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# Controlled growth of TiO<sub>2</sub>/Zeolite nanocomposites for simultaneous removal of ammonium and phosphate ions to prevent eutrophication

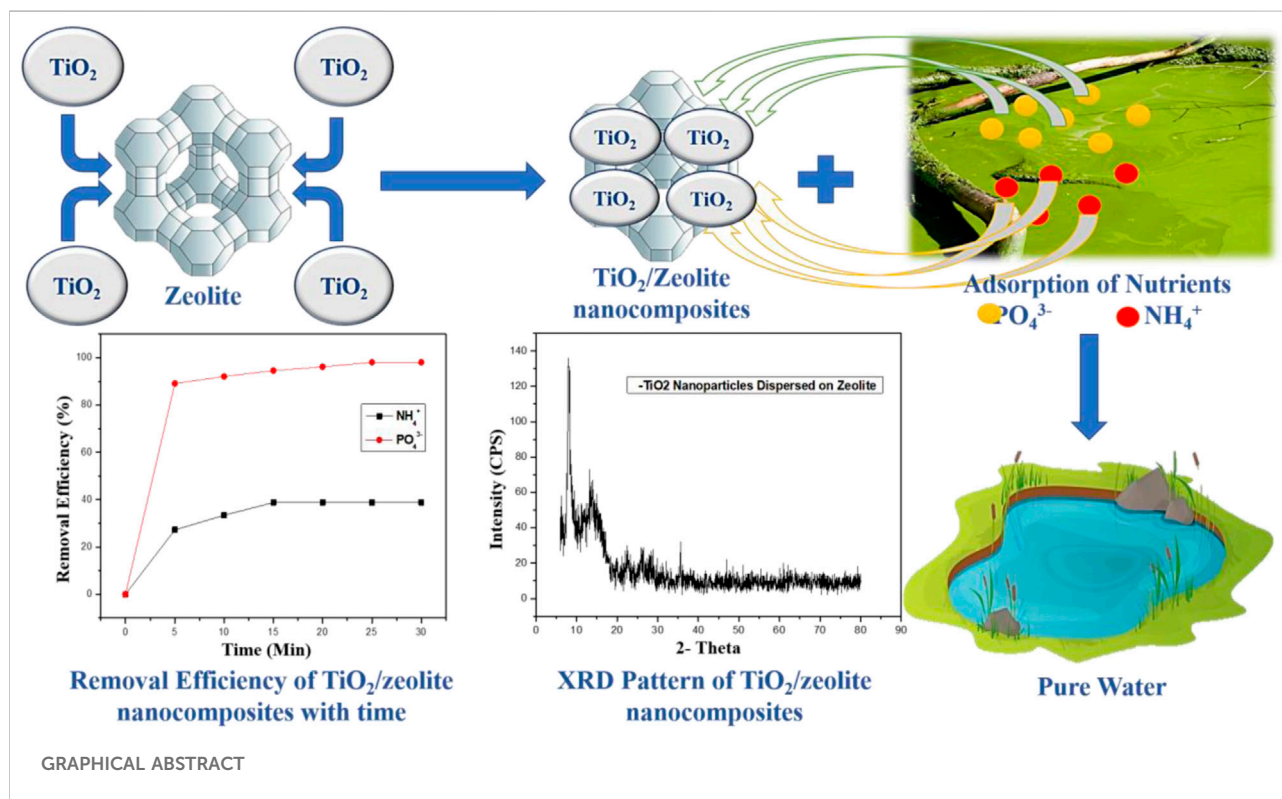
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In the modern era, problems like eutrophication caused by increased nutrients such as ammonia and phosphorous in freshwater bodies have become the cause of freshwater ecosystem deterioration. To save freshwater by reducing eutrophication, new cost-effective strategies and methods are urgently needed. In this study, titanium oxide nanoparticles dispersed on zeolite were chemically synthesized for the simultaneous removal of phosphate and ammonium ions from aqueous solutions. SEM and XRD analysis were used to characterize the synthesized TiO<sub>2</sub>/zeolite nanocomposites, which revealed that the synthesized material was more stable and dispersed than zeolite. The nanocomposites removed 38.8% NH<sub>4</sub><sup>+</sup> and 98.1% PO<sub>4</sub><sup>3-</sup> from an initial concentration of both ions of 20 mg 100 ml<sup>-1</sup>. The removal of both ions was investigated under various conditions including different concentrations of nanocomposites, initial concentration of the solution, temperature, time, and pH. The maximum adsorption of nanocomposites for PO<sub>4</sub><sup>3-</sup> was 38.63 mg g<sup>-1</sup> at optimal conditions, and 3.75 mg g<sup>-1</sup> for NH<sub>4</sub><sup>+</sup>. Kinematics studies showed that both the ions were adsorbed by a pseudo-second-order model. Ion chemisorption occurred as a result of ligand exchange or electrostatic adsorption between ions and nanocomposites. Overall, it was determined that this strategy is a viable and efficient method for simultaneously removing both ions (anionic phosphate and cationic ammonium) from eutrophic waters.

