be explained that ΔS and ΔH were the key factors for determining the overall sign and magnitude of the binding free energy (ΔG). Only when the free energy change was negative, the adsorption can occur spontaneously. And the positive ΔS along with negative ΔH contributed favorably to the overall binding free energy (ΔG) [53]. Besides, the positive value of ΔS suggests increased randomness at the solid/solution interface during the adsorption [55, 57, 58].

Table 4. Thermodynamic parameters of phosphate adsorption onto FeOOH@CR material.

| Thermodynamic parameters | Temperature (K) | Value     |
|--------------------------|----------------|-----------|
| ΔG (kJ/mol)              | 278 K          | -0.845    |
|                          | 393 K          | -4.389    |
|                          | 303 K          | -6.751    |
|                          | 313 K          | -9.114    |
| ΔH (kJ/mol)              |                | 64.84     |
| ΔS (kJ/(mol.K))          |                | 0.24      |

3.3. Effect of coexisted ions, durability, and comparison with other studies

Figure 7 shows the impacts of anions on the phosphate adsorption capacity of FeOOH@CR material. Anions such as Cl⁻, SO₄²⁻, NO₃⁻, and HCO₃⁻ commonly coexist with PO₄³⁻ in water and wastewater. The anions HCO₃⁻, at a concentration of 100 mg/L, had the greatest impact on the phosphate adsorption capacity. Other anions, such as Cl⁻, NO₂⁻, and SO₄²⁻ had a lower effect than HCO₃⁻ on the adsorption process, demonstrating the specific interaction and adsorption of FeOOH@CR material with HCO₃⁻ and PO₄³⁻ anions.
As seen in Figure 7, the presence of cations such as calcium and magnesium in the solution increased the phosphate adsorption. The fundamental reason for this is that the presence of Ca and Mg increases the positive charge of the material surface, which makes negative phosphate anions easier to adsorb. The material was also capable of eliminating Ca\(^{2+}\) from 210 to 128 mg/L and Mg\(^{2+}\) from 202 to 142 mg/L at the same time. One probable explanation is that after treating the resin with NH\(_3\) solution, iron and other cations dissociate from their ionic bonds with the resin, forming oxides/hydroxides particles inside the pores. As a result, the ion exchange resin is still capable of accepting new Ca\(^{2+}\) and Mg\(^{2+}\) cations as they arrive in the solution, positively charging the surface to aid phosphate adsorption. In the addition of Ca\(^{2+}\) and Mg\(^{2+}\), the phosphate adsorption capacity increased by 1.21 times, reaching 3.652 mgPO\(_4^{3-}\)/g in Table 5.

**Figure 7.** Effect of other anions on the adsorption of phosphate.

(Condition: 48 h, 5 g FeOOH@CR/L, 20 mgPO\(_4^{3-}\)/L, pH 6.5, room temperature of ~ 30 °C)
Figure 8. Effect of Ca and Mg cations on the adsorption of phosphate.
(Condition: 48 h, 5 gFeOOH@CR/L, 20 mgPO$_4^{3-}$/L, pH 6.5, room temperature of ~ 30 °C)

Table 5. The comparison of phosphate adsorption capacity.

| Parameters       | Solution (PO$_4^{3-}$ without Ca$^{2+}$ and Mg$^{2+}$) | Solution (PO$_4^{3-}$, Ca$^{2+}$, Mg$^{2+}$) |
|------------------|--------------------------------------------------------|-----------------------------------------------|
|                  | (mgPO$_4^{3-}$/g)                                       | (mgPO$_4^{3-}$/g) (mgCa$^{2+}$/g) (mgMg$^{2+}$/g) |
| Adsorption capacity | 3.1 ± 0.049                                             | 3.625 ± 0.043 16.4 ± 0.057 12 ± 0.096 |

Besides, this material showed that the total adsorption capacity of phosphate (3.625 mg/g) and hardness (28.4mg/g) was 32.025 mg/g compared to a commercial product (INDION MB-6 SR, Ion Exchange (India) Ltd., India) which had a total adsorption capacity of phosphate (4.4 mg/g) and hardness (8.6 mg/L) was 13 mg/g. This can be seen that the adsorption capacity of the material in this study was 2.46 times higher than that of the INDION MB-6 SR material. INDION MB-6 SR was a commercially available material on the market, it had the ability to remove both cations and anions in water.

