Effective Sequestration of Phosphate and Ammonium Ions by the Bentonite/Zeolite Na−P Composite as a Simple Technique to Control the Eutrophication Phenomenon: Realistic Studies

Mostafa R. Abukhadra,* Samar Mohamed Ali, Emad Abouel Nasr, Haitham Abbas Ahmed Mahmoud, and Emad Mahrous Awwad

ABSTRACT: A bentonite/Zeolite-P (BE/ZP) composite was synthesized by controlled alkaline hydrothermal treatment of bentonite at 150 °C for 4 h for effective sequestration of phosphate and ammonium pollutants. The composite is of 512 m²/g surface area, 387 meq/100 g ion-exchange capacity, and 5.8 nm average pore diameter. The experimental investigation reflected the strong effect of the pH value in directing the uptake behavior and the best results were attained at pH 6. The kinetic properties showed an excellent agreement for phosphate and ammonium adsorption results with the pseudo-second-order model showing equilibrium intervals of 600 and 360 min, respectively, and maximum experimental capacities of 170 and 155 mg/g, respectively. Additionally, their equilibrium modeling confirmed excellent fitness with the Langmuir hypothesis, signifying homogeneous and monolayer uptake processes with a theoretical $q_{\text{max}}$ of 179.4 and 166 mg/g for phosphate and ammonium, respectively. Moreover, the calculated Gaussian adsorption energies of phosphate (0.8 kJ/mol) and ammonium (0.72 kJ/mol) suggested physisorption for them with mechanisms close to the zeolitic ion-exchange process or the coulombic attractive forces. This was supported by the assessed thermodynamic parameters which also suggested spontaneous uptake by endothermic reaction for phosphate and exothermic reaction for ammonium. The BE/ZP composite is of excellent reusability and used for eight recyclability runs achieving removal percentages of 61.5 and 74.5% for phosphate and ammonium, respectively, in run 8. Finally, the composite was applied in the purification of sewage water and groundwater, achieving complete removal for phosphate from sewage water and ammonium from groundwater and reduction of the ammonium ions in the sewage water to 2.3 mg/L.

1. INTRODUCTION

Contamination of the water resources by different types of contaminants resulted in several environmental and health hazards. The eutrophication process is a common phenomenon associated with the extensive and uncontrolled growth of algae and other phytoplankton biomass in the present water bodies. This related mainly to the overloading of the water resources by huge quantities of nutrients, especially nitrogen- and phosphorus-bearing compounds. The occurrence of eutrophication commonly causes considerable depletion in the dissolved oxygen, which reduces the quality of the water resources and negatively affects the present aquatic ecosystems.

However, phosphorous is a vital element in several industries especially in fertilizers, and its discharge as drainage water from agricultural activities can increase its abundance in water resources above the accepted limit (0.03 mg/L), which induces rapid and random growth of algae and microorganisms. This was also observed for the saturation of the water resources by ammonium ions with a concentration higher than 3 mg/L. Additionally, the over concentrations of ammonium cause disorder effects on the tissues of fish and other aquatic organisms and physiological parameters, especially disease resistance and the growth rate. Thus, developing effective and advanced techniques to reduce the ammonium and phosphate ions from sewage water and drainage water is a critical challenge for modern civilization.

Utilizing novel materials of significant ion exchange and adsorption properties in the elimination of phosphate and ammonium ions from water was evaluated as a promising technique that can be applied at low cost with environmentally friendly properties. Synthetic adsorbents and ion exchangers based on natural resources such as natural clays,
bentonite, muscovite, activated carbon, synthetic zeolite, biochars, struvite, cellulose-based adsorbents, and magnetite were applied commonly for this target.\textsuperscript{12−17} Zeolite-based materials either of natural or synthetic forms were studied extensively in the elimination of phosphate and ammonium from sewage water and polluted lakes.\textsuperscript{18} This controlled mainly by their unique microporous structures, superior surface areas, and ion-exchange properties as well as their environmental values.\textsuperscript{16} This was also recorded for natural layered aluminosilicate structures (clays) that were applied extensively in their natural and modified phases as favorable adsorbents for different types of pollutants including phosphate and ammonium.\textsuperscript{4,10,21} Bentonite is one of the most studied clays in water remediation technologies for its exceptional physicochemical features, flexible crystalline and chemical structure, superior surface area, environmental value, high ion replacement, high uptake capacities, and high natural availability.\textsuperscript{10,20}

The integration between zeolite and clay minerals was inspected recently as an innovative methodology to produce a hybrid product of improved physicochemical properties.\textsuperscript{4} Such materials were synthesized by controlled hydrothermal alkaline alteration of clays and were inspected as potential adsorbents for dyes and some chemical ions.\textsuperscript{4,10,21} In our previous studies, we investigated the synthesis of bentonite/zeolite-P and muscovite/phillipsite composites as novel materials with enhanced textural and physicochemical properties as compared to the integrated phases.\textsuperscript{4} Unfortunately, the investigation of the bentonite/zeolite-P composite as an adsorbent for phosphate and ammonium and its application in the purification of sewage and groundwater has not been carried out until now.

The aim of the introduced study is to investigate the synthetic bentonite/zeolite-P composite as a promising adsorbent for phosphate and ammonium ions with effective adsorption capacity, low preparation cost, and high recyclability properties. The adsorption tests were accomplished considering prepared aqueous solutions to investigate the optimized conditions and the capacity of the material, and then, the composite was applied in the purification of realistic groundwater and sewage water samples to avoid their effects in the eutrophication phenomenon. The expected nature of the uptake processes was evaluated considering the commonly studied kinetic and equilibrium theoretical models.

2. RESULTS AND DISCUSSION

2.1. Characterization. 2.1.1. Structural and Chemical Properties. The X-ray diffraction (XRD) pattern of bentonite confirmed the presence of montmorillonite as the main clay mineral. The principal peaks of the montmorillonite as a crystalline phase were observed at 6.55, 19.85, 25.1, and 28.35\textdegree as the characteristic 2Theta angles showing a crystallite size of 12.9 nm (card nos: 00-003-0010 and 00-058-2010) (Figure 1AA). The crystallite size was calculated considering the commonly used Scherrer equation ($D = 0.9\lambda / W \cos \theta$), where $D$, $W$, $\theta$, and $\lambda$ symbols refer to the crystallite size, the full width at the mean peak at the half maximum (radians), the Bragg’s angle, and the wavelength of the used X-ray (CuK\textalpha = 0.15405 nm), respectively. After the activation of the sample by heating, the obtained pattern declared a significant reduction in the intensities of the detected montmorillonite peaks reflecting partial destruction and dehydration for its crystalline structure (Figure 1AB). Under the alkaline transformation process, the obtained pattern confirmed the formation of hybrid material between bentonite represented by the montmorillonite peaks and the synthetic zeolite represented by zeolite Na−P (Figure 1AC). The main peak of montmorillonite mineral appeared as a strongly reduced peak with a noticeable deviation from its position to be detected at 6.73\textdegree (Figure 1AC). Synthetic zeolite Na−P showed several characteristic peaks at 12.46, 16.6, 21.66, 28.1, 33.38, and 38\textsuperscript{10} (Figure 1AC).

This was also supported by the chemical properties of both BE and BE/ZP from the FT-IR spectra (Figure 1BA). The original bentonite showed its main groups of crystalline OH, interlayer water molecules, Si−O, and Al−O at the absorption bands of 3400, 1640, 1000, and 918 cm\textsuperscript{−1}, respectively.\textsuperscript{10,22} Also, the characteristic bands of Si−O−Al, Si−O−Mg, and Mg−Fe−OH were identified by the detected minor bands within the area from about 400 to 1000 cm\textsuperscript{−1} (Figure 1BA). The synthetic BE/ZP showed the same bands but with significant deviation for their positions and a noticeable increase in the intensities of the characteristic bands of structural OH and bounded water (Figure 1BB). This might be related to the role of the alkaline modification processes in causing etching for the surficial siloxane groups of the present montmorillonite minerals which induce the exposure of Si−OH groups as well as the Al−OH group\textsuperscript{10} (Figure 1BB). Additionally, the formation of zeolite-P is associated with an increase in the water content because of the entrapment of the water molecules within the interchannels of zeolite. This was supported by the distinguished band at 1429 cm\textsuperscript{−1} which was the characteristic band of structural OH and bounded water of zeolites.

Figure 1. XRD patterns of bentonite, thermally activated bentonite, and synthetic BE/ZP composite (A) and FTIR spectra of bentonite and the synthetic BE/ZP composite (B).
cm⁻¹ which signifies the coordinated water molecules within the pores of the synthetic zeolite²⁰ (Figure 1B). The observed disappearance for some bentonite-related bands confirmed the partial destruction of the montmorillonite structure and the hydration of the interunit water layers by the alkaline transformation.

This supported by the obtained full chemical analysis for both bentonite and BE/ZP composite. The used bentonite as a precursor is of 54.82% SiO₂, 9.5% Fe₂O₃, 17.56% Al₂O₃, 2.4% CaO, 2.5% MgO, 1.45% TiO₂, 2.6% Na₂O, and 9.2% LOI. The synthetic BE/ZP is composed mainly of 51.46% SiO₂, 14.52% Al₂O₃, 7.5% Fe₂O₃, 10.3% Na₂O, 1.52% MgO, 1.62% CaO, 0.77% TiO₂, and 12.6% LOI. The observed declination in the Si content re

Figure 2. SEM images of bentonite (A) and the synthetic BE/ZP composite showing the distribution of zeolite-P cubes on the surface of bentonite particles (B–D).

 synthetic BE/ZP, the bentonite grains appeared as a substrate of numerous zeolite cubes (Zeolite Na−P) that randomly distributed on them (Figure 2B–D). Such a morphology confirms the formation of the composite without extensive destruction for montmorillonite as the main mineral of bentonite. This is of strong influence in the textural properties as compared to both bentonite and commercial synthetic zeolite Na−P (Table 1). The surface area increased to 512 m²/g as compared to 91 and 123 m²/g for bentonite and zeolite-P, respectively. Also, the determined average pore diameter demonstrated changes in the value for BE/ZP (5.8 nm) as compared to bentonite (10.4 nm) and synthetic zeolite Na−P (1.2 nm). Moreover, the composite showed considerable enhancement in the ion-exchange capacity to be 387 meq/100 g which is of very high value considering the measured values for both bentonite and synthetic zeolite Na−P (Table 1).

2.2. Adsorption Results. 2.2.1. Effect of the Main Parameters. In any studied adsorption process for its influence in regulating the H⁺/OH⁻ competition within the present receptor sites as well as its vital effect in direct the speciations of both phosphate and ammonium ions. Generally, phosphate ions were identified in four species at the different pH values including H₂PO₄⁻, HPO₄²⁻, H₂PO₄⁻, and PO₄³⁻. This reflected in the observed trend for the uptake of phosphate by BE/ZP at different pH values (Figure 3A). The achieved adsorption quantity increased from 10 to 37 mg/g with the regular expansion in the adjusted pH from pH 2 to pH 6 (Figure 3A). Beyond pH 6, the BE/ZP composite showed noticeable declination in its uptake capacity until pH 8 (Figure 3A). This behavior related to the existence of phosphate as H₂PO₄⁻ within the pH range from pH 3 to pH 6 which induced the electrostatic attraction between them and the BE/ZP surface which is positively charged within this range. Below pH 3, the phosphate ions were detected in their neutral form and of significant difficulty to be adsorbed by BE/ZP. Beyond pH 6, the dominance of HPO₄²⁻ and PO₄³⁻ as the phosphate species resulted in highly repulsive forces with BE/ZP functional groups which are of negative charges within this pH range under the deprotonation processes.

The uptake trend of ammonium displayed continuous enhancement in the adsorbed quantity from 5.2 to 36.5 mg/g with the regular expansion in the adjusted pH from pH 2 to pH 8 (Figure 3A). This was assigned to the continuous deprotonation of BE/ZP characteristic groups with the augmentation in the studied pH values to be of higher attractive forces for the positively charged ammonium ions as compared to the acidic conditions. The increment in the pH from pH 6 to pH 8 is of slight impact on the BE/ZP capacity for ammonium ions which might be credited to the transformation of NH₄⁺ ions into NH₃ as well as the reported reduction in the ion-exchange properties of the natural silicate minerals in the high alkaline environments. The saturation of the system by the hydronium ions at the acidic environments induced the stability of ammonium ions in their normal forms and the depletion of the system in the hydronium ions in the alkaline environments accelerates the transformation of ammonium into ammonia gas which might be released out of the system. This was supported by the determined value of pH of the zero point charge (pH (PZC)) which is 6.74. That is, the BE/ZP composite is of negative charge above this value.

Table 1. Textual and Physical Properties of the B/ZP Catalyst in Comparison With Bentonite and Zeolite-P

| sample          | cation exchange capacity (meq/100 g) | swelling capacity | specific surface area (m²/g) | micropores volume (mL/g) | mesopores volume (mL/g) | total volume (mL/g) | average pore size (nm) |
|-----------------|-------------------------------------|-------------------|-----------------------------|-------------------------|-------------------------|-------------------|-----------------------|
| bentonite       | 104                                 | 8.37              | 91                          | 0.013                   | 0.262                   | 0.312             | 10.4                  |
| zeolite Na−P    | 320                                 | 2.54              | 123                         | 0.36                    | 0.01                    | 0.37              | 1.2                   |
| bentonite/zeolite Na−P | 387                           | 5.62              | 512                         | 0.244                   | 0.175                   | 0.422             | 5.8                   |
2.2.1.2. Time Intervals. Investigation of the adsorption properties of BE/ZP for both phosphate and ammonium within different intervals is of critical importance in the detection of the equilibration time to achieve the best uptake capacities. The recognized curves for the both ions highlighted two segments related to low different adsorption rates (Figure 3B). The first segment exhibited a rapid change in the uptake rates which appeared in the experimental adsorbed quantities. This was signified from 30 to 600 min for the phosphate ions and from 30 to 360 min for the ammonium ions (Figure 3B). The second segment was identified from 600 and 360 min for phosphate and ammonium, respectively, to 1320 min showing slight or fixed adsorption rates indicating the attendance of their equilibration states (Figure 3B). The recorded experimental uptake capacities at their equilibrium time intervals are 82 and 71 mg/g for phosphate and ammonium, respectively (Figure 3B). This was reported extensively in the literature and explained as a considerable result for the regular occupation of the BE/ZP active receptor sites by phosphate and ammonium ions with expanding the tested time intervals until achieving the full occupation of all the present sites demonstrating the saturation or the equilibration stage.10,25

2.2.1.3. Initial Concentration. The investigation of the adsorption properties of BE/ZP as a function of the pollutant concentrations is of vital role to detect the experimental maximum uptake capacities as well as the uptake behaviors. The plotted results showed an increase in the adsorbed quantities with expanding the studied concentrations from 25 to 300 mg/L for phosphate and from 25 to 250 mg/L for ammonium (Figure 3C). 300 and 250 mg/L are the equilibrium concentrations for phosphate and ammonium, respectively. The fixed adsorption capacities at such equilibration concentrations reflected the complete saturation of the BE/ZP surface by the adsorbed ions achieving maximum experimental capacities of 170 and 155 mg/g for phosphate and ammonium, respectively (Figure 3C). The recounted increment in the adsorbed quantities at the studied higher concentrations might be related to the effect of such concentrations in promoting the driving forces of both phosphate and ammonium ions in the direction of the BE/ZP receptor sites.26

2.2.1.4. BE/ZP Dosages. The role of BE/ZP dosages in inducing the removal percentages of both phosphate and ammonium ions was studied within the range from 0.02 to 0.14 g (Figure 3D). The results revealed an excellent increase in the reported removal percentages with the regular incorporation of higher dosages of BE/ZP from 0.02 to 0.14 g for the two ions achieving complete removal for them using the highest dosage (0.14 g) (Figure 3D). This enhancement in the recognized removal percentages might be related to the predicted increase in the BE/ZP receptor sites, ion-exchange sites, and the total surface area with the incorporation of higher masses of it in the addressed system.17

2.2.2. Kinetic and Equilibrium Studies. 2.2.2.1. Kinetic Properties. The kinetic properties of BE/ZP adsorption systems for phosphate- and ammonium-dissolved ions were evaluated according to the commonly investigated models of pseudo-first-order, pseudo-second-order, Elovich, and intraparticle-diffusion models, and their illustrative equations are documented in Table S1. Considering the acquired nonlinear fitting results, the uptake of both phosphate and ammonium is of higher fitting with the pseudo-second-order than pseudo-first-order model based on the correlation coefficient and the Chi-square values (Figure 4A,B; Table 2). However, the pseudo-first-model suggested physical uptake reactions, and the pseudo-second-order model
suggested reactions of more chemical affinity which might include the electron-sharing process, electron exchange, surface complexation, and internal diffusion.

The reported good fitness with the Elovich model gives indication about the energetic heterogeneity of the BE/ZP surface during the uptake reactions and support the estimated conclusion from the pseudo-second-order model. The reported fitness reflected complex adsorption process or the dominance of surface complexation and/or ion exchange (Coulombic attractive forces) as the main mechanisms without the formation or destruction of ionic or covalent bonds. The isotherm models will give support and more explanation for the nature of the adsorption reactions.

The intraparticle-diffusion kinetic model was assessed to provide more information about suggested mechanisms that can control the uptake reactions of phosphate and ammonium by BE/ZP. The recognized intraparticle diffusion curves displayed three observable segments without intersection between them and the original points, signifying the operation of different types of adsorption mechanisms in addition to the diffusion of dissolved phosphate and ammonium ions (Figure 4C). The adsorption process first involved the uptake of the ions by the surficial or the external receptors forming the first segment which appears as the dominant mechanism and characterizes the initial stages of the reactions. After the saturation of the external receptors, the process appeared to be controlled by the layered adsorption mechanism with restricted diffusion for the phosphate and ammonium ions forming the second adsorption segments in the curves. After attending the equilibration or the complete saturation, the third segment of the curves was identified which refers to the formation of thick layers from the adsorbed phosphate and ammonium on the BE/ZP surface. This stage characterized by an interionic attraction and/or molecular association as the principal uptake mechanisms.

### Table 2. Theoretical Parameters of Kinetic, Isothermal, and Thermodynamic Studies

| model | parameters | phosphate | ammonium |
|-------|------------|-----------|-----------|
| Kinetic Models | | | |
| pseudo-first order | $K_1$ (min$^{-1}$) | 0.015 | 0.002 |
| | $q_{e(Cal)}$ (mg/g) | 92.3 | 80.35 |
| | $R^2$ | 0.88 | 0.77 |
| | $X^2$ | 0.66 | 1.19 |
| pseudo-second order | $k_2$ (g mg$^{-1}$ min$^{-1}$) | 0.0028 | 0.0013 |
| | $q_{e(Cal)}$ (mg/g) | 89.26 | 77.95 |
| | $R^2$ | 0.99 | 0.96 |
| | $X^2$ | 0.04 | 0.17 |
| Elovich | $\beta$ (g/mg) | 0.05 | 0.056 |
| | $\alpha$ (mg/g min) | 1.47 | 1.27 |
| | $R^2$ | 0.93 | 0.88 |
| | $X^2$ | 0.41 | 0.57 |
| Isotherm Models | | | |
| Langmuir | $q_{max}$ (mg/g) | 179.4 | 161.72 |
| | $b$ (L/mg) | $5.13 \times 10^{-5}$ | $2.54 \times 10^{-4}$ |
| | $R^2$ | 0.99 | 0.99 |
| | $X^2$ | 0.13 | 0.24 |
| | $R_L$ | 0.98 | 0.998 |
| Freundlich | $1/n$ | 0.66 | 0.5 |
| | $k_f$ (mg/g) | 195 | 170.3 |
| | $R^2$ | 0.98 | 0.98 |
| | $X^2$ | 0.45 | 0.55 |
| D–R model | $\beta$ (mol$^2$/kJ$^2$) | 0.77 | 0.95 |
| | $q_{a}$ (mg/g) | 174.6 | 166.2 |
| | $R^2$ | 0.97 | 0.985 |
| | $X^2$ | 0.86 | 0.51 |
| | $E$ (kJ/mol) | 0.8 | 0.72 |
| Thermodynamic Parameters | | | |
| $\Delta G^\circ$ (kJ mol$^{-1}$) | 303 K | $-15.09$ | $-14.93$ |
| | 308 K | $-15.59$ | $-15.05$ |
| | 313 K | $-16.16$ | $-15$ |
| | 318 K | $-16.85$ | $-14.73$ |
| | 323 K | $-17.43$ | $-14.42$ |
| | 328 K | $-17.93$ | $-14.02$ |
| | 333 K | $-18.36$ | $-13.27$ |
| | 338 K | $-18.75$ | $-12.49$ |
| | 343 K | $-19.06$ | $-11.85$ |
| $\Delta H^\circ$ (kJ mol$^{-1}$) | 16.2 | $-39.6$ |
| $\Delta S^\circ$ (J K$^{-1}$ mol$^{-1}$) | 103.49 | $-79.34$ |

Figure 4. Nonlinear fitting of phosphate (A) and ammonium (B) adsorption results with pseudo-first-order, pseudo-second-order, and Elovich models and the intraparticle-diffusion model (C).
with Langmuir, Freundlich, and Dubinin–Radushkevich models (Figure S1A,B). The representative theoretical equations of the inspected models are listed in Table S1 and the isotherm parameters appear in Table 2. The supposition of the Langmuir model suggested homogeneous and monolayer uptake of both phosphate and ammonium by BE/ZP while the Freundlich model suggested multilayer and heterogeneous uptake processes for them. Moreover, the values of Chi-squared ($\chi^2$) and the correlation coefficient, the adsorption results of phosphate and ammonium by BE/ZP are of strong agreement with Langmuir as well as Freundlich model with a preference for the Langmuir model as the fitting results are of low Chi-squared ($\chi^2$) values (Figure S1A,B; Table 2). The calculated theoretical values of the RL parameter are less than one for both phosphate and ammonium (Figure 5A,B; Table 2). The theoretical values for the maximum uptake of phosphate and ammonium capacities are 179.4 and 161.7 mg/g, respectively (Table 2). The increase in the calculated $Q_e$ values with negative signs at all the studied temperature values for both phosphate and ammonium ions suggested spontaneous uptake of them by the BE/ZP composite (Figure S3A,B; Table 2). The theoretical adsorption energies of phosphate and ammonium by BE/ZP are of strong agreement with Langmuir as well as Freundlich model with a preference for the Langmuir model as the fitting results are of low Chi-squared ($\chi^2$) values (Figure S1A,B; Table 2). The calculated theoretical values of the RL parameter are less than one for both phosphate and ammonium (Figure 5A,B; Table 2). The theoretical values for the maximum uptake of phosphate and ammonium capacities are 179.4 and 161.7 mg/g, respectively (Table 2). Additionally, the theoretical adsorption energies of phosphate and ammonium are 0.8 and 0.72 kJ/mol, respectively (Table 2). Such values imply physisorption uptake of both phosphate and ammonium contaminants by BE/ZP (physical or chemical) depending on the role of its related parameters in calculating the Gaussian adsorption energy. The fitted adsorption results of phosphate and ammonium are of excellent agreement with the D–R model, and the theoretical parameters of the model showed 174.6 and 166 mg/g as the theoretical values for the maximum uptake of phosphate and ammonium by BE/ZP, respectively (Figure S1A,B; Table 2).

The recognition of $\Delta G^\circ$ values with negative signs at all the studied temperature values for both phosphate and ammonium ions suggested spontaneous uptake of them by the BE/ZP composite (Figure S3A,B; Table 2). The increase in the calculated adsorption $\Delta G^\circ$ values for phosphate related to the decrease in the favorability of the reaction at the tested higher temperature values and the reverse behavior was observed for the uptake of ammonium by BE/ZP. For $\Delta H^\circ$ values, the observed positive sign for phosphate and negative sign for ammonium reflected endothermic and exothermic uptake reactions, respectively (Table 2). The positive sign of $\Delta S^\circ$ during the uptake of phosphate reflected increase in the randomness degree of the reaction with the tested temperature values and suggested high affinity of BE/ZP for phosphate ions, and the negative sign of $\Delta S^\circ$ for the ammonium ions reflected a strong decrease in the randomness degree of the reaction with the tested temperature values and suggested high affinity of BE/ZP for ammonium ions.
significant decrease in the reaction randomness\textsuperscript{30,34} (Table 2).

Finally, the values of the Gibbs free energies and enthalpies for the uptake of both phosphate and ammonium within the range of physiosorption mechanisms support the previously estimated conclusion from the isotherm studies (Table 2).

2.2.3. Reusability Properties. The evaluation of the BE/ZP composite as a sustainable adsorbent for phosphate and ammonium which can be reused effectively is of commercial and economic value. The reusability properties of BE/ZP were assessed eight times and the experimental results proved excellent stability and reusability for the BE/ZP composite (Figure 7). For the phosphate removal reusability tests, the observed higher stability of BE/ZP during the uptake of ammonium as compared to the uptake of phosphate might be related to the tendency of the adsorbed phosphate ions to form a strong complex with the external functional groups of both the synthetic zeolite Na\textsuperscript{−}P and the bentonite substrate which will be discussed further in the mechanism section.

2.2.4. Suggested Mechanism. The investigated adsorbent in this study is a novel composite from two types of silicate minerals. The composite is advanced integration between layered silicate montmorillonite and tectosilicate microporous zeolite Na\textsuperscript{−}P which was formed by the controlled alkaline transformation of the raw bentonite sample (Figure 8). Such an integration process resulted in a hybrid product of higher porous properties, higher surface area, and higher ion-exchange properties than the single phases of bentonite and zeolite. Additionally, the alkaline treatment affected greatly the crystalline and surficial properties of montmorillonite layers. The montmorillonite became enriched in the sodium ions as substituted ions within the tetrahedral and octahedral units, as trapped ions in molecular cavities of the tetrahedral sheets, and as free ions within the interunit water layer\textsuperscript{10} (Figure 8). Moreover, alkaline modification is of strong etching effect in the silicate and aluminosilicate minerals as it causes more exposure for the surficial siloxane functional groups.\textsuperscript{10} This is of positive impact on the ion exchange and the adsorption properties under the reported modifications in the structural and surficial properties.\textsuperscript{38}

The adsorption mechanisms of phosphate and ammonium by such heterogeneous structures can be explained for each structure as a separate phase. The uptake of them by the synthetic zeolite Na\textsuperscript{−}P was controlled mainly by both the ion exchange and adsorption mechanisms in addition to minor effects for other assist processes.\textsuperscript{39,40} The ion-exchange process in the zeolite adsorption system is known as the outer surface complexation mechanism and involves the replacement of either the free or the structural cations by the dissolved ions in the surrounding environments.\textsuperscript{41} The adsorption mechanism which is known as the inner surface complexation process involves the formation of chemical bonds between the adsorbed ions and the
main functional groups of zeolite Na−P and/or the electrostatic attractions for the ions by these groups. For the adsorption mechanisms of montmorillonite, the adsorption properties were significant to the ion exchange between the free ions in the interunit water layer and the tested dissolved ions in addition to the electrostatic attractions with its chemical groups.

Generally, the phosphate adsorption by silicate minerals occurred by both the chemical interaction and the electrostatic attraction. The electrostatic process was represented mainly by the Coulombic attractive forces between the present phosphate ions and the main binding sites of BE/ZP (Figure 8). This mechanism involved the formation of monodentate and bidentate complexes within the pH range from the values lower than the point of zero charge (PZC) to the value higher than the PZC according to eqs 3 and 4.

\[ \text{BE/ZP} - \text{OH}^+ + \text{H}_2\text{PO}_4^- \leftrightarrow \text{BE/ZP} - \text{O} - \text{P} - \text{OH} + \text{H}_2\text{O} \quad (3) \]

\[ \text{BE/ZP} - \text{OH} + \text{H}_2\text{PO}_4^- \leftrightarrow \text{BE/ZP} - \text{O} - \text{P} - \text{OH} + \text{OH}^- \quad (4) \]

The adsorption of ammonium either by montmorillonite or by zeolite Na−P was controlled mostly by the ion-exchange processes, as summarized in eqs 5−7. Other studies demonstrated the controlling of the ammonium adsorption by (A) the successful replacement of the zeolitic interchannel water and the montmorillonite interlayer water by the dissolved ammonium ions creating coordination complexes with the existing replaceable ions, (B) the occurrence of physical trapping for the ammonium ions within the interchannel of the zeolite structure or between the montmorillonite units, and (C) the normal electrostatic attraction processes (Figure 8).

\[ \text{Zeolite P} - \text{Na}^+ + \text{NH}_4^+ \leftrightarrow \text{Na}^+ + \text{zeolite P} - \text{NH}_4^+ \quad (5) \]

\[ \text{Montmorillonite} - \text{Na}^+ + \text{NH}_4^+ \leftrightarrow \text{Na}^+ + \text{montmorillonite} - \text{NH}_4^+ \quad (6) \]

\[ \text{BE/ZP} - \text{Na}^+ + \text{NH}_4^+ \leftrightarrow \text{Na}^+ + \text{BE/ZP} - \text{NH}_4^+ \quad (7) \]

### 2.2.5. Comparison Study.

The adsorption capacities of BE/ZP for phosphate and ammonium were compared with different types of synthetic and natural adsorbents in the literature considering the estimated theoretical capacities (Table 3). As compared to the presented natural and synthetic adsorbents, BE/ZP exhibited higher uptake capacities for both phosphate and ammonium pollutants. It achieved better results than natural and synthetic zeolites as well as their modified products, natural clay minerals and their modified products, and carbonaceous adsorbents from different resources (Table 3). Also, the composite displayed higher results than some advanced adsorbents as graphene and graphene oxide-based adsorbents, nanometal oxide-based adsorbents, different types of modified mesoporous silica, and layered double hydroxide (Table 3). Considering the obtained results, the synthetic BE/ZP is an advanced adsorbent for phosphate and ammonium which can be used to capture them effectively from real water samples and can be reused again as a fertilizer carrier.

### 2.2.6. Realistic Study.

The appropriateness of BE/ZP to be used directly in realistic remediation of sewage water and groundwater samples from the present phosphate and ammonium contaminants was evaluated by mixing 0.14 g of

| Adsorbents | Phosphate | Ammonium |
|------------|-----------|----------|
| MCM-41/rice husk | 21 | 10.72 |
| Mg(OH)₂/ZrO₂ | 87.2 | 39.8 |
| Lanthanum hydroxides | 107.5 | 28.43 |
| Titanium modified zeolite | 37.60 | 4.9 |
| L₆₀SBA-15 | 45.6 | 30.0 |
| Calcined Mg–Al-LDHs | 40.78 | 26.63 |
| ZrO₂ nanoparticles | 99 | 27.47 |
| Smeectic clay | 42.19 | 22.6 |
| Zirconia/graphite oxide | 149.3 | 50.06 |
| Titania/GO | 33.11 | 51.48 |
| La doping magnetic graphene | 116.28 | 76.92 |
| Hydrous zirconium oxide | 51.8 | 46.9 |
| Milled furnace slag | 43.1 | 125.0 |
| Kaolinitic clay | 38.46 | 43.47 |
| Fe–Mn binary oxide | 36 | 109.0 |
| Zeolite A | 52.91 | 237.6 |
| Biochar | 133 | 80.65 |
| MgO | 75.13 | 121.07 |
| Fe-based MOFs of MIL-101 | 106.67 | 61.0 |
| NH₄–Fe-based MOFs of MIL-101 | 121.67 | 61.0 |
| Halloysite | 3.56 | 62.0 |
| Fe₂O₃ doped halloysite | 5.13 | 62.0 |
| MgO/diatomite | 63.3 | 11.0 |
| BE/ZP | 179.4 | this study |

**Structure or between the montmorillonite units, and (C) the normal electrostatic attraction processes (Figure 8).**
Table 4. Chemical Analysis of Sewage Water and Groundwater Sample before and after Treating Them with the BE/ZP Composite

|                      | sewage water analyses | groundwater analyses |                |                |               |                |               |               |               |               |               |               |               |               |               |               |               |               |               |
|----------------------|-----------------------|----------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                      | sample | after treatment | limit (max) | sample | after treatment | limit (max) |                |                |               |               |               |               |               |               |               |               |               |               |               |               |
| pH                   | 7.8     | 8.4     | 6.5–9 | turbidity (NTU) | 0.45 | 0.35 | 1 |                |                |               |               |               |               |               |               |               |               |               |               |
| TSS (mg/L)           | 18      | 16      | 50     | pH | 7.49 | 8.1 | 6.5–8.5 |                |                |               |               |               |               |               |               |               |               |               |               |
| TDS (mg/L)           | 634     | 612     | 2000   | alkalinity (mg/L) | 189 | 124 |                |                |               |               |               |               |               |               |               |               |               |               |               |
| BOD (mg/L)           | 6       | 3.8     | 60     | conductivity (U/cm) | 1315 | 578 |                |                |               |               |               |               |               |               |               |               |               |               |               |
| COD (mg/L)           | 30      | 9.8     | 80     | total hardness (mg/L) | 191 | 80.6 | 500 |                |                |               |               |               |               |               |               |               |               |               |               |
| oil & grease (mg/L)  | 7       | 1.77    | 10     | Ca hardness (mg/L) | 112 | 47.2 | 350 |                |                |               |               |               |               |               |               |               |               |               |               |
| sulphide (mg/L)      | 0.01    | nil     | 1      | Mg hardness (mg/L) | 79 | 33.4 | 150 |                |                |               |               |               |               |               |               |               |               |               |               |
| ammonium (mg/L)      | 12.3    | 2.3     | 10     | chloride (mg/L) | 103 | 95.4 | 250 |                |                |               |               |               |               |               |               |               |               |               |               |
| nitrate (mg/L)       | 27      | 6.2     | 30     | sulfate (mg/L) | 150 | 112.3 | 250 |                |                |               |               |               |               |               |               |               |               |               |               |
| phosphate (mg/L)     | 4       | nil     | 2      | ammonia (mg/L) | 0.62 | nil | 0.45 |                |                |               |               |               |               |               |               |               |               |               |               |
| iron (mg/L)          | 0.5     | nil     | 3.5    | nitrite (mg/L) | 0.009 | nil | 0.9 |                |                |               |               |               |               |               |               |               |               |               |               |
| Cu (mg/L)            | 0.01    | nil     | 0.5    | nitrate (mg/L) | 7.05 | nil | 45 |                |                |               |               |               |               |               |               |               |               |               |               |
| Zn (mg/L)            | 0.011   | nil     | 0.2    | iron (mg/L) | 0.38 | nil | 0.3 |                |                |               |               |               |               |               |               |               |               |               |               |
|                      |         |         |        | manganese (mg/L) | 0.91 | nil | 0.4 |                |                |               |               |               |               |               |               |               |               |               |               |
|                      |         |         |        | Cu (mg/L) | 0.009 | nil | 2 |                |                |               |               |               |               |               |               |               |               |               |               |
|                      |         |         |        | Zn (mg/L) | 0.02 | nil | 3 |                |                |               |               |               |               |               |               |               |               |               |               |

BE/ZP with 100 mL of the tested water samples for 600 min. After that, the solid adsorbents were separated and the treated water samples were evaluated depending on the full chemical analysis of the samples. The chemical analysis of the studied sewage water sample demonstrated the existence of phosphate, ammonium, and nitrate in concentrations higher than the permitted limits. Additionally, other types of metal ions as iron, zinc, and copper in addition to COD were detected but at concentrations lower than the limits (Table 4). After the real remediation of the sewage water by BE/ZP, the chemical analysis reflected the reduction of phosphate, ammonium, and nitrate to concentrations lower than the permitted limits for purified sewage water (Table 4). Moreover, the results reflected a significant reduction in the COD content and complete decontamination of the detected metal ions and sulfide (Table 4).

For the evaluated groundwater sample, it showed significant concentrations of the total hardness elements and the sulfate, ammonia, and nitrate pollutants without detection of phosphate ions (Table 4). Also, the iron (Fe) and manganese (Mn) contents were identified at concentrations above the acceptable limits for groundwater (Table 4). The results after the remediation process accomplished complete decontamination of the existing ammonia, nitrate, iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn) pollutants (Table 4). Also, the application of BE/ZP resulted in an excellent reduction in the content of the total hardness and sulfate pollutants from the water sample. Such results either for the sewage water or the groundwater support the suitability of BE/ZP materials to be used effectively in the realistic water remediation applications.

4. EXPERIMENTAL SECTION

4.1. Materials. Natural bentonite samples collected from the Western desert bentonite quarry and NaOH pellets (97%, Sigma-Aldrich) were used in the preparation of the composite. The studied aqueous solutions of phosphate and ammonium pollutants were prepared by dilution processes for standard solutions of them (1000 mg/L, Sigma-Aldrich).

4.2. Preparation of the Bentonite/Zeolite Composite (BE/ZP). The composite was prepared according to Abukhadra et al. The bentonite sample was ground to fine fractions of size less than 70 μm and heated to about 750 °C for 4 h as a thermal activation step to produce a chemically reactive aluminosilicate product of a more flexible chemical structure. The activated bentonite (6 g) was treated by NaOH solution (12 g in 100 mL of distilled water) under vigorous stirring (500 rpm) for 2 h at 70 °C. Then, the mixture was set into a conversion reactor consisting of a Teflon autoclave and lined by stainless as a closed alteration system after fixing the conditions at 150 °C for 4 h. By the end of the alteration time and after cooling the system, the
solid fractions were separated by centrifugation, washed extensively, and dried at 65 °C for 24 h.

4.3. Characterization Techniques. The structural properties of bentonite (BE) and the synthetic BE/ZP composite were examined based on the XRD patterns which were obtained using a PANalytical X-ray diffractometer (Empyrean). A scanning electron microscope (Gemini, Zeiss-Ultra 55) was used to study the changes in the morphological features. Additionally, the chemical functional groups were investigated using the FTIR-FT Raman spectrometer (Vertex 70). The changes in the textural properties especially the surface area, as well as the pore-size distribution, were studied based on the plotted nitrogen adsorption/desorption curves depending on Brunauer–Emmett–Teller and Barrett–Joyner–Halenda, respectively.

4.4. Phosphate and Ammonium Decontamination. The adsorption tests were conducted as triplicate tests and the mentioned results are the average values with the standard deviation less than 4.2 and 3.5% for the uptake of phosphate and ammonium, respectively. The BE/ZP fractions which were used in the adsorption tests are in the size range from 10 to 23 μm (50% of the sample with size less than 12 μm and 95% of the sample with size less than 20 μm).

4.4.1. Effect of the pH Value. The pH value is the main controlling parameter in the adsorption systems as it controls the surface properties of BE/ZP and the dissolved ion speciation. The influences of pH values were studied within a range from pH 2 to pH 8 after fixing the other factors at 0.02 g as BE/ZP dosage, 100 mg/L as ammonium and phosphate concentrations, 100 mL as aqueous solution volumes, 120 min as contact time, and 30 °C as reaction temperature. By the end of each test, the residual concentrations were determined using the ion chromatography technique.

4.4.2. Kinetics. The influence of the uptake time and the kinetic behaviors was studied for different selected time intervals within a systematic range from about 30 min to about 1320 min. The other reacting factors were adjusted at 0.02 g of BE/ZP as dosage, 100 mL as volume, 100 mg/L as ammonium and phosphate concentrations, pH 6, and reaction temperature of 30 °C. The kinetic behavior of both phosphate and ammonium was examined by mathematical fitness between the obtained results and four theoretical kinetic models (pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models).

4.4.3. Effect of Adsorbent Dose. The role of the composite masses on enhancing the decontamination percentages was studied for different dosages from 0.02 g to about 0.14 g. This was accomplished after adjusting the conditions at pH 6, 30 °C as temperature, 100 mL as volume, 1320 min as time interval, and 100 mg/L as concentration.

4.4.4. Equilibrium Studies. The equilibrium behavior and the isotherm studies were assessed to investigate the adsorption mechanism of the BE/ZP composite. The experiment tests were designed to be accomplished at a fixed time of 1320 min, a fixed BE/ZP dose of 0.02 g, a fixed volume of 100 mL, pH 6, and the concentration within a range from 25 mg/L to about 400 mg/L. The investigated equilibrium models involved Langmuir, Freundlich, and Dubinin–Radushkevich models.

4.4.5. Thermodynamic Studies. The adsorption behavior of ammonium and phosphate at different temperature values is a vital factor in controlling the adsorption capacity and detecting the nature of the reactions. The thermodynamic tests were accomplished after fixing the conditions at 120 min as uptake time, 0.02 g as BE/ZP mass, 100 mL as volume, and 100 mg/L as the studied concentrations, and the inspected temperature was adjusted within a range from about 303 to 343 K.

4.4.6. Reusability of the Adsorbent. Applicability of reusing the BE/ZP in several cycles of adsorption removal for the ammonium and phosphate is of critical value in the commercial sale. The reusability experiments were conducted for eight cycles by mixing 0.14 g of BE/ZP with 100 mL of distilled water contaminated with ammonium and phosphate ions (100 mg/L) for 1320 min at pH 6. After each experiment, the solid fractions were separated, washed, dried at 80 °C, and reused again in the next cycle.

4.4.7. Realistic Application. After the experimental detection of the best adsorption parameters, the synthetic BE/ZP composite was used directly in the elimination of ammonium and phosphate ions from real water samples (groundwater and sewage water). The inspected groundwater samples were collected as representative samples for groundwater from different wells in Beni-Suef Governorate, Egypt, and the sewage samples were collected from some sewage water stations as final treated products. The water samples were preserved within polypropylene bottles and acidified using diluted nitric acid. Finally, the samples were kept in a refrigerator at 2 °C for further studies.
The authors declare no competing financial interest. Further studies will be accomplished to investigate the adsorption mechanism of the synthetic composite using low-energy ion scattering and X-ray photoelectron spectroscopy as well as different analytical techniques to investigate the composite surface properties after the adsorption processes.

**ACKNOWLEDGMENTS**

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding this work through research group number RG-1439-009.

**REFERENCES**

(1) Abbas, M.; Adil, M.; Ehtisham-ul-Haque, S.; Munir, B.; Yameen, M.; Ghaffar, A.; Shag, A. G. A.; Tahir, M. A.; Iqbal, M. Vibrio fischeri bioluminescence inhibition assay for ecotoxicity assessment: A review. *Sci. Total Environ.* 2018, 626, 1295−1309.

(2) Iqbal, M. Vicia faba bioassay for environmental toxicity monitoring: a review. *Chemosphere* 2016, 144, 785−802.

(3) Iqbal, M.; Abbas, M.; Nisar, J.; Nazir, A.; Qamar, A. Bioassays based on higher plants as excellent dosimeters for ecotoxicity monitoring: a review. *Chem. Int.* 2019, 5, 1−80.

(4) Abukhodr, M. R.; Mostafa, M. Effective decontamination of phosphate and ammonium utilizing novel muscovite/philippsite composite; equilibrium investigation and realistic application. *Sci. Total Environ.* 2019, 667, 101−111.

(5) Shi, Z.; Xu, C.; Guan, H.; Li, L.; Fan, L.; Wang, Y.; Liu, L.; Meng, Q.; Zhang, R. Magnetic metal organic frameworks (MOFs) composite for removal of lead and malachite green in wastewater. *Colloids Surf., A* 2018, 539, 382−390.

(6) Bhatti, H. N.; Hayat, J.; Iqbal, M.; Noreen, S.; Nawaz, S. Biocomposite application for the phosphate ions removal in aqueous medium. *J. Mater. Res. Technol.* 2018, 7, 300−307.

(7) Kiani, D.; Silva, M.; Sheng, Y.; Baltrusaitis, J. Experimental Insights into the Genesis and Growth of Struvite Particles on Low-Solubility Dolomite Mineral Surfaces. *J. Phys. Chem. C* 2019, 123, 25135−25145.

(8) Vu, T. M.; Trinh, V. T.; Doan, D. P.; Van, H. T.; Nguyen, T. V.; Vigneswaran, S.; Ngo, H. H. Removing ammonium from water using modified corncob-biochar. *Sci. Total Environ.* 2017, 579, 612−619.

(9) Shaban, M.; Abukhodr, M. R.; Nasief, F. M.; El-Salam, H. A. Removal of ammonia from aqueous solutions, ground water, and wastewater using mechanically activated clinoptilolite and synthetic zeolite-a: kinetic and equilibrium studies. *Water, Air, Soil Pollut.* 2017, 228, 450.

(10) Shaban, M.; Abukhodr, M. R.; Shahien, M. G.; Ibrahim, S. S. Novel bentonite/zeolite-NaP composite efficiently removes methylene blue and Congo red dyes. *Environ. Chem. Lett.* 2018, 16, 275−280.

(11) Li, J.; Wang, X.; Wang, J.; Li, Y.; Xia, S.; Zhao, J. Simultaneous recovery of microalgae, ammonium and phosphate from simulated wastewater by MgO modified diatomite. *Chem. Eng. J.* 2019, 362, 802−811.

(12) Du, Y.; Wang, L.; Wang, J.; Zheng, G.; Wu, J.; Dai, H. Flower−wire−, and sheet-like MnO2-deposited diatomites: Highly efficient absorbents for the removal of Cr(VI). *J. Environ. Sci.* 2015, 29, 71−81.

(13) Fu, H.; Yang, Y.; Zhu, R.; Liu, J.; Usman, M.; Chen, Q.; He, H. Superior adsorption of phosphate by ferrhydrate-coated and lanthanum-decorated magnetite. *J. Colloid Interface Sci.* 2018, 530, 704−713.

(14) Lu, B.; Kiani, D.; Taifan, W.; Barasauskas, D.; Honer, K.; Zhang, L.; Baltrusaitis, J. Spatially Resolved Product Spéciation during Struvite Synthesis from Magnesium (MgCO3) Particles in Ammonium (NH4+)+ and Phosphate (PO43−) Aqueous Solutions. *J. Phys. Chem. C* 2019, 123, 8908−8922.

(15) Seliem, M. K.; Komarenii, S.; Abu Khadra, M. R. Phosphate removal from solution by composite of MCM-41 silica with rice husk: kinetic and equilibrium studies. *Microporous Mesoporous Mater.* 2016, 224, 51−57.
nanotubes: determination of equilibrium and kinetics parameters. J. Ind. Eng. Chem. 2016, 34, 130–138.
(34) Lin, H.; Wu, X.; Zhu, J. Kinetics, equilibrium, and thermodynamics of ammonium sorption from swine manure by natural chabazite. Sep. Sci.Technol. 2016, 51, 202–213.
(35) Ingezakis, V. J.; Zorpas, A. A. Heat of adsorption, adsorption energy and activation energy in adsorption and ion exchange systems. Desalin. Water Treat. 2012, 39, 149–157.
(36) Lima, E. C.; Hosseini-Bandeghariaei, A.; Moreno-Piraján, J. C.; Anastopoulos, I. A critical review of the estimation of the thermodynamic parameters on adsorption equilibria. Wrong use of equilibrium constant in the Van’t Hoff equation for calculation of thermodynamic parameters of adsorption. J. Mol. Liq. 2019, 273, 425–434.
(37) Lima, E. C.; Hosseini-Bandeghariaei, A.; Moreno-Piraján, J. C.; Anastopoulos, I. Response to “Some remarks on a critical review of the estimation of the thermodynamic parameters on adsorption equilibria. Wrong use of equilibrium constant in the van’t Hoff equation for calculation of thermodynamic parameters of adsorption.” J. Mol. Liq. 2019, 273, 425–434.
(38) Abukhadra, M. R.; Sayed, M. A. K’ trapped kaolinite (Kaol/K’) as low cost and eco-friendly basic heterogeneous catalyst in the transesterification of commercial waste cooking oil into biodiesel. Energy Convers Manag. 2018, 177, 468–476.
(39) Abukhadra, M. R.; Mohamed, A. S. Adsorption Removal of Safranin Dye Contaminants from Water Using Various Types of Natural Zeolite. Silicon 2019, 11, 1635–1647.
(40) Gedik, K.; Imamoglu, I. Removal of cadmium from aqueous solutions using clinoptilolite: influence of pretreatment and regeneration. J. Hazard. Mater. 2008, 155, 385–392.
(41) Benhammou, A.; Yaacoubi, A.; Nibou, L.; Tanouti, B. Adsorption of metal ions onto Moroccan stevensite: kinetic and isotherm studies. J. Colloid Interface Sci. 2005, 282, 320–326.
(42) Shaban, M.; Abukhadra, M. R.; Shahien, M. G.; Ibrahim, S. S. Novel bentonite/zeolite-NaP composite efficiently removes methylene blue and Congo red dyes. Environ. Chem. Lett. 2018, 16, 275–280.
(43) Morali, N. I.H A. N. Investigation of zinc and lead removal from aqueous solutions using clinoptilolite. Degree Of Master of Science MIDDLE EAST TECHNICAL UNIVERSITY, 2006.
(44) Onyango, M. S.; Kuchar, D.; Kubota, M.; Matsuda, H. Adsorptive removal of phosphate ions from aqueous solution using synthetic zeolite. Ind. Eng. Chem. Res. 2007, 46, 894–900.
(45) Bentabol, M.; Cruz, M. D.; R. NH4 for K substitution in diotahedral micas synthesized at 200 °C. Appl. Clay Sci. 2012, 66, 268–277.
(46) Sugahara, H.; Takanou, Y.; Ogawa, N. O.; Chikaraishi, Y.; Ohkouchi, N. Nitrogen isotopic fractionation in Ammonia during 268 2019 composite: adsorption behavior and mechanism. ACS Omega http://pubs.acs.org/journal/acsodf chabazite.
(47) Anastopoulos, I. A critical review of the estimation of the thermodynamic parameters on adsorption equilibria. Wrong use of equilibrium constant in the Van’t Hoff equation for calculation of thermodynamic parameters of adsorption. J. Mol. Liq. 2019, 273, 425–434.
(50) Xie, J.; Wang, Z.; Zhang, H.; Zhan, Y. Removal of phosphate from aqueous solution by a Fe-Mn binary oxide adsorbent. J. Colloid Interface Sci. 2009, 335, 168–174.
(51) Yao, Y.; Gao, B.; Inyang, M.; Zimmerman, A. R.; Cao, X.; Pulimmanapalli, P.; Yang, L. Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. J. Hazard. Mater. 2011, 190, 501–507.
(52) Zhou, J.; Yang, S.; Yu, J. Facile fabrication of mesoporous MgO microspheres and their enhanced adsorption performance for phosphate from aqueous solutions. Colloids Surf, A 2011, 379, 102–108.
(53) Zong, E.; Wei, D.; Wan, H.; Zheng, S.; Xu, Z.; Zhu, D. Adsorptive removal of phosphate ions from aqueous solution using zirconia-functionalized graphite oxide. Chem. Eng. J. 2013, 221, 193–203.
(54) Sukulpaisan, S.; Vongsetskul, T.; Reamouppaturