Remarkable phosphate removal from saline solution by using a novel trimetallic oxide nanocomposite
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ABSTRACT
Phosphate removal is an important measure to control eutrophication in aquatic environments, as it inhibits algal bloom. Salinity exists in these media along with high phosphate and currently available phosphate removal methods function poorly under this condition. In this study, the main objective is to fabricate a nanocomposite to improve and accelerate phosphate removal from saline solutions. To achieve this goal, Fe₃O₄/ZnO and a novel nanoadsorbent, Fe₃O₄/ZnO/CuO, were synthesized. Their characteristics were determined using FE-SEM, EDX, FT-IR, and XRD analyses, and their capability to adsorb phosphate from saline solutions was investigated and compared. The overall results suggest that the trimetallic oxide nanocomposite has great potential for the efficient removal of phosphate, in comparison with Fe₃O₄/ZnO. Experiments showed that Fe₃O₄/ZnO/CuO exhibited a remarkable sorption capacity of 156.35 mg P/g, fast sorption kinetic, strong selectivity for phosphate even in the presence of a high concentration of salinity (60 mg/L), and a wide applicable pH range of 3–6.
Furthermore, using Fe₃O₄/ZnO/CuO, even a low dosage of 0.1 g/L was sufficient to reach an adsorption efficiency of 96.13% within 15 min compared to Fe₃O₄/ZnO (80.47% within 30 min). Moreover, the pseudo-second-order kinetic model best described the experimental adsorption data for both nanocomposites.

Key words | adsorption, eutrophication, Fe₃O₄/ZnO, salinity, trimetallic

HIGHLIGHTS
- High adsorption capacity of the trimetallic oxide nanocomposite.
- Wide applicable pH range of 3–6 of Fe₃O₄/ZnO/CuO nanocomposite.
- Enhanced PO₄³⁻ removal from saline solution by Fe₃O₄/ZnO/CuO.
- More than 45% adsorption rate increase in saline solution by modifying Fe₃O₄/ZnO.
- The pseudo-second-order kinetic model perfectly described PO₄³⁻ removal.

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INTRODUCTION

Phosphorus (P), as an indispensable element, holds a vital nourishing role in the growth of all living organisms (Shan et al. 2020). However, their excessive presence in the environment originating from industries, agricultural, and domestic wastewater sources could accelerate the overgrowth of undesirable algae and aquatic plants. This algae bloom leads to the eutrophication phenomenon, an important issue that damages the biodiversity and functionality of the aquatic ecosystem (Wu et al. 2017; Li et al. 2018; Ma et al. 2020). Therefore, controlling the amount of phosphorus is of great importance.

High amounts of salt are used in oil, textile, and leather industries. During their processes, a large amount of saline wastewater is produced, which finally enters surface waters. Moreover, high amounts of NaCl and Na₂SO₄ salts exist naturally in free waters as well (Stewart 2008). According to the results of various studies, the phosphorous removal efficiency decreases significantly with an increase in the amount of salinity in the solution (Lefebvre & Moletta 2006). Therefore, it is of high significance to find a method that functions well under this condition.

Thus far, conventional approaches such as chemical precipitation and biological treatment are incapable of removing low concentrations of phosphate; therefore, other methods are required so as to overcome the mentioned problems (Wu et al. 2017). Due to the simplicity in design, the effectiveness even at low concentrations of phosphorus, and the recycling capability, the adsorption method has been widely accepted as a preferable approach for phosphate removal (Wu et al. 2017; Yin et al. 2018; Dong et al. 2020). Since conventional adsorbents show low selectivity for phosphate adsorption in the presence of other competing anions (such as sulfate, chloride, and bicarbonate), the identification and development of adsorbents with high selectivity for this nutrient are crucial (Acelas et al. 2015). Recently, therefore, nano-based adsorbents have been developed due to their ease of use, low cost, and contamination removal capability from water and wastewater. So far, various nanocomposites have been used for phosphate adsorption. For example, Nie et al. (2019) achieved 44.14 mg P/g adsorption capacity by using Ti–NS nanocomposite at pH 6.5–7.5, nanocomposite dosage of 500 mg/L, initial phosphate concentration of 10 mg/L, and at 25 °C. In Zhou et al.’s (2018) study, the adsorption capacity of 37.86 mg P/g was reported by the use of nHFZO@I402 nanocomposite at pH 7, nanocomposite dosage of 750 mg/L, phosphate concentration of 5 mg/L, and at 25 °C. In another study, Wu et al. (2017) achieved the adsorption capacity of 83.5 mg P/g by using La(OH)₃/Fe₃O₄ nanocomposite at pH 4.3–6, nanocomposite dosage of 100 mg/L, initial phosphate concentration of 0.5–15 mg/L, and at 25 °C. In Nodeh et al.’s (2017) research, the adsorption capacity of 116.28 mg P/g was achieved by using MG@La nanocomposite at pH 6, nanocomposite dosage of 100 mg/L, initial phosphate concentration of 50 mg/L, and at 25 °C.

Moreover, the recyclability of an adsorbent is of great importance to evaluate its performance for practical applications (Hu et al. 2016). Nanoparticles are difficult to separate after usage in wastewater treatment, and commonly used adsorbent recycling systems suffer from several
disadvantages. While separation methods such as centrifuge consume a lot of energy, and filtration is susceptible to clogging, magnetic separation is a faster and more effective method (Wu et al. 2017; Cai et al. 2019). Accordingly, the combination of magnetic nanoparticles (such as Fe₃O₄) with other nanomaterials makes the separation and recycling of the synthesized adsorbent more facile.