3.4. Application to real wastewater, durability, and comparisons with other studies

After that, the FeOOH@CR material was used to treat real wastewater. As shown in Figure S6, the phosphate concentration in synthetic wastewater decreased from 20 to 4.76 mgPO$_4^{3-}$/L, while domestic wastewater decreased from 14.34 to 2.15 mgPO$_4^{3-}$/L, meeting the requirement of QCVN 14: 2008/BTNMT (Column A). Although competing ions may exist in domestic wastewater, they had less effect on the
phosphate adsorption process. Figure 9 shows five cycles of adsorption-regeneration that were used to verify the material durability. After five reuse cycles, the adsorption capacity was only 1.75 mgPO$_4^{3-}$/g, which was approximately 56.68% of the capacity of the fresh material. Table 6 compares the adsorption capacity of various nanomaterials, showing that FeOOH@CR is potential for phosphate application.

![Figure 9. Durability test of FeOOH@CR material for phosphate adsorption. (Condition: 48 h, 5 gFeOOH@CR/L, 20 mgPO$_4^{3-}$/L, pH 6.5, room temperature of ~ 30 °C)](image)

Table 6. Phosphate adsorption capacity from various developed adsorbents.

| Materials                      | Experimental conditions          | Adsorption capacity (mg P per g of adsorbent) | References |
|--------------------------------|----------------------------------|-----------------------------------------------|------------|
| Akagenite                     | 25 °C, pH 7, $C_e = 1$-250 mgP/L | 60                                            | [59]       |
| Akagenite granulated          | 20 °C, pH 5.5, $C_e = 0$-4 mgP/L | 17-23                                         | [60]       |
| Activated alumina             | 20 °C, pH 5.5, $C_e = 0$-4 mgP/L | 12-14                                         | [60]       |
| Activated alumina             | $C_e = 0$-2 mgP/L                | 3.3                                           | [61]       |
| Iron/zirconium binary oxide   | 25 °C, pH 4, $C_e = 0$-80 mgP/L  | 13.7                                          | [12]       |
| MgAlLDH (granular)            | 25 °C, pH 6.9, $C_e = 0$-150 mgP/L | 47.3                                          | [62]       |
| Activated carbon              | $C_e = 0$-28 mgP/L               | 3.2                                           | [63]       |
Anion exchange resin from soybean hulls

- Temperature: 25 °C, pH 7
- Dose: 10 g
- Initial concentration: 10-620 mgP/L

Purolite A500P anion exchange resin

- Dose: 0.5-10 g/L
- Initial concentration: 1-15 mgP/L

Iron oxide tailings (23% w/w Fe)

- Temperature: 20-21 °C, pH 6.6-6.8
- Dose: 0.2-4.0 g/L
- Initial concentration: 0-130 mgP/L
- Adsorption capacity: 30.435 (mgPO₄³⁻/gFe)

Hydrated Fe(III) oxide nanoparticles on anion exchange resin (35% w/w Fe)

- pH 6.5
- Dose: 0.2-4.0 g/L
- Initial concentration: 7 mgP/L
- Adsorption capacity: 19.97 (mgPO₄³⁻/gFe)

FeOOH@CR (5%)

- Temperature: 25-30 °C, pH 6
- Dose: 2-10 g/L
- Initial concentration: 2-20 mgPO₄³⁻/L
- Adsorption capacity: 3.1 (mg PO₄³⁻/g Fe)

| Material | Temperature | pH | Dose | Initial concentration | Adsorption capacity |
|----------|-------------|----|------|-----------------------|---------------------|
| Anion exchange resin from soybean hulls | 25 °C, pH 7 | | 10 g | 10-620 mgP/L | 20 |
| Purolite A500P anion exchange resin | | | Dose = 0.5-10 g/L | C₀ = 1-15 mgP/L | 23.55 |
| Iron oxide tailings (23% w/w Fe) | 20-21 °C, pH 6.6-6.8 | | Dose = 0.2-4.0 g/L | C₀ = 0-130 mgP/L | 7 |
| Hydrated Fe(III) oxide nanoparticles on anion exchange resin (35% w/w Fe) | pH 6.5 | | Dose = 0.2-4.0 g/L | | 30.435 (mgPO₄³⁻/gFe) |
| FeOOH@CR (5%) | 25-30 °C, pH 6 | | Dose = 2-10 g/L | C₀ = 2-20 mgPO₄³⁻/L | 3.1 |