## KEYWORDS

phosphate, ammonium, eutrophication, titanium oxide nanocomposites, zeolite



## Highlights

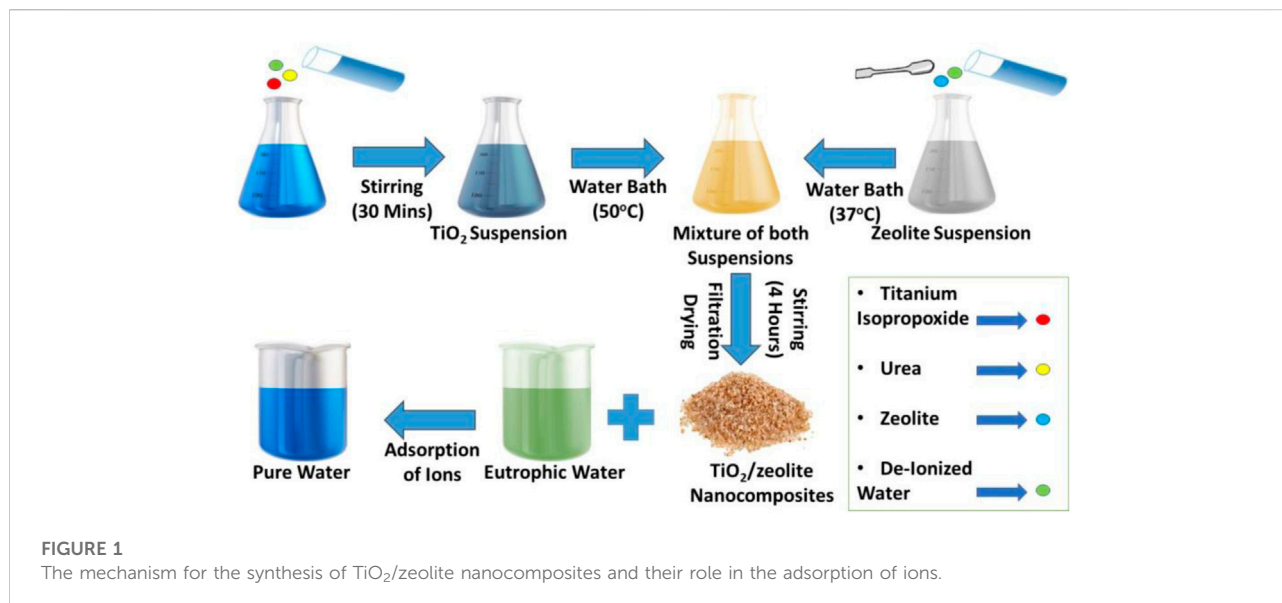
- 1) Loading of  $\text{TiO}_2$  nanoparticles on the surface of zeolites by functional group and electrostatic interactions.
- 2) Greater stability and disperse ability of  $\text{TiO}_2/\text{zeolite}$  nanocomposite than natural zeolite.
- 3) The synthesized system Hybrid  $\text{TiO}_2/\text{zeolites}$  showed efficient potential for removing ammonium and phosphate ions from water.
- 4) It is believed that  $20^\circ\text{C}$  is the ideal temperature for removing ammonium and phosphate ions from a mixed solution.
- 5) The chemisorption process follows a pseudo-second-order kinetic model.

## Introduction

Eutrophication has emerged as a major global issue. It occurs when seaweeds form in water as a result of abnormal algae growth. The structure of the ecosystem changes as nutrient salts in the water increase. Human activities have caused a variety of changes in the biosphere, one of which is eutrophication (Howarth et al., 2002; Smith, 2003). When limiting growth

ingredients, such as phosphate, are released into water bodies and accumulate there, it results in eutrophication, one of the major environmental challenges. The natural equilibrium of the aquatic ecosystem is impacted by eutrophication conditions, which are marked by an algal bloom followed by oxygen deficiency. Aquatic ecosystems are being harmed by eutrophication (Smith et al., 2006). The removal of phosphorous and nitrogen is critical to preserving the water and the ecosystem's integrity (Schindler, 2006; Smith & Schlinder, 2009). Nutrient enrichment is caused by factors such as ecosystem stability and the presence of disease-causing agents (Smith & Schlinder, 2009). Phosphorus and nitrogen levels in Pakistan's rivers, coastal waters, and lakes have increased due to human activities. As a result, eutrophication is on the rise, and toxic algal blooms are on the rise (Søndergaard & Jeppesen, 2007).

Composites are the outstanding materials of the modern world, having two components consisting of continuous and noncontinuous phases. Composites possess the best features due to the reinforcement (less than 100 nm in size) of the material of each component (Ates et al., 2017). Nanocomposites have vast applications in almost every field of life such as automotive, engineering, energy storage, plastic, adhesive, coating, rubber,



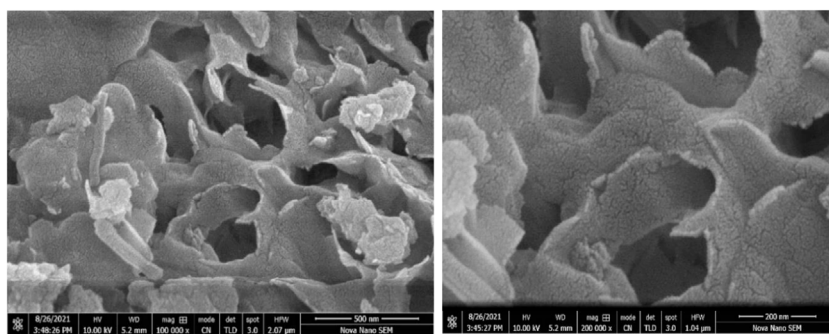
food, wastewater treatment, electronics, optics, electro analysis, biomedical, etc.  $\text{TiO}_2/\text{zeolite}$  nanocomposites synthesized in the present study have large applications but here the main concern is their use in wastewater treatment. The heterointerface between  $\text{TiO}_2$  nanoparticles and zeolite has proved beneficial particularly in wastewater treatment.  $\text{TiO}_2/\text{geopolymer}$  composites are used for the removal of antibiotics from hospital wastewater (Sanguanpak et al., 2022).  $\text{TiO}_2/\text{zeolite}$  composites are also used for the removal of atenolol from water by photocatalytic degradation or adsorption. These composites can be reused four times until their activity has been reduced (Stojanović et al., 2022).  $\text{TiO}_2/\text{zeolite}$  composite sheet is equipped with an oxidation contractor to remove the organic contaminants from industrially treated water by adsorption (Nomura et al., 2022).  $\text{TiO}_2$  nanoparticles act as good adsorbers for organic contaminants and inorganic ions. Zeolite is also a natural adsorber and has many applications in wastewater treatment. A Hybrid of both these materials will prove to be more effective in wastewater treatment by adsorption of contaminants. Because dispersion of nanoparticles on zeolite increases the adsorption capacity of zeolite (Xu et al., 2020).

To remove phosphorous and nitrogen from the water, various methods such as adsorption, biological processes, precipitation, crystallization, and ion exchange have been reported (Huo et al., 2012). The best and most efficient way to remove ions is through adsorption (Zheng and Wang, 2010). Activated carbon, copper oxides, iron oxides, titanium oxides, clay minerals, and zeolites are examples of naturally occurring adsorbents that remove phosphorous and nitrogen (Bonetto et al., 2015; Fernández-Catalá et al., 2020). As a result, many researchers are working on developing green materials (Gao et al., 2008) that can be used to remove phosphorous and

nitrogen from wastewater at the same time (Wang & Peng, 2010; Liu et al., 2013; Wan et al., 2017). Because they are biocompatible, cost-effective, and environmentally friendly, green synthesized titanium oxide nanoparticles can remove phosphorous and nitrogen. Nanoparticles made from plant extracts (Parsons et al., 2007) are widely used to remove phosphorous (Cao et al., 2016) and nitrogen from water (Devatha et al., 2016). Agglomeration in aqueous solution due to high surface area is a disadvantage of water treatment methods because it reduces dispersibility and reactivity. The dispersion of nanoparticles on natural supports such as zeolite solves this problem.

Zeolites are aluminosilicate minerals that are microporous and frequently utilized as catalyst and adsorbent materials in the industry. Numerous materials have been used to support  $\text{TiO}_2$ , but natural zeolite has emerged as the most preferred of these (Liao et al., 2019). Zeolites are considered to be great supporting materials because of their characteristics like higher cation exchange capacity, microporous structure, and large surface area (Bowman, 2003; Alshameri et al., 2014). Zeolites and modified zeolites play a vital role in the removal of organic, cationic, and anionic pollutants and thus reducing environmental pollution (Wang and Peng, 2010, Ning et al., 2008). Zeolites are appealing adsorbents because they remove phosphorous and ammonia from wastewater effectively and simultaneously (Huang et al., 2014). Secondary chemical reagents should not be used to modify zeolites because this type of modification produces secondary pollution.

Phosphate and ammonium ion adsorption was adsorbed using a variety of materials. Natural zeolite removed  $17.68 \text{ mg g}^{-1}$  ammonium and  $2.73 \text{ mg g}^{-1}$  phosphate ions in the batch experiments (Wan et al., 2017). Based on these



**FIGURE 2**  
Scanning electron microscopy images of  $\text{TiO}_2/\text{Zeolite}$  nanocomposites at 500 nm (A) and 200 nm (B).

findings, titanium oxide nanoparticle-zeolite ( $\text{TiO}_2/\text{Zeolite}$ ) nanocomposites were created to determine the factors that influence phosphate and ammonium ion removal efficiency (Belhadj et al., 2022). In order to combat eutrophication in wastewater treatment processes, the systematic, in-depth strategy used in the current experiment with the produced composite material may be crucial (Italiya et al., 2022). This research focused on 1) characterization of  $\text{TiO}_2/\text{Zeolite}$  nanocomposites for the recognition of changes in chemical and surface species before and after the calcination process; and 2) batch experiments for the evaluation of phosphate and ammonium ions' adsorption by  $\text{TiO}_2/\text{Zeolite}$  nanocomposites using thermodynamic and adsorption kinetic isotherms.

## Experimental

### Materials

Titanium Isopropoxide ( $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ , 98% Analytical Grade), Urea ( $\text{CH}_4\text{N}_2\text{O}$ , 99% Analytical Grade), and Zeolite ( $(\text{SiO}_2)_x(\text{Al}_2\text{O}_3)_y$ , 86.33% Analytical Grade) were bought from Sigma-Aldrich and used as such. In all the experiments, deionized (DI) water was used.

### Preparation of $\text{TiO}_2/\text{Zeolite}$ nanocomposites

Pour 0.5 g Urea into 25 ml deionized water for the synthesis of  $\text{TiO}_2/\text{Zeolite}$  Nanocomposites (Figure 1). After 5 min of stirring, 5.5 ml of Titanium Isopropoxide was poured dropwise into the solution. The obtained suspension was placed in a water bath at  $50^\circ\text{C}$  for 30 min after stirring it for 30 min. Meanwhile, took 50 ml of deionized water and dissolved 4 g of zeolite in it and the resulting suspension was placed in a  $37^\circ\text{C}$  water bath for 30 min. The first suspension was poured dropwise into the zeolite suspension, and the final mixture was

stirred for 4 h. The final mixture was cooled at room temperature before being aged for 16 h. The product was washed three times with deionized water after filtration. The filtrate was dried for 2–4 h at  $60\text{--}70^\circ\text{C}$ . The finished product was placed in a vial for future use. Titanium oxide nanoparticles are charged, and because different functional groups are present on the surface of zeolites, nanoparticles can be loaded on the surface of zeolites by functional group and electrostatic interactions.

## Characterization

Scanning Electron Microscope was used to examine the particle size distribution and morphology of the synthesized titanium oxide/zeolite nanocomposites (FEI Nova Nano SEM 450, America). An X-Ray Powder Diffractometer (Bruker AXS D8 Advance) with a high-power radioactive source in the  $10\text{--}80^\circ$  range of  $2\theta$  was used to examine the crystalline structure of synthesized titanium oxide/zeolite nanocomposites.