Earlier research conducted by Nezhadheydari et al. (2019) showed that Fe₃O₄/ZnO nanocomposite has a phosphate removal efficiency of 50% in 12 h, requiring modification. For this purpose, CuO nanoparticles were used because of their cost-efficiency, simple synthesis, and the fact that the combination of ZnO and CuO creates environmentally friendly nanocomposites. Also, through the formation of inner-sphere and/or outer-sphere complexes, CuO nanoparticles show a strong ligand sorption (of HPO₄²⁻ and H₂PO₄⁻) (Mahdavi & Akhzari 2016).

However, to the best of our knowledge, there are no reports available on the application of Fe₃O₄/ZnO/CuO for phosphate removal. In addition, the functionality of this trimetallic oxide nanocomposite for phosphate adsorption remains unclear and requires more investigations.

Motivated by these concepts, the main objectives of this study are to (1) fabricate and characterize a novel recyclable trimetallic oxide nanocomposite for phosphate removal, (2) improve the phosphate sorption efficiency and the capacity of the trimetallic oxide adsorbent, (3) accelerate phosphate removal by modifying Fe₃O₄/ZnO, and (4) investigate the kinetic studies of phosphate removal in the presence and absence of salinity by Fe₃O₄/ZnO/CuO. This study proposed a novel adsorbent as a promising candidate for effective phosphate removal from saline solutions.

MATERIAL, EQUIPMENT, AND METHODS

Material

In this study, all chemicals were of analytical grade and used without further purification. Iron(III) chloride hexahydrate (FeCl₃·6H₂O), zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O), ethylene glycol, polyethylene glycol, sodium acetate (C₂H₅NaO₂), copper(II) acetate dihydrate (Cu(CO₂CH₃)₂·2H₂O), sodium hydroxide (NaOH), ethanol and distilled water were used for synthesizing the nanocomposites. KH₂PO₄ was used as a pollutant, and NaCl and Na₂SO₄ were used for investigating the effect of salinity on phosphate adsorption. Molybdenum reagent was also used for analyzing the concentration of phosphate in the solution, all of which were purchased from Merck.

Equipment

The equipment used in this research was Hach DR4000 U spectrophotometer, Metrohm 691 pH meter, Korea Tech DSA-series ultrasonic bath, Shafaq magnetic stirrer (made in Iran), Fara Azma vacuum oven (made in Iran), 101 Sigma centrifuge, Stainless Teflon autoclave (Made in Iran), Tescan MIRA3 (for FE-SEM and EDX analysis), XRD Philips X’pert XPD, and Frontier FT-IR (made in the USA).

Synthesis of nanocomposites

To synthesize the nanoadsorbents, the following steps were taken for each of the nanocomposites.

Preparation of Fe₃O₄/ZnO

Fe₃O₄ and ZnO nanoparticles were synthesized by co-precipitation and sol-gel methods, respectively (Fu & Zhu 2016; Hasnida et al. 2016). To prepare the nanoparticles, 1 g of FeCl₃·6H₂O was poured into 40 ml of ethylene glycol and stirred to obtain a clear solution. Then, 4.3 g of sodium acetate and 1 g of polyethylene glycol were added to the solution, stirred at room temperature for 30 min, and put in an autoclave for 8 h at 200 °C. Then, it was washed several times with ethanol and dried at room temperature.

The final solution was kept at room temperature for 1 h to allow all sediments to settle. Then, it was centrifuged several times with ethanol and was dried at room temperature.
Preparation of Fe₃O₄/ZnO/CuO

CuO nanoparticles were synthesized using the hydrolysis method (Tran & Nguyen 2014). To prepare these nanoparticles, 0.6 g of copper acetate (II) was dissolved in 50 ml of distilled water on a stirrer at 100 °C, and 0.01 g of NaOH was added. Then, 0.1 g of the synthesized Fe₃O₄/ZnO nanocomposite was dispersed in 25 ml of distilled water, added to the copper solution, and stirred for 1 h at 80 °C. After hydrolysis, the precipitate in the solution was washed several times with distilled water and ethanol, and then the resulting substance was dried at 200 °C for 2 h.

Methods

Phosphate adsorption from the synthesized wastewater using Fe₃O₄/ZnO and Fe₃O₄/ZnO/CuO nanocomposites was investigated by the one-factor-at-a-time (OFAT) method. The values of the examined parameters are presented in Table 1.

A 100 ml glass beaker was used for phosphate removal examinations at a temperature of 25 ± 0.5 °C, and all experiments were performed three times, the error rate of which was less than 1.5%. After each test, the used nanocomposite was separated with a magnet to avoid a possible metal leakage. The remaining liquid in the beaker was used to determine the concentration of residual phosphate in the solution by the colorimetric method using the UV–Vis spectrophotometer and the molybdovanadate reagents (0.5 ml) (Eaton et al. 2005). Then, the phosphate adsorption efficiency was calculated using the following equation:

\[
E\% = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]  

where \( C_0 \) (mg/L) is the initial concentration of the phosphate solution, \( C_e \) (mg/L) is the concentration of phosphate solution after adsorption, and \( E \) (%) is the efficiency of phosphate adsorption.

The capacity of phosphate adsorption by Fe₃O₄/ZnO and Fe₃O₄/ZnO/CuO adsorbents was calculated using the following equation (Lin et al. 2020):

\[
q_e = \frac{(C_0 - C_e)V}{M_s}
\]  

where \( C_0 \) and \( C_e \) (mg/L) are initial and equilibrium concentrations of the phosphate solution, respectively, \( V \) (L) is the volume of the phosphate solution, and \( M_s \) (g) is the mass of the utilized nanocomposite.