4. Conclusions

The FeOOH@CR material was successfully synthesized and applied for phosphate and hardness removal in water. The equilibrium adsorption time was determined to be 48 h while the suitable pH was around 6.5. The adsorption capacity increased with the increase of phosphate concentration and adsorption temperature. The maximum adsorption capacity of FeOOH@CR material is 3.1 mgPO₄³⁻/g (62 mgPO₄³⁻/gFe). The presence of Ca²⁺ and Mg²⁺ cations enhanced the phosphate adsorption up to 1.21 times, suggesting the use of the material for simultaneous phosphate and hardness removal. In both synthetic and domestic wastewater, the FeOOH@CR was effective for removal phosphate to meet the discharging standards, indicating the practicability of the material in wastewater treatment.

Supplementary Data
**Figure S1.** SEM image and EDX-mapping result of CR.

**Figure S2.** SEM image and EDX-mapping result of FeOOH@CR after phosphate adsorption.
Figure S3. SEM image and EDX-mapping result of fresh FeOOH@CR.

Figure S4. Pseudo- first-order kinetic plot of phosphate adsorption onto FeOOH@CR material.
Figure S5. Plot for determining the point of zero charge ($\text{pH}_{\text{ZPC}}$) of FeOOH@CR material.

Figure S6. The concentration before and after treatment of synthetic wastewater and domestic wastewater.

References

[1] Sun L, Tong H, Gao C, Liu Y and Feng C 2021 Removal of antibiotic resistance genes from secondary effluent by processes combining nano-iron, ultrasound-activated persulfate, and ultrafiltration Water Sci Technol 83 1578-90

[2] Zhao D and Sengupta A K 1998 Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers Water Research 32 1613-25
[3] Conley D J, Paerl H W, Howarth R W, Boesche D F, Seitzinger S P, Havens K E, Lancelot C and Likens G E 2009 Controlling eutrophication: nitrogen and phosphorus *Science* **323** 1014-5

[4] Anzecc A 2000 Australian and New Zealand guidelines for fresh and marine water quality *Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra* 1-103

[5] Ren J, Li N, Zhao L and Ren N 2014 Enhanced adsorption of phosphate by loading nanosized ferric oxyhydroxide on anion resin *Frontiers of Environmental Science & Engineering* **8** 531-8

[6] Zhang T, Ding L and Ren H 2009 Pretreatment of ammonium removal from landfill leachate by chemical precipitation *Journal of Hazardous Materials* **166** 911-5

[7] Oguz E 2005 Thermodynamic and kinetic investigations of PO$_3^-$ adsorption on blast furnace slag *Journal of Colloid and Interface Science* **281** 62-7

[8] Awual M R, Jyo A, Ihara T, Seko N, Tamada M and Lim K T 2011 Enhanced trace phosphate removal from water by zirconium(IV) loaded fibrous adsorbent *Water Research* **45** 4592-600

[9] Awual M R, Shenashen M, Jyo A, Shiwaku H and Yaita T 2014 Preparing of novel fibrous ligand exchange adsorbent for rapid column-mode trace phosphate removal from water *Journal of Industrial and Engineering Chemistry* **20** 2840-7

[10] Wiriyathamcharoen S, Sarkar S, Jienvrangkul P, Nguyen T T, Klysubun W and Padunghson S 2020 Synthesis optimization of hybrid anion exchanger containing triethylamine functional groups and hydrated Fe (III) oxide nanoparticles for simultaneous nitrate and phosphate removal *Chemical Engineering Journal* **381** 122671