## Batch experiments

Using the following experimental conditions, four batch experiments were performed to investigate the simultaneous adsorption of phosphate and ammonium ions by  $\text{TiO}_2/\text{Zeolite}$  nanocomposites. The initial concentrations ( $20\text{ mg } 100\text{ ml}^{-1}$ ), pH (6.00), and temperature ( $30^\circ\text{C}$ ) were fixed in the first experiment. However, the concentration of nanocomposites was varied ( $0.4, 0.6, 0.7, 0.8,$  and  $1\text{ g } 100\text{ ml}^{-1}$ ). The concentration of nanocomposites ( $0.7\text{ g } 100\text{ ml}^{-1}$ ) was fixed in the second experiment, as was the pH (6.00) and temperature ( $30^\circ\text{C}$ ). While, the initial concentrations of the ions ( $20, 40, 60, 80,$  and  $100\text{ mg } 100\text{ ml}^{-1}$ ) were altered. The initial concentrations ( $20\text{ mg } 100\text{ ml}^{-1}$ ), nanocomposites concentration ( $0.7\text{ g } 100\text{ ml}^{-1}$ ), and pH (6.00) were all fixed in the third experiment. However, the temperature ( $20, 30,$  and  $40^\circ\text{C}$ ) was changed. The starting

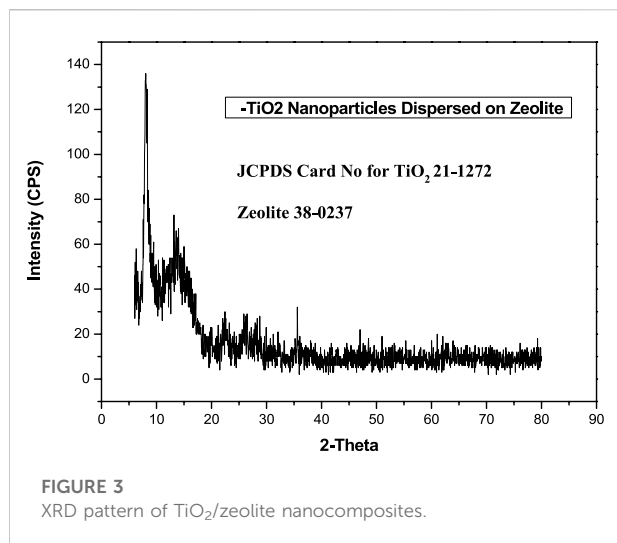


FIGURE 3  
XRD pattern of TiO<sub>2</sub>/zeolite nanocomposites.

concentrations of the ions (20 mg 100 ml<sup>-1</sup>), nanocomposites concentration (0.7 g 100 ml<sup>-1</sup>), and temperature (30°C) were all fixed in the fourth experiment. However, the pH (4.00, 6.00, 8.00, 10.00, and 12.00) was altered. Final solutions were stirred for 30 min in all four experiments to ensure that the maximum amount of phosphate and ammonium ions were adsorbed by TiO<sub>2</sub>/zeolite nanocomposites. The solutions were filtered after shaking for the desired amount of time to remove the adsorbents. A UV-Spectrophotometer (Metash UV-9000S) was utilized for the observation of the adsorption of ions from the solution before and after the addition of TiO<sub>2</sub>/zeolite nanocomposites, and all experimental conditions were analyzed to find the best conditions. The efficiency of ion removal from the solution was then found with the help of the following equation:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

Here  $\eta$  (%) is the removal efficiency of phosphorous and nitrogen,  $C_0$  is the starting phosphorous and nitrogen concentration (mg 100 ml<sup>-1</sup>) and  $C_e$  is the remaining phosphorous and nitrogen concentration (mg 100 ml<sup>-1</sup>) after removal (Weng et al., 2013). All experiments were carried out in triplicate, with two parallel samples each.

## Results and discussion

### Characterization

A small spherical structure of TiO<sub>2</sub> nanoparticles with an average size of 50 nm was revealed by SEM images of TiO<sub>2</sub>/zeolite nanocomposites (Figure 2A). It has been suggested that urea can reduce metal ions to produce nanoparticles. Nanoparticles with an amorphous appearance are evenly

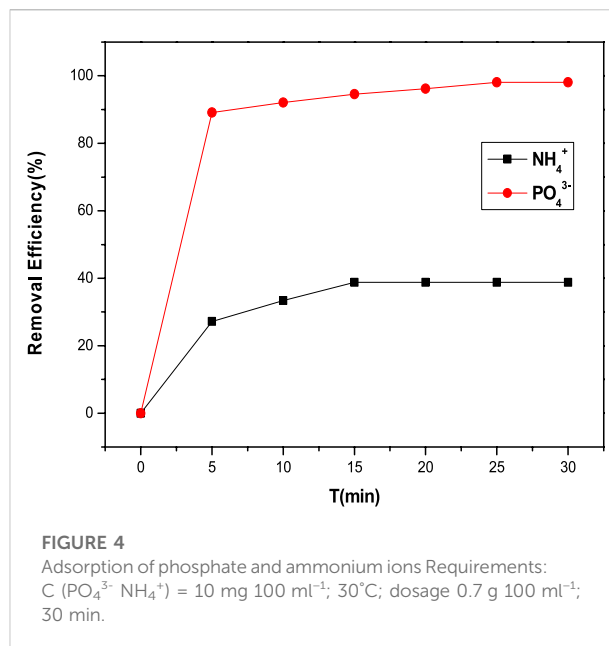


FIGURE 4  
Adsorption of phosphate and ammonium ions Requirements:  
C (PO<sub>4</sub><sup>3-</sup>, NH<sub>4</sub><sup>+</sup>) = 10 mg 100 ml<sup>-1</sup>; 30°C; dosage 0.7 g 100 ml<sup>-1</sup>;  
30 min.