After obtaining the optimum conditions for phosphate removal, phosphate adsorption tests were conducted in the presence of NaCl and Na₂SO₄ salts, which are the predominant salts in both industrial wastewater and free waters (Stewart 2008). Then, the amount of adsorption efficiency was determined.

Adsorption kinetics were also investigated by pseudo-first-order and pseudo-second-order kinetic equations (Equations (3) and (4)) (Ho & McKay 1998):

\[
\frac{dq}{dt} = K_1(q_e - q)
\]  

\[
\frac{dq}{dt} = K_2(q_e - q)^2
\]  

where \( K_1 \) (L/h) is the rate constant of the pseudo-first-order model, \( K_2 \) (g/mg h) is the rate constant of the pseudo-second-order model, and \( q \) and \( q_e \) (mg/g) are the amount of phosphate adsorbed to the adsorbent at time \( t \) (min).

To determine pH at the point of zero charge (pH_{pzc}) for each nanocomposite, the following approach was used. First, 0.01 M NaCl solution was added to sealed vials, and the initial pH of each vial was adjusted to the values between 2 and 10 using pH regulator solution. 30 mg of each nanocomposite was added to vials with different initial pH and shaken for 48 h at room temperature. Using a pH meter, the final pH of each solution was determined. The initial and final graphs were plotted, and pH_{pzc} is the
interception point of the $pH_{final}$ vs. $pH_{initial}$ curve and the $pH_{initial} = pH_{final}$ line (Órfão et al. 2006).

RESULTS AND DISCUSSIONS

Magnetic adsorbent characteristics

To determine the characteristics of the synthesized nanocomposites, FE-SEM, EDX, FT-IR, and XRD analyses were performed, the results of which are presented in Figures 1–4.

FE-SEM analysis

To investigate the morphology and dimensions of Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/CuO, FE-SEM images of both fabricated nanocomposites are presented in Figure 1. Figure 1(a) shows the morphology of Fe$_3$O$_4$/ZnO, which has a rod-shaped structure, and the dimension of this nanocomposite varies from 20 to 30 nm. In Hong et al.’s (2008) and Xia et al.’s (2011) studies, the average dimension of Fe$_3$O$_4$/ZnO nanocomposite was in the ranges of 25–30 and 20–30 nm, respectively. As can be seen in Figure 1(b), Fe$_3$O$_4$/ZnO/CuO has a spherical structure, and the dimension of this nanocomposite varies in the range of 25–36 nm.

EDX analysis

X-ray diffraction analysis was performed to identify the chemical composition of the synthesized samples. X-ray diffraction spectra for Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/CuO are shown in Figure 2(a) and 2(b), respectively. The constituent materials of the two synthesized nanocomposites are presented in Table 2. Based on results, Fe$_3$O$_4$/ZnO has O, Fe, and Zn elements, and the trimetallic oxide adsorbent contains O, Fe, Zn, and Cu. According to Figure 2(a) and 2(b), broad peaks of Zn, O, Fe, and Cu elements indicate a strong bond between Fe$_3$O$_4$ and ZnO nanoparticles in Fe$_3$O$_4$/ZnO and between Fe$_3$O$_4$, ZnO, and CuO nanoparticles in the Fe$_3$O$_4$/ZnO/CuO nanocomposite (Farrokhi et al. 2014; Tju et al. 2017).

FT-IR analysis

FT-IR was used to qualify the chemical bonds between the functional groups of Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/CuO nanocomposites. The synthesized samples were subjected to wavenumbers in the range of 400–4,000 cm$^{-1}$, the results of which are presented in Figure 3. According to Figure 3(a), the adsorption in 400 and 590 cm$^{-1}$ are associated with stretching bands of Zn–O and Fe–O, respectively. Moreover, the broad peak around 1,700–3,400 cm$^{-1}$ is related to the stretching vibrations of O–H bond in water molecules adsorbed on the surface of Fe$_3$O$_4$/ZnO nanocomposite. As shown in Figure 3(b), the adsorption in 400, 420, and 590 cm$^{-1}$ are related to stretching bands of Zn–O, Cu–O, and Fe–O, respectively. Besides, the wide peak in 1,700–3,400 cm$^{-1}$ is due to the stretching vibrations of O–H bond in water molecules adsorbed on the surface of Fe$_3$O$_4$/ZnO/CuO (Xie et al. 2015; Kulkarni et al. 2017; Tju et al. 2017). The agreement of XRD and EDX analyses indicates the successful formation of fabricated nanocomposites (Taufik & Saleh 2017).

XRD analysis

XRD patterns were generated using Cu Kα radiation (40 kV, 40 mA) to identify the crystalline components of both adsorbents. All XRD patterns were obtained over a 2θ range of 5–80°. Figure 4(a) and 4(b) illustrates XRD patterns of Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/CuO nanoadsorbents, respectively. Fe$_3$O$_4$ nanoparticles have diffraction angles at about 2θ = 30, 35, 43, 53, 57, 62, 66, 71, 74, 75, and 79, ZnO nanoparticles at 2θ = 32, 34, 36, 47, 56, 63, 66, 68, and 69 (Farrokhi et al. 2014; Vakili Tajareh et al. 2019), and CuO particles have diffraction angles at 2θ = 32, 35, 38, 48, 53, 58, 61, 65, 66, and 67 (Taufik et al. 2016).
Figure 2 | EDS spectra of (a) Fe₃O₄/ZnO nanocomposite and (b) Fe₃O₄/ZnO/CuO nanocomposite.
Determining the optimal condition of the two nanoadsorbents for phosphate removal

To determine the optimum values of parameters (the initial pH of the solution, the concentration of nanocomposite, and the initial concentration of phosphate), required examinations were conducted. Then, the optimum conditions for each of the desired parameters were determined. The effect of different dosages of salinity and adsorption kinetics under optimum conditions were also investigated.