[11] Xu X, Gao B Y, Yue Q Y and Zhong Q Q 2010 Preparation of agricultural by-product based anion exchanger and its utilization for nitrate and phosphate removal *Bioresource Technol* **101** 8558-64

[12] Long F, Gong J-L, Zeng G-M, Chen L, Wang X-Y, Deng J-H, Niu Q-Y, Zhang H-Y and Zhang X-R 2011 Removal of phosphate from aqueous solution by magnetic Fe–Zr binary oxide *Chemical Engineering Journal* **171** 448-55

[13] Nur T, Johir M A H, Loganathan P, Nguyen T V and Kandasamy J 2014 Phosphate removal from water using an iron oxide impregnated strong base anion exchange resin *Journal of Industrial and Engineering Chemistry* **20** 1301–7

[14] Awual M R, Urata S, Jyo A, Tamada M and Katakai A 2008 Arsenate removal from water by a weak-base anion exchange fibrous adsorbent *Water Research* **42** 689-96

[15] Awual M R and Jyo A 2011 Assessing of phosphorus removal by polymeric anion exchangers *Desalination* **281** 111–7

[16] Chubar N I, Kanibolotskyy V A, Strelko V V, Gallios G G, Samanidou V F, Shaposhnikova T O, Milgrandt V G and Zhuravlev I 2005 Adsorption of phosphate ions on novel inorganic ion exchangers *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **255** 55-63

[17] Reddy D H K and Lee S-M 2013 Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions *Advances in Colloid and Interface Science* **201-202** 68-93

[18] Chen J, Kong H, Wu D, Chen X, Zhang D and Sun Z 2007 Phosphate immobilization from aqueous solution by fly ashes in relation to their composition *Journal of Hazardous Materials* **139** 293-300

[19] Jellali S, Wahab M A, Hassine R B, Hamzaoui A H and Bousselmi L 2011 Adsorption characteristics of phosphorus from aqueous solutions onto phosphate mine wastes *Chemical Engineering Journal* **169** 157-65

[20] Huang W, Wang S, Zhu Z, Li L, Yao X, Rudolph V and Haghseresht F 2008 Phosphate removal from wastewater using red mud *Journal of Hazardous Materials* **158** 35-42

[21] Nie G, Wang J, Pan B and Lv L 2015 Surface chemistry of polymer-supported nano-hydrated ferric oxide for arsenic removal: effect of host pore structure *Science China Chemistry* **58** 722-30
[22] Ren J, Li N and Zhao L 2012 Adsorptive Removal of Cr(VI) from Water by Anion Exchanger Based Nanosized Ferric Oxyhydroxide Hybrid Adsorbent Chemical and Biochemical Engineering Quarterly 26 111-8

[23] Ding M, de Jong B H W S, Roosendaal S J and Vredenberg A 2000 XPS studies on the electronic structure of bonding between solid and solutes: adsorption of arsenate, chromate, phosphate, Pb2+, and Zn2+ ions on amorphous black ferric oxyhydroxide Geochimica et Cosmochimica Acta 64 1209-19

[24] Nur T, Johir M A H, Loganathan P, Nguyen T, Vigneswaran S and Kandasamy J 2014 Phosphate removal from water using an iron oxide impregnated strong base anion exchange resin Journal of Industrial and Engineering Chemistry 20 1301-7

[25] Yan M, Wang D, Ni J, Qu J, Yan Y and Chow C W 2008 Effect of polyaluminum chloride on enhanced softening for the typical organic-polluted high hardness North-China surface waters Separation and purification technology 62 401-6

[26] Sepehr M N, Zarrabi M, Kazemian H, Amran A, Yaghmaian K and Ghaafari H R 2013 Removal of hardness agents, calcium, and magnesium, by natural and alkaline modified pumice stones in single and binary systems Applied Surface Science 274 295-305

[27] Suzuki K, Tanaka Y, Osada T and Waki M 2002 Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration Water research 36 2991-8

[28] Rubenowitz E, Axelsson G and Rylander R 1996 Magnesium in drinking water and death from acute myocardial infarction American journal of epidemiology 143 456-62