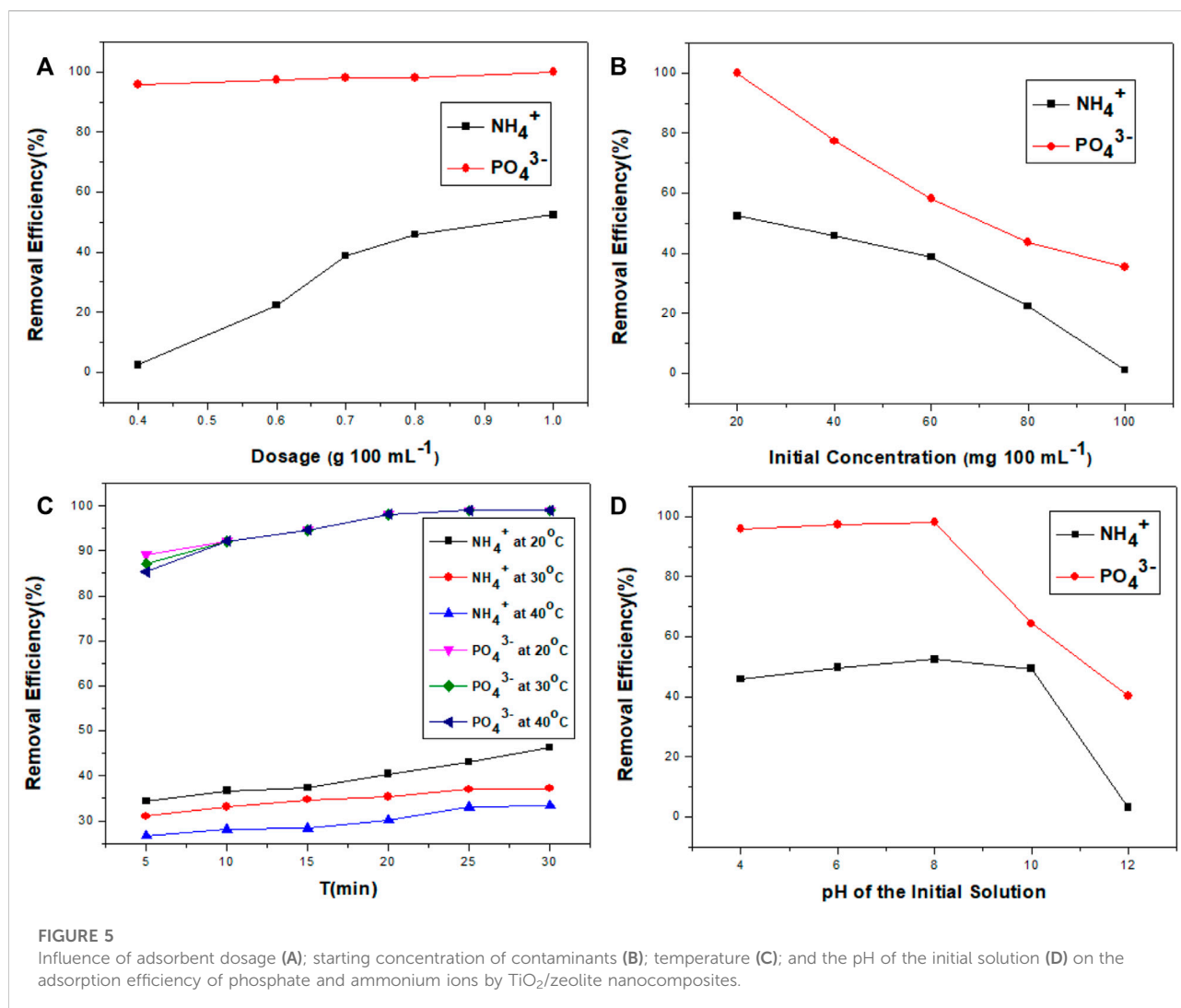
distributed above zeolites and dispersed in their pore spaces. The zeolite has the appearance of a hollow tube (Figure 2B). The sizes of the nanocomposites vary. Some particles are large, while others are small. The size mainly depends upon the dispersion of nanoparticles on zeolite. Some particles are large due to more dispersion of nanoparticles on zeolite and some particles are small due to less dispersion. Dispersion of the particles on zeolite varies with the synthetic conditions (Monpezat et al., 2019). The aggregation of high-energy surface particles causes large size. The resulting hybrid product had greater potential and advantages for removing ammonium and phosphate ions from water.

The XRD pattern of TiO<sub>2</sub>/zeolite nanocomposites revealed a clear, sharp peak, the values were compared to the JCPDS values (Figure 3). JCPDS value confirmed a broad peak at  $2\theta = 8.04^\circ$  as a zeolite characteristic peak (Ren et al., 2018). All of the peaks are rougher, indicating that the surface of the zeolite is covered by a stabilizer or capping agent. In this case, nano titanium acts as a stabilizer or capping agent, roughening the zeolite peaks. Specific peaks at  $2\theta$  of 13.16°, 35.6°, and 10–35° have appeared and are due to rutile, anatase, and brookite (TiO<sub>2</sub> polymorphs) (Li et al., 2014). The XRD pattern also followed Bragg's equation (Yuzhen & Shangmin, 1998), indicating that TiO<sub>2</sub>/zeolite nanocomposites were formed in all aspects.