Effect of pH

Both the dominant phosphate species and surface charges of a nanocomposite in water are highly dependent on pH. Therefore, experiments were conducted to understand the effect of solution pH on the phosphate removal efficiency with the use of both adsorbents. Using pH regulator solution, all phosphate solutions were adjusted to a wide pH range of 2–11, the results of which are displayed in Figure 5. As can be seen in Figure 5(a), the acidity or alkalinity of the solution had a significant effect on the phosphate removal efficiency. Experimental data showed that the efficiency of the process was increased sharply and then decreased to further increase of pH. According to the results, both nanocomposites had a better performance in the acidic range (Fe$_3$O$_4$/ZnO at pH = 3
and Fe$_3$O$_4$/ZnO/CuO at pH = 4). As known, the phosphate in the solution changes into distinct types at different pH ranges, as shown in the following equation:

$$H_3PO_4 \leftrightarrow pK_1 H_2PO_4^- + H^+$$
$$pH = 2.12$$
$$H_2PO_4^- \leftrightarrow pK_2 HPO_4^{2-} + H^+$$
$$pH = 7.21$$
$$HPO_4^{2-} \leftrightarrow pK_3 PO_4^{3-} + 2H^+$$
$$pH = 12.67$$

where $pK_1 = 2.12$, $pK_2 = 7.21$, and $pK_3 = 12.67$, respectively (Hong et al. 2017; Othman et al. 2018). $pH_{pzc}$ was calculated for both adsorbents. As shown in Figure 5(c) and 5(d), $pH_{pzc}$ of Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/CuO are 6 and 6.76, respectively. At lower pH (under $pH_{pzc}$), due to protonation, both nanocomposite surfaces were positively charged, and the dominant phosphate ions $H_2PO_4^-$ were more easily adsorbed on the adsorbents’ surface. Therefore, the adsorption efficiency was higher in acidic pH. As pH increases (more than $pH_{pzc}$), through deprotonation, the positively charged surface of both the nanocomposites gradually changes into negative. As a result, the adsorption efficiency...
dropped due to the negligible attraction between the dominant anion species and the negative charges on the adsorbents’ surface (Nezamzadeh-Ejhieh & Hushmandrad 2010; Farrokhi et al. 2014; Taufik & Saleh 2017; Karthikeyan & Meenakshi 2020; Salehi & Hosseinifard 2020). In many studies, a similar tendency was indicated regarding the removal of phosphate (Liu et al. 2011; Eljamal et al. 2016; Hong et al. 2017; Salehi & Hosseinifard 2020).

Since the optimum pH value of the trimetallic oxide nanocomposite (pH = 4) is higher than that of Fe₃O₄/ZnO (pH = 3), the amount of material needed to reduce pH will decrease. Moreover, Fe₃O₄/ZnO/CuO has an efficiency of 96.13% at pH = 4, with an increase of nearly 16% compared to Fe₃O₄/ZnO with a removal efficiency of 80.46% at pH = 3. Furthermore, at pH in the wide range of 3–6, the trimetallic oxide adsorbent is highly efficient. These results show a significant improvement in the quality of Fe₃O₄/ZnO/CuO and its more economical use.

The effect of the initial concentration of nanocomposite

To investigate the effect of the adsorbents dosage, different amounts of them were tested, the results of which are presented in Figure 6. As can be observed in Figure 6(a), at first, the adsorption efficiency rises with an increase in the concentration of both nanocomposites and decreases slightly after reaching the maximum value. This trend can be ascribed to an increase in adsorbent dosage, which leads to the lack of access to the unsaturated active sites in the adsorbents (Farrokhi et al. 2014; Salehi & Hosseinifard 2020). Also, when the adsorbent dosage exceeds 100 mg/L, the particles become agglomerated, which culminates in a decrease in surface area, and thus a reduction in the adsorption efficiency (Keramati & Ayati 2019). Another important point is that the value of adsorption capacity increased while using a solution that contains 100 mg/L of the trimetallic oxide nanocomposite (156.35 mg/g) in comparison with the same amount of Fe₃O₄/ZnO (130.76 mg P/g). This increment can be attributed to the CuO nanoparticles. Since these particles exhibit a strong ligand sorption (of H₂PO₄⁻) through the formation of inner-sphere and/or outer-sphere complexes, the phosphate adsorption efficiency and capacity increase significantly (Mahdavi & Akhzari 2016).

Effect of initial phosphate concentration

To determine the optimum phosphate concentration, different amounts of this contaminant were examined, the results of which are presented in Figure 7. Based on

![Figure 6](http://example.com/figure6.png)

Figure 6 | (a) Effect of nanocomposite amount on phosphate absorption efficiency in optimum conditions and (b) effect of Fe₃O₄/ZnO and Fe₃O₄/ZnO/CuO nanocomposites on the phosphate uptake efficiency over time (pH = 3, [Fe₃O₄/ZnO] = 20–200 mg/L, [PO₄³⁻] = 50 mg/L, and T = 25 ± 0.5 °C; pH = 4, [Fe₃O₄/ZnO/CuO] = 20–200 mg/L, [PO₄³⁻] = 50 mg/L, and T = 25 ± 0.5 °C).
the results, by increasing the initial concentration of phosphate, the adsorption rate raised at first and then decreased. This trend could be related to the presence of sufficient active sites in the adsorbent compared to the initial concentration of the contaminant. By increasing the concentration to 50 mg/L, the adsorption rate for Fe₃O₄/ZnO and Fe₃O₄/ZnO/CuO nanocomposites reached 80.46% and 96.31%, respectively. Then the adsorption efficiency, in concentrations of more than 50 mg/L, decreased due to the reduction in the number of active sites in comparison to the dosage of contaminant (Hallaji et al. 2015; Nakarmi et al. 2020). In several studies, increasing the initial phosphate concentration has been associated with a decrease in the phosphate removal efficiency (Bozorgpour et al. 2016; Nodeh et al. 2017). Besides, by comparing the graphs in Figure 7(a), it can be concluded that the trimetallic oxide nanocomposite can maintain its high adsorption efficiency even at a low concentration of phosphate (10 mg/L) in comparison to Fe₃O₄/ZnO.