[29] Rosborg I, Soni V and Kozisek F 2015 Impact of Calcium and Magnesium in Groundwater and Drinking Water on the Health of Inhabitants of the Slovak Republic International Journal of Environmental Research and Public Health 14 278

[30] Sheikholeslami R 2011 Composite scale formation and assessment by the theoretical Scaling Potential Index (SPI) proposed previously for a single salt Desalination 278 259-67

[31] Fu L, Wang J and Su Y 2009 Removal of low concentrations of hardness ions from aqueous solutions using electrodeionization process Separation and Purification Technology 68 390-6

[32] Park J-S, Song J-H, Yeon K-H and Moon S-H 2007 Removal of hardness ions from tap water using electromembrane processes Desalination 202 1-8

[33] Seo S-J, Jeon H, Lee J K, Kim G-Y, Park D, Nojima H, Lee J and Moon S-H 2010 Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications Water research 44 2267-75

[34] Li C-W, Liao J-C and Lin Y-C 2005 Integrating a membrane and a fluidized pellet reactor for removing hardness: effects of NOM and phosphate Desalination 175 279-88

[35] Apell J N and Boyer T H 2010 Combined ion exchange treatment for removal of dissolved organic matter and hardness Water Research 44 2419-30

[36] Kazemian H, Modarres H and Mobtaker H G 2003 Iranian natural clinoptilolite and its synthetic zeolite P for removal of cerium and thorium from nuclear wastewaters Journal of Radioanalytical and Nuclear Chemistry 258 551-6

[37] Torabian A, Kazemian H, Seifi L, Bidhendi G N, Azimi A A and Ghadiri S K 2010 Removal of petroleum aromatic hydrocarbons by surfactant-modified natural zeolite: the effect of surfactant CLEAN–Soil, Air, Water 38 77-83

[38] Seifi L, Torabian A, Kazemian H, Bidhendi G N, Azimi A A, Nazmara S and AliMohammadi M 2011 Adsorption of BTEX on surfactant modified granulated natural zeolite nanoparticles: parameters optimizing by applying Taguchi experimental design method CLEAN–Soil, Air, Water 39 939-48
[40] Hifumi H, Ewing A V and Kazarian S G 2016 ATR-FTIR spectroscopic imaging to study the drying and dissolution of pharmaceutical polymer-based films *International Journal of Pharmaceutics* **515** 57-68
[41] Ruan H D, Frost R L, Kloprogge J T and Duong L 2002 Infrared spectroscopy of goethite dehydroxylation. II. Effect of aluminium substitution on the behaviour of hydroxyl units *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **58** 479-91
[42] Liao S, Wang J, Zhu D, Ren L, Lu J, Geng M and Langdon A 2007 Structure and Mn2+ adsorption properties of boron-doped goethite *Applied Clay Science* **38** 43-50
[43] Rahimi S, Moatatri R M, Rajabi L, Derakhshan A A and Keyhani M 2015 Iron oxide/hydroxide (α, γ-FeOOH) nanoparticles as high potential adsorbents for lead removal from polluted aquatic media *Journal of Industrial and Engineering Chemistry* **23** 33-43
[44] Lochaiwatana Y, Poolthong S, Hirata I, Okazaki M, Swasdison S and Vongsavan N 2015 The synthesis and characterization of a novel potassium chloride-fluoridated hydroxyapatite varnish for treating dentin hypersensitivity *Dental Materials Journal* **34**
[45] Gheisari H, Karamian E and Abdellahi M 2015 A novel hydroxyapatite–Hardystonite nanocomposite ceramic *Ceramics International* **41** 5967-75
[46] Furuzono T, Yasuda S, Kimura T, Kyotani S, Tanaka J and Kishida A 2004 Nano-scaled hydroxyapatite/polymer composite IV. Fabrication and cell adhesion properties of a three-dimensional scaffold made of composite material with a silk fibroin substrate to develop a percutaneous device *Journal of Artificial Organs* **7** 137-44
[47] Raul P, Devi R, Umlong I, Banerjee S and Purkait M 2012 Removal of Fluoride from Water Using Iron Oxide-Hydroxide Nanoparticles *Journal of nanoscience and nanotechnology* **12** 3922-30
[48] Wiriyathamcharoen S, Sarkar S, Jienvrangkul P, Nguyen T T, Klysubun W and Padunghiton S 2020 Synthesis optimization of hybrid anion exchanger containing triethylamine functional groups and hydrated Fe(III) oxide nanoparticles for simultaneous nitrate and phosphate removal *Chemical Engineering Journal* **381** 122671
[49] Nguyen T T, Le T T, Phan P T and Nguyen N H 2020 Preparation, Characterization, and Application of Novel Ferric Oxide-Amine Material for Removal of Nitrate and Phosphate in Water *Journal of Chemistry* **2020** 8583543
[50] Belhachemi M and Addoun F 2011 Comparative adsorption isotherms and modeling of methylene blue onto activated carbons *Applied Water Science* **1** 111-7
[51] Chabani M, Amrane A and Bensmaili A 2009 Equilibrium sorption isotherms for nitrate on resin Amberlite IRA 400 *Journal of Hazardous Materials* **165** 27-33
[52] Limousin G, Gaudet J P, Charlet L, Szenknect S, Barthès V and Krimissa M 2007 Sorption isotherms: A review on physical bases, modeling and measurement *Applied Geochemistry* **22** 249-75
[53] Venkiteshwaran K, Wells E and Mayer B K 2020 Kinetics, Affinity, Thermodynamics, and Selectivity of Phosphate Removal Using Immobilized Phosphate-Binding Proteins *Environmental Science & Technology* **54** 10885-94
[54] Das R, Das Tuhi S and Zaidi S M J 2018 *Carbon Nanotubes for Clean Water*, ed R Das (Cham: Springer International Publishing) pp 85-106
[55] Bekçi Z, Seki Y and Kadir Yurdakoç M 2007 A study of equilibrium and FTIR, SEM/EDS analysis of trimethoprim adsorption onto K10 *Journal of Molecular Structure* **827** 67-74
[56] Du X, Li Y, Xia Y-L, Ai S-M, Liang J, Sang P, Ji X-L and Liu S-Q 2016 Insights into Protein–Ligand Interactions: Mechanisms, Models, and Methods *International Journal of Molecular Sciences* **17** 144
[57] Manju G N, Raji C and Anirudhan T S 1998 Evaluation of coconut husk carbon for the removal of arsenic from water *Water Research* **32** 3062-70
[58] Namasivayam C and Ranganathan K 1995 Removal of Cd(II) from wastewater by adsorption on “waste” Fe(III)Cr(III) hydroxide Water Research 29 1737-44
[59] Deliyanni E A, Peleka E N and Lazaridis N K 2007 Comparative study of phosphates removal from aqueous solutions by nanocrystalline akaganéite and hybrid surfactant-akaganéite Separation and Purification Technology 52 478-86
[60] Genz A, Kornmüller A and Jekel M 2004 Advanced phosphorus removal from membrane filtrates by adsorption on activated aluminium oxide and granulated ferric hydroxide Water Research 38 3523-30
[61] Wang J, N L I, Meng H and Fang C 2009 Research of LUCC for Industrial Zone Based on the Landsat TM Image. In: 2009 International Conference on Environmental Science and Information Application Technology, pp 260-2
[62] Kuzawa K, Jung Y-J, Kiso Y, Yamada T, Nagai M and Lee T-G 2006 Phosphate removal and recovery with a synthetic hydrotalcite as an adsorbent Chemosphere 62 45-52
[63] Mahmudov R and Huang C P 2011 Selective adsorption of oxyanions on activated carbon exemplified by Filtrasorb 400 (F400) Separation and Purification Technology 77 294-300
[64] Marshall W E and Wartelle L H 2004 An anion exchange resin from soybean hulls Journal of Chemical Technology & Biotechnology 79 1286-92
[65] Martin B D, Parsons S A and Jefferson B 2009 Removal and recovery of phosphate from municipal wastewaters using a polymeric anion exchanger bound with hydrated ferric oxide nanoparticles Water Science and Technology 60 2637-45
[66] Zeng L, Li X and Liu J 2004 Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings Water Research 38 1318-26