### Batch experiments

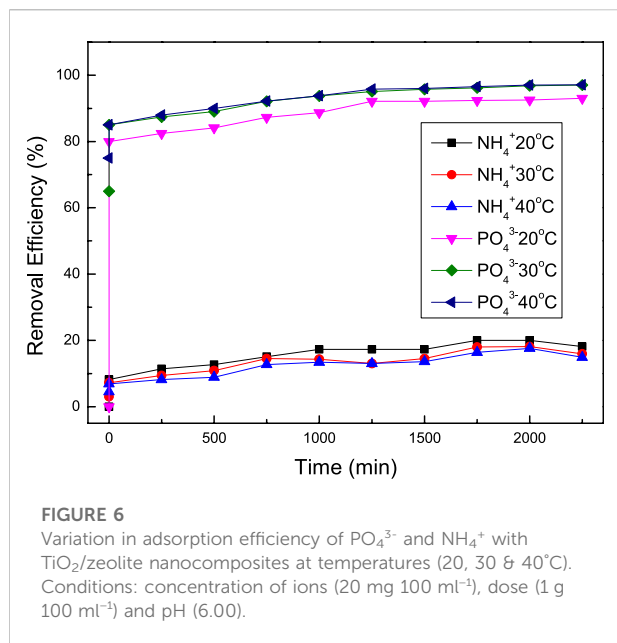
Both ammonium (NH<sub>4</sub><sup>+</sup>) and phosphate (PO<sub>4</sub><sup>3-</sup>) ions were removed with extremely fast kinetics (Figure 4). The removal efficiency for NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> ions increased to 27.2 and 89.1%, respectively, within the first 5 min. Within 30 min, however,





efficiency increased to 38.8% for NH<sub>4</sub><sup>+</sup> ions and 94.6% for PO<sub>4</sub><sup>3-</sup> ions, respectively. Phosphate removal is more efficient and effective than ammonium ion removal. Furthermore, after 15 min, the removal of ammonium ions became constant, whereas the removal of phosphate took 25 min. The adsorption efficiency increased by increasing the time until the equilibrium is reached (Chen et al., 2011). More the time, more will be the chances of agitation of TiO<sub>2</sub> nanoparticles with zeolite (Popuri et al., 2009). But at equilibrium, the surface of the composites is completely blocked by the ions resulting in constant adsorption efficiency. At this point, the adsorption of ions on the surface of the composites becomes equal to the desorption of ions (Dotto & Pinto, 2011). It has been seen that the removal of phosphate ions by these composites is faster. While removal of ammonium ions is also fast but not as efficient as phosphate ions because the removal efficiency also depends upon many factors other than time which is discussed further.

In adsorption experiments, increasing the dose of nanocomposites increased the adsorption efficiency of ammonium ions while decreasing the dose of nanocomposites decreased it. However, the adsorption efficiency of phosphate ions was unaffected (Figure 5A). This nanocomposite has a high capacity for phosphate ions but a low capacity for ammonium ions. As a result, increasing the dose of nanocomposites creates more binding sites for ammonium ions. Adsorption efficiency of ammonium and phosphate ions increased from 2.4 to 52.4 percent and 95.9 to 100 percent. By increasing the dose of the nanocomposites, the available surface area increased. As a result, the interactive absorption sites for both ions were expanded, increasing overall efficiency. However, the static unit volume adsorption capacity and adsorbent dose were reduced. If we keep the contaminant concentration constant, increasing the adsorbent dose will increase the points of contact and thus the adsorbability of the nanocomposites (Chen et al.,



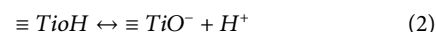
2013). The adsorbent activity was reduced at the peak value of the adsorbent dose, resulting in fewer binding sites. As a result, the appropriate dosage of nanocomposites is 0.7 g 100 ml<sup>-1</sup>.

When the concentrations of the ions were raised from 20 to 100 mg 100 ml<sup>-1</sup>, the removal efficiency of ammonium ions decreased from 52.4 to 1% and for phosphate ions from 100 to 35.4 percent (Figure 5B). Because of the limited adsorption sites on  $\text{TiO}_2/\text{zeolite}$  nanocomposites, this decrease occurred. In this experiment, the adsorbent dose was held constant while the number of contaminants increased. As a result, competitive adsorption between contaminants occurred (Wan et al., 2017). As a result, adsorption efficiency is reduced. When the initial concentration is lower, more adsorption sites are available to remove contaminants from the nanocomposites' surface. As a result, maximum adsorption took place. When the initial concentration is higher, however, the minimum adsorption sites are available to remove contaminants from

the nanocomposites' surface. As a result, there was minimal adsorption.

At the optimum temperature, the majority of experiments yield satisfactory results. The removal of ammonium and phosphate ions was studied at three temperatures for the determination of the optimal temperature for ion adsorption. At these three temperatures, the removal efficiencies of ammonium ions were 34.4, 31.0, and 26.7 percent in the first 5 min. However, after 30 min of reaction equilibrium, the ammonium ion removal efficiencies stabilized at 46.3, 37.2, and 33.4 percent, respectively. While phosphate ion removal was high, at 99 percent at all three temperatures, and remained stable (Figure 5C). Because ammonium ion adsorption was an exothermic process, the removal of ammonium ions decreased as the temperature increased. As a result, at higher temperatures, ammonium ion removal was not favored. However, temperature change had not affected the adsorption of phosphate ions. The optimal temperature for the removal of phosphate and ammonium ions from a mixed solution is thought to be 20°C.

At high pH levels, the adsorption efficiency of phosphate and ammonium ions is greatly influenced (Figure 5D). Phosphate adsorption was unaffected until the pH reached 8.00. However, if the pH value raised from 8.00 to 12.00, the phosphate removal decreased from 98.1 to 40.2 percent. The ammonium removal was 52.4 percent at pH 4.00. It stayed at this level until pH 10.00. The removal of ammonium ions dropped to 3.1 percent at pH 12.00, as shown below (Figure 5D). Because of the following reason, the removal efficiency varied with pH. The adsorption sites on the nanocomposites were in a more deprotonated state between pH 4.00 and 10.00 of an aqueous solution, producing a more negative surface charge due to the following mechanism:



Ammonium ions can interact more with maximum anion binding sites at pH 4.00 to 10.00. However, at lower pH, more  $\text{H}^+$  ions were produced, which competed with  $\text{NH}_4^+$  for adsorption sites and reduced ammonium ion removal

TABLE 1 Values of adsorption kinetics for co-adsorption of phosphate and ammonium ions on  $\text{TiO}_2/\text{zeolite}$  nanocomposites at three temperatures.

	Temperature (K)	Pseudo-first-order			Pseudo-second-order		
		$q_e$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$	$q_e$ (mg g <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$
$\text{NH}_4^+$	293	39.28	0.390	0.941	4.06	0.0020	0.987
	303	35.71	0.414	0.953	3.75	0.0022	0.966
	313	7.14	0.360	0.878	3.53	0.0021	0.974
$\text{PO}_4^{3-}$	293	6,428.57	1.390	0.553	37.51	0.0136	1.000
	303	19,285.71	1.507	0.592	38.63	0.0153	1.000
	313	322,857.14	1.847	0.826	36.99	0.0032	1.000

TABLE 2 Isotherm co-adsorption values of phosphate and ammonium ions on TiO<sub>2</sub>/zeolite nanocomposites.

Temperature (°C)	Freundlich			Langmuir		
	1/n	K <sub>F</sub> (mg g <sup>-1</sup> )	R <sup>2</sup>	Q <sub>m</sub> (mg g <sup>-1</sup> )	K <sub>L</sub> (L mg <sup>-1</sup> )	R <sup>2</sup>
30						
NH <sub>4</sub> <sup>+</sup>	0.45	1.09	0.781	6.25	0.130	0.964
PO <sub>4</sub> <sup>3-</sup>	0.54	14.69	0.954	52.63	0.54	0.987

efficiency (Huang et al., 2014; Wan et al., 2017). At higher pH, more OH<sup>-</sup> ions were produced, which competed with PO<sub>4</sub><sup>3-</sup> for adsorption sites and reduced phosphate ion removal efficiency. An optimal pH of 6.00 is required for ion removal.

## Adsorption kinetics, thermodynamics, and isothermal studies

For a better calculation of adsorption and kinetic isothermal models, different values of removal efficiencies of ammonium and phosphate ions at three temperatures were analyzed for 20–30 h (Figure 6).

Pseudo-first-order and second-order kinetic models were applied for the study of the adsorption mechanism.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (4)$$

$$h = k_2 q_e^2 \quad (5)$$

Where  $q_t$  and  $q_e$  are adsorption capacities at the time (min) and equilibrium and  $k_1$  (min<sup>-1</sup>) and  $k_2$  (g mg<sup>-1</sup> h<sup>-1</sup>) are the pseudo-first-order adsorption and pseudo-second-order adsorption rate constants, respectively. Table 1 shows the proper values for all parameters.

The pseudo-first-order correlation coefficient (R<sup>2</sup>) values for NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> are 0.941, 0.953, 0.878 and 0.553, 0.592, 0.862, respectively. While the pseudo-second-order values for NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> are 0.987, 0.966, 0.974 and 1.000, 1.000, 1.000, respectively. As a result, it was determined that pseudo-second order is a more consistent kinetic model for hybrids' removal behavior. Both the correlation coefficient (R<sub>2</sub>) values for NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> ions at three temperatures are greater than 0.990, indicating that these ions are removed entirely by chemical adsorption. Values of correlation coefficient at lower temperature are greater than 0.990 suggested that the adsorption process was not first order reaction but followed the pseudo second order kinetic model (Wu et al., 2009). The adsorption process took place in many steps and the rate determining step involved the sharing or exchange of electrons suggesting that the adsorption process was mainly

chemisorption. The adsorption of the ions followed an exothermic reaction and should be taken place at lower temperature for the maximum adsorption of the ions.

Thus, high values of correlation coefficient for ions are due to the pseudo second order kinetics and chemisorption exothermic process (Ho & McKay, 1999). As a result of the interaction between ions and nanocomposites, good removal efficiency of both NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> ions was observed. This interaction occurred *via* ligand exchange or electron sharing between NH<sub>4</sub><sup>+</sup>—PO<sub>4</sub><sup>3-</sup> ions and nanocomposites. The rate constants  $k_2$  of NH<sub>4</sub><sup>+</sup> ions for pseudo-second-order remained unaffected by increasing the temperature, but PO<sub>4</sub><sup>3-</sup> ions varied more efficiently. It was discovered that this method is faster, more practical, and simple for controlling pollution caused by these ions. The temperature had not affected the removal of NH<sub>4</sub><sup>+</sup> ions with nanocomposites; it demonstrated that NH<sub>4</sub><sup>+</sup> ion adsorption with nanocomposites remained stable at these three temperatures. While increasing the temperature reduced PO<sub>4</sub><sup>3-</sup> ion adsorption with nanocomposites, it revealed that PO<sub>4</sub><sup>3-</sup> ion adsorption with nanocomposites is an exothermic process. At a lower temperature, it would remain stable.

The adsorption data were also fitted into Freundlich and Langmuir equations (Table 2) to determine the precise adsorption capacity of the nanocomposites for these two water pollutants (Zhang et al., 2011). Eq. 6 depicts the Freundlich model equation:

$$\ln q_e = \ln K_F - \frac{1}{n} \ln C_e \quad (6)$$

While  $q_e$  is called equilibrium adsorption capacity (mg g<sup>-1</sup>),  $K_F$  is known as the Freundlich equilibrium constant (L g<sup>-1</sup>),  $1/n$  is constant for adsorption capacity, and  $C_e$  is NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> equilibrium concentration (mg L<sup>-1</sup>).

While Eq. 7 is used to express the Langmuir isotherm model:

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{q_0 K_L} \quad (7)$$

$K_L$  (L mg<sup>-1</sup>) is called the Langmuir adsorption constant and  $q_m$  (mg g<sup>-1</sup>) is known as the maximum adsorption capacity.

Based on correlation coefficient (R<sup>2</sup>) values for the Freundlich & Langmuir models, ammonium and phosphate ions adsorb on nanocomposites *via* a monolayer adsorption process. Because



TABLE 3 Thermodynamic values for co-adsorption of phosphate and ammonium ions on TiO<sub>2</sub>/zeolite nanocomposites.

	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )	$\Delta S^\circ$ (KJ mol <sup>-1</sup> )	$\Delta G^\circ$ (KJ mol <sup>-1</sup> )		
			293 K	303 K	313 K
NH <sub>4</sub> <sup>+</sup>	-3.21	0.0089	-0.599	-0.402	-0.398
PO <sub>4</sub> <sup>3-</sup>	-10.91	0.0051	-9.121	-9.001	-0.898

ammonium and phosphate ions have a positive and a negative charge, NH<sub>4</sub><sup>+</sup> is less adsorbed on nanocomposites than PO<sub>4</sub><sup>3-</sup>. Adsorption is aided by negative charges. The 1/n values of ammonium and phosphate ions are both very low, indicating that the adsorption process was mainly chemical.

K<sub>d</sub> (Thermodynamic distribution coefficient),  $\Delta G^\circ$  (kJ mol<sup>-1</sup> Gibbs free energy),  $\Delta H^\circ$  (kJ mol<sup>-1</sup> Enthalpy change) and  $\Delta S^\circ$  (J mol<sup>-1</sup> K<sup>-1</sup> Entropy change) were used for the calculation of thermodynamic values by using Eqs 8, 9:

$$\ln K_d = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

$$\Delta G^\circ = -RT \ln K_d \quad (9)$$

When a graph was plotted between  $\ln K_c$  and 1/T,  $\Delta S^\circ$ ,  $\Delta H^\circ$ , and  $\Delta G^\circ$  parameters were found from the intercept and slope of the graph (Table 3).

The  $\Delta H^\circ$  and  $\Delta S^\circ$  values for ammonium ion adsorption confirmed that the process of adsorption of these ions was exothermic.  $\Delta G^\circ$  negative values for ammonium ion adsorption confirmed that this was a highly favorable and spontaneous process. Phosphate ion adsorption  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  values confirmed that the process was exothermic and spontaneous.  $\Delta G^\circ$  values decreased as temperature increased, confirming that higher temperatures were unfavorable for the removal process. The above calculations and conclusions confirmed that the removal of NH<sub>4</sub><sup>+</sup> by TiO<sub>2</sub>/zeolite nanocomposites was a physical adsorption process because the surface of the nanocomposites has a negative charge in water that electrostatically attracts NH<sub>4</sub><sup>+</sup> ions. While phosphate adsorption was caused by the addition of nanocomposites to water, Ti-OH bonds form as a result of hydrolysis at the titanium surface. TiPO<sub>4</sub><sup>2-</sup> is formed when this bond exchanges with phosphate.

## Evaluation of adsorption measurements

TiO<sub>2</sub>/zeolite nanocomposites absorbed fewer ammonium ions (3.75 mg g<sup>-1</sup>) than natural zeolite (17.68 mg g<sup>-1</sup>), modified zeolite combined with struvite crystallization (17.55 mg g<sup>-1</sup>), and iron nanoparticles (9.70 mg g<sup>-1</sup>), but more than eucalyptus magnetic nanocomposites (3.47 mg g<sup>-1</sup>). Phosphate adsorption by TiO<sub>2</sub>/zeolite nanocomposites (38.63 mg g<sup>-1</sup>) was greater than that of natural zeolite (2.73 mg g<sup>-1</sup>) and modified zeolite

combined with struvite crystallization (8.25 mg g<sup>-1</sup>), but it was slightly lower or nearly equal to that of eucalyptus magnetic nanoparticles dispersed on zeolite (38.91 mg g<sup>-1</sup>) (Huang et al., 2014; Wang et al., 2014; Wan et al., 2017; Xu et al., 2020). The prepared TiO<sub>2</sub>/zeolite nanocomposites have selective adsorption for NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup>, with PO<sub>4</sub><sup>3-</sup> adsorption being greater than NH<sub>4</sub><sup>+</sup> adsorption.

## Conclusion

TiO<sub>2</sub>/Zeolite nanocomposites were chemically synthesised in this study, where titanium nanoparticles were successfully dispersed on zeolite. The role of zeolite as an inorganic carrier improved titanium nanoparticle dispersion. Titanium nanoparticles were also protected from oxidation and agglomeration by zeolite. Furthermore, it enhanced the number of adsorption sites, which improved the simultaneous adsorption of NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup>. The removal process depends upon factors like time, adsorbent concentration, pH, and temperature. Removal efficiency increased by increasing the agitation time but became constant after some time. The removal process is primarily determined by the adsorbent concentration because more concentration increased the adsorption sites but adsorption decreased as the reaction pH increased (pH > 8.00). PO<sub>4</sub><sup>3-</sup> and NH<sub>4</sub><sup>+</sup> removal efficiencies were 98.1 percent and 38.8 percent, respectively. The adsorption process was exothermic, and TiO<sub>2</sub>/Zeolite nanocomposites were more effective at removing both ions at low temperatures (20°C). The process of adsorption followed pseudo-second-order kinetics and was primarily chemical in nature.

## Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

## Author contributions

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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