**Equilibrium time**

Phosphate adsorption for both nanocomposites was tested in 1 h. Considering the graphs illustrated in Figures 5(b), 6(b), and 7(b), the equilibrium time for Fe₃O₄/ZnO and Fe₃O₄/ZnO/CuO nanocomposites was attained in 30 and 15 min, respectively. This noticeable decrease in the equilibrium time indicates a significant improvement of the trimetallic oxide adsorbent in comparison to Fe₃O₄/ZnO due to the reduction in the consumed energy during the process.

**The effect of salinity on the phosphate removal efficiency**

To investigate the ability of the synthesized nanocomposites in phosphate removal in the presence of salinity, the influence of different anions was investigated. The effect of chloride and sulfate anions, as a predominant ion that generally coexists with phosphate in both industrial wastewater and free waters, was examined. These ions were tested at concentrations of 10, 20, 30, 40, 50, and 60 mg/L, and their results are presented in Figure 8(a) and 8(b) for Fe₃O₄/ZnO and Fe₃O₄/ZnO/CuO nanocomposites, respectively. As can be seen, the effect of both salts on the phosphate removal efficiency was almost constant. The presence of both ions had an interfering effect on the phosphate adsorption and led to a decrease in the adsorption efficiency. The investigated anions' chemical attraction to the adsorption sites can be explained by the Hofmeister order,
i.e., $\text{PO}_3^{4-} < \text{CO}_2^{4-} < \text{SO}_2^{3-} < \text{Cl}^- < \text{Br}^- < \text{NO}_3^-$ (Luo et al. 2020). However, salinity had less effect on the trimetallic oxide adsorbent in comparison to Fe$_3$O$_4$/ZnO. Also, Fe$_3$O$_4$/ZnO/CuO had a higher adsorption capability even at high salinity concentrations (60 mg/L) (less than 16% decrease in efficiency). On the other hand, Fe$_3$O$_4$/ZnO had a significant efficiency reduction in the presence of salinity (more than 36%). Moreover, Fe$_3$O$_4$/ZnO/CuO achieved higher efficiency in less time, indicating its higher ability for phosphate removal. According to the results, the phosphate removal efficiency in the presence of the mentioned concentrations of NaCl salinity using Fe$_3$O$_4$/ZnO was 70.95, 66.12, 56.31, 57.4, 48.6, and 39.81%, respectively, while this efficiency for trimetallic oxide nanocomposite was 90.74, 89.32, 88.02, 85.62, 83.45, and 80.37%, respectively. The phosphate removal efficiency in the presence of the mentioned concentrations of Na$_2$SO$_4$ salinity while using Fe$_3$O$_4$/ZnO was 76.4, 75.3, 55.3, 53.9, 49.5, and 43.72%, respectively, and this efficiency using Fe$_3$O$_4$/ZnO/CuO was 90.13, 88.48, 87.23, 86.33, 83.69, and 81.05%, respectively. The decrease in the contaminant removal efficiency in the presence of salinity can be due to the competition that occurs between ions. Similar results have been reported in several studies. In Hong et al.’s (2017) study, Fe$_3$O$_4$@SiO$_2$ nanocomposite was used in the presence of HCO$_3$ anion, which reduced the phosphate removal efficiency by 29%. In a study by Hu et al. (2020), Zr@MCS nanoadsorbent was used for phosphate removal in the presence of SO$_4^{2-}$ anion, which reduced the adsorption efficiency by more than 15%.

Equilibrium and kinetic adsorption studies

To evaluate the rate of phosphate adsorption on the surface of the nanocomposites, pseudo-first-order and pseudo-second-order kinetic models were applied to the adsorption data. Their results under two situations – the presence and absence of salinity – are presented in Table 3. The pseudo-second-order kinetics has a higher correlation coefficient ($R^2$) than the pseudo-first-order (closer to 1) in the absence of salinity in the system. So, it can be concluded that phosphate adsorption kinetics follows the pseudo-second-order model. Different types of adsorbents had similar results (Bozorgpour et al. 2016; Nodeh et al. 2017; Wu et al. 2017; Zhou et al. 2018; Hao et al. 2019; He et al. 2020). According to the results, the rate constant in the kinetic equation for Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/CuO is 0.001 and 0.0015, respectively. The 50% increase in the adsorption rate while using Fe$_3$O$_4$/ZnO/CuO indicates its higher capability in phosphate adsorption. Moreover, the Fe$_3$O$_4$/ZnO/CuO maximum adsorption capacity (156.35 mg P/g) is approximately 16.37% higher than that of Fe$_3$O$_4$/ZnO (130.76 mg P/g).

Adsorption kinetics was also applied on phosphate removal in the presence of salinity (NaCl and Na$_2$SO$_4$ salts with a concentration of 60 mg/L) in the system.
concentration of 60 mg/L was chosen due to its substantial effect on the reduction of phosphate removal efficiency, the results of which are presented in Table 3. By comparing the values of the correlation coefficient ($R^2$), it can be seen that the phosphate adsorption in the presence of salinity follows the pseudo-second-order model.

According to Table 3, the adsorption rate by using Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/CuO nanocomposites in the presence of NaCl in the system ($K_2$ = 0.0007 and $K_2$ = 0.0013, respectively) is approximately 28 and 30%, respectively. This rate is higher than the condition that Na$_2$SO$_4$ exists in the system ($K_2$ = 0.0005 and $K_2$ = 0.0009, respectively), which shows that the interfering effect of NaCl on the adsorption efficiency is slightly less than Na$_2$SO$_4$. According to the results, Fe$_3$O$_4$/ZnO/CuO had an adsorption rate of about 45% higher than Fe$_3$O$_4$/ZnO. Also, using Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/CuO adsorbents in the presence of NaCl in the system reduced the reaction rate by 30 and 13%, respectively, and by 50 and 40% in the presence of Na$_2$SO$_4$, respectively, compared to the absence of salinity in the system. Generally, the results indicate the better quality and performance of the modified trimetallic oxide nanocomposite.

### Table 3 | Kinetics parameters for phosphate adsorption by Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/ZnO/CuO nanocomposites

| Nanocomposite Type of salinity | $q_e$ (mg P/g) | $K_1$ | $R^2$ | $K_2$ | $R^2$ | $q_e$ (mg P/g) |
|------------------------------|---------------|------|------|------|------|---------------|
| Without salinity             |               |      |      |      |      |               |
| Fe$_3$O$_4$/ZnO              | –             | 0.1924 | 0.7734 | 0.001  | 0.8426 | 130.76        |
| Fe$_3$O$_4$/ZnO/CuO          | –             | -0.4054 | 0.8614 | 0.0015 | 0.999  | 156.35        |
| With salinity                |               |      |      |      |      |               |
| Fe$_3$O$_4$/ZnO NaCl (60 mg/L)| –             | -0.1753 | 0.9017 | 0.0007 | 0.9618 | 64.91         |
| Na$_2$SO$_4$ (60 mg/L)       |               | 0.1647 | 0.8122 | 0.0005 | 0.939  | 71.29         |
| Fe$_3$O$_4$/ZnO/CuO NaCl (60 mg/L)| –             | -0.4311 | 0.7289 | -0.0013 | 0.7468 | 131.1         |
| Na$_2$SO$_4$ (60 mg/L)       |               | -0.3745 | 0.7392 | 0.0009 | 0.8684 | 132.17        |

1 mol/L NaOH solution with a contact time of 20 min. This desorption reagent could efficiently regenerate both of the adsorbents due to the tendency to replace OH$^-$ particles with H$_2$PO$_4^-$ particles. The NaOH-regenerated nanocomposites were reused for phosphate removal under optimum conditions. As illustrated in Figure 9, the results showed that with the use of Fe$_3$O$_4$/ZnO, the phosphate removal efficiency had a 2–3% decrease in each cycle and after the 10th cycle, the efficiency declined up to 20%. On the other hand, by using the modified trimetallic oxide nanocomposite, the phosphate adsorption efficiency had less than 1% decrease after each cycle, while, in the 10th cycle, it declined to less than 10%.

### CONCLUSION

In this study, two magnetically separable Fe$_3$O$_4$/ZnO and modified Fe$_3$O$_4$/ZnO/CuO nanocomposites were synthesized and characterized. Then, their ability to adsorb phosphate and the effect of salinity on their performance were investigated and compared. According to the results, the trimetallic oxide nanocomposite had a high capacity to adsorb phosphate in the absence and particularly in the presence of salinity, while Fe$_3$O$_4$/ZnO showed less resistance to salinity and had a lower phosphate removal efficiency. Results demonstrated about 50% increase in phosphate adsorption rate by using Fe$_3$O$_4$/ZnO/CuO and its significant improvement in comparison to Fe$_3$O$_4$/ZnO, due to the decrease in reaction time and energy, and the increase in the phosphate removal efficiency. Regeneration and reusability studies showed that the trimetallic oxide nanocomposite had a notable improvement in comparison to Fe$_3$O$_4$/ZnO due to its negligible adsorption efficiency reduction after regeneration.
each cycle. Moreover, the pseudo-second-order kinetic model perfectly described phosphate removal for both nanocomposites in the presence and absence of salinity.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Acelas, N. Y., Martin, B. D., López, D. & Jefferson, B. 2015 Selective removal of phosphate from wastewater using hydrated metal oxides dispersed within anionic exchange media. *Chemosphere* 119, 1353–1360.

Bozorgpour, F., Ramandi, H. F., Jafari, P., Samadi, S., Yazd, S. S. & Aliabadi, M. 2016 Removal of nitrate and phosphate using chitosan/Al₂O₃/Fe₃O₄ composite nanofibrous adsorbent: comparison with chitosan/Al₂O₃/Fe₃O₄ beads. *Int. J. Biol. Macromol.* 93, 557–565.

Cai, W., Fu, F., Zhu, L. & Tang, B. 2019 Simultaneous removal of chromium (VI) and phosphate from water using easily separable magnetite/pyrite nanocomposite. *J. Alloys Compd.* 803, 118–125.

Dong, S., Ji, Q., Wang, Y., Liu, H. & Qu, J. 2020 Enhanced phosphate removal using zirconium hydroxide encapsulated in quaternized cellulose. *J. Environ. Sci.* 89, 102–112.

Eaton, A., Clesceri, L. & Greenberg, A. 2005 *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association (APHA), Washington, DC, 20001-3710.

Eljamal, O., Khalil, A. M., Sugihara, Y. & Matsunaga, N. 2016 Phosphorus removal from aqueous solution by nanoscale zero valent iron in the presence of copper chloride. *Chem. Eng. J.* 293, 225–231.

Farrokhi, M., Hosseini, S.-C., Yang, J.-K. & Shirzad-Siboni, M. 2017 Application of ZnO–Fe₃O₄ nanocomposite on the removal of azo dye from aqueous solutions: kinetics and equilibrium studies. *Water Air Soil Pollut.* 225, 2113.

Fu, R. & Zhu, M. 2016 Synthesis and characterization of structure of Fe₃O₄@ graphene oxide nanocomposites. *Adv. Compos. Lett.* 25, 096369531602500604.

Hallaji, H., Keshtkar, A. R. & Moosavian, M. A. 2015 A novel electrospun PVA/ZnO nanofiber adsorbent for U (VI), Cu (II) and Ni (II) removal from aqueous solution. *J. Taiwan Inst. Chem. Eng.* 46, 109–118.

Hao, H., Wang, Y. & Shi, B. 2019 *Nala (CO₃)₂ hybridized with Fe₃O₄ for efficient phosphate removal: synthesis and adsorption mechanism study*. *Water Res.* 155, 1–11.

Hasnidanawani, J., Azlina, H., Norita, H., Bonnia, N., Ratim, S. & Ali, E. 2016 Synthesis of ZnO nanostructures using sol-gel method. *Procedia Chem.* 19, 211–216.

He, J., Xu, Y., Wang, W., Hu, B., Wang, Z., Yang, X., Wang, Y. & Yang, L. 2020 Ce (III) nanocomposites by partial thermal decomposition of Ce-MOF for effective phosphate adsorption in a wide pH range. *Chem. Eng. J.* 379, 122431.

Ho, Y. & Mckay, G. 1998 A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Saf. Environ. Prot.* 76, 332–340.

Hong, R., Zhang, S., Di, G., Li, H., Zheng, Y., Ding, J. & Wei, D. 2008 Preparation, characterization and application of
Fe$_3$O$_4$/ZnO core/shell magnetic nanoparticles. *Mater. Res. Bull.* **43**, 2457–2468.

Hong, D., Yanling, Z., Qianlin, D., Junwen, W., ZHANG, K., Guangyue, D., Xianmei, X. & Chuanmin, D. 2017 Efficient removal of phosphate from aqueous solution using novel magnetic nanocomposites with Fe$_3$O$_4$@SiO$_2$ core and mesoporous CeO$_2$ shell. *J. Rare Earths* **35**, 98–994.

Hu, L., Li, Y., Zhang, X., Wang, Y., Cui, L., Wei, Q., Ma, H., Yan, L. & Du, B. 2016 Fabrication of magnetic water-soluble hyperbranched polyol functionalized graphene oxide for high-efficiency water remediation. *Sci. Rep.* **6**, 28924.

Hu, Y., Du, Y., Nie, G., Zhu, T., Ding, Z., Wang, H., Zhang, L. & Xu, Y. 2020 Selective and efficient sequestration of phosphate from waters using reusable nano-Zr (IV) oxide impregnated agricultural residue anion exchanger. *Sci. Total Environ.* **700**, 134999.

Karthekeyan, P. & Meenakshi, S. 2020 Enhanced removal of phosphate and nitrate ions by a novel ZnFe LDHs-activated carbon composite. *Sustain. Mater. Technol.* **25**, e00154.

Keramati, M. & Ayati, B. 2019 Petroleum wastewater treatment using a combination of electrocoagulation and photocatalytic process with immobilized ZnO nanoparticles on concrete surface. *Process Saf. Environ. Prot.* **126**, 356–365.

Kulkarni, S. D., Kumbar, S. M., Menon, S. G., Choudhari, K. & Santhosh, C. 2017 Novel magnetically separable Fe$_3$O$_4$@ZnO core–shell nanocomposite for UV and visible light photocatalysis. *Adv. Sci. Lett.* **23**, 1724–1729.

Lefebvre, O. & Moletta, R. 2006 Treatment of organic pollution in industrial saline wastewater: a literature review. *Water Res.* **40**, 5671–5682.

Li, T., Su, X., Yu, X., Han, B., Zhu, Y. & Zhang, Y. 2018 Preparation of cobalt-containing spinel oxides as novel adsorbents for efficient phosphate removal. *Environ. Sci. Water Res. Technol.* **4**, 1671–1684.

Lin, D., Wu, F., Hu, Y., Zhang, T., Liu, C., Hu, Q., Hu, Y., Xue, Z., Han, H. & Ko, T.-H. 2020 Adsorption of dye by waste black tea powder: parameters, kinetic, equilibrium, and thermodynamic studies. *J. Chem.* **2020**, 5431046.

Liu, J., Wan, L., Zhang, L. & Zhou, Q. 2011 Effect of pH, ionic strength, and temperature on the phosphate adsorption onto lanthanum-doped activated carbon fiber. *J. Colloid Interface Sci.* **364**, 490–496.

Luo, W., Huang, Q., Zhang, X., Antwi, P., Mu, Y., Zhang, M., Xing, J., Chen, H. & Ren, S. 2020 Lanthanum/Gemini surfactant-modified montmorillonite for simultaneous removal of phosphate and nitrate from aqueous solution. *J. Water Process. Eng.* **33**, 101036.

Ma, P., Ding, W., Yuan, J., Yi, L. & Zhang, H. 2020 Total recycle strategy of phosphorus recovery from wastewater using granule chitosan inlaid with γ-AlOOH. *Environ. Res.* **184**, 109309.

Mahdavi, S. & Akhzari, D. 2016 The removal of phosphate from aqueous solutions using two nano-structures: copper oxide and carbon tubes. *Clean Technol. Environ. Policy* **18**, 817–827.

Nakarmi, A., Bourdo, S. E., Ruhl, L., Kanel, S., Nadagouda, M., Alla, P. K., Pavel, I. & Viswanathan, T. 2020 Benign zinc oxide betaine-modified biochar nanocomposites for phosphate removal from aqueous solutions. *J. Environ. Manage.* **272**, 111048.

Nezamzadeh-Ejhieh, A. & Hushmandrad, S. 2010 Solar photodecolorization of methylene blue by CuO/X zeolite as a heterogeneous catalyst. *Appl. Catal. A-Gen.* **368**, 149–159.

Nezhadheydari, H., Tavabe, K. R., Mirvaghefi, A., Heydari, A. & Frinsko, M. 2019 Effects of different concentrations of Fe$_3$O$_4$/ZnO and Fe$_3$O$_4$/CNT magnetic nanoparticles separately and in combination on aquaculture wastewater treatment. *Environ. Technol. Innov.* **15**, 100414.

Nie, G., Wu, L., Du, Y., Wang, H., Xu, Y., Ding, Z. & Liu, Z. 2019 Efficient removal of phosphate by a millimeter-sized nanocomposite of titanium oxides encapsulated in positively charged polymer. *Chem. Eng. J.* **360**, 1128–1136.

Nodeh, H. R., Sereshki, H., Afsharian, E. Z. & Nouri, N. 2017 Enhanced removal of phosphate and nitrate ions from aqueous media using nanosized lanthanum hydrous doped on magnetic graphene nanocomposite. *J. Environ. Manage.* **197**, 265–274.

Órfão, J., Silva, A., Pereira, J., Barata, S., Fonseca, I., Faria, P. & Pereira, M. 2006 Adsorption of a reactive dye on chemically modified activated carbons – influence of pH. *J. Colloid Interface Sci.* **296**, 480–489.

Othman, A., Dumitrescu, E., Andreea, D. & Andreescu, S. 2018 Nanoporous sorbents for the removal and recovery of phosphorus from eutrophic waters: sustainability challenges and solutions. *ACS Sustain. Chem. Eng.* **6**, 12542–12561.

Salehi, S. & Hosseinifard, M. 2020 Optimized removal of phosphate and nitrate from aqueous media using zirconium functionalized nanochitosan-graphene oxide composite. *Cellulose* **27**, 8859–8883.

Shan, S., Wang, W., Liu, D., Zhao, Z., Shi, W. & Cui, F. 2020 Remarkable phosphate removal and recovery from wastewater by magnetically recyclable La$_2$O$_2$CO$_3$/γ-Fe$_2$O$_3$ nanocomposites. *J. Hazard. Mater.* **397**, 122597.

Stewart, R. H. 2008 *Introduction to physical oceanography*. Texas A & M University, College Station, TX. Open Textbook Library. https://open.umn.edu/opentextbooks/textbooks/introduction-to-physical-oceanography

Taufik, A. & Saleh, R. 2017 Synthesis of iron (II, III) oxide/zinc oxide/copper (II) oxide (Fe$_3$O$_4$/ZnO/CuO) nanocomposites and their photosonocatalytic property for organic dye removal. *J. Colloid Interface Sci.* **491**, 27–36.

Taufik, A., Tju, H. & Saleh, R. 2016 Comparison of catalytic activities for sonocatalytic, photocatalytic and sonophotocatalytic degradation of methylene blue in the presence of magnetic Fe$_3$O$_4$/CuO/ZnO nanocomposites. *J. Phys. Conf. Ser.* **710**, 012004.

Tju, H., Taufik, A. & Saleh, R. 2017 Photocatalytic, sonocatalytic, and photosonocatalytic of Fe$_3$O$_4$/CuO/ZnO nanocomposites with addition of 2 different types of carbon. *AIP Conf. Proc.* **1788**, 030131.
Tran, T. & Nguyen, V. 2014 Copper oxide nanomaterials prepared by solution methods, some properties, and potential applications: a brief review. Int. Sch. Res. Not. 2014, 856592.

Vakili Tajareh, A., Ganjidoust, H. & Ayati, B. 2019 Synthesis of TiO₂/Fe₃O₄/MWCNT magnetic and reusable nanocomposite with high photocatalytic performance in the removal of colored combinations from water. J. Water Environ. Nanotechnol. 4, 198–212.

Wu, B., Fang, L., Fortner, J. D., Guan, X. & Lo, I. M. 2017 Highly efficient and selective phosphate removal from wastewater by magnetically recoverable La(OH)₃/Fe₃O₄ nanocomposites. Water Res. 126, 179–188.

Xia, J., Wang, A., Liu, X. & Su, Z. 2011 Preparation and characterization of bifunctional, Fe₃O₄/ZnO nanocomposites and their use as photocatalysts. Appl. Surf. Sci. 257, 9724–9732.

Xie, X., Chen, L., Pan, X. & Wang, S. 2015 Synthesis of magnetic molecularly imprinted polymers by reversible addition fragmentation chain transfer strategy and its application in the Sudan dyes residue analysis. J. Chromatogr. A 1405, 32–39.

Yin, Q., Wang, R. & Zhao, Z. 2018 Application of Mg-Al-modified biochar for simultaneous removal of ammonium, nitrate, and phosphate from eutrophic water. J. Clean. Prod. 176, 230–240.

Zhou, K., Wu, B., Su, L., Xin, W. & Chai, X. 2018 Enhanced phosphate removal using nanostructured hydrated ferric-zirconium binary oxide confined in a polymeric anion exchanger. Chem. Eng. J. 345, 640–647.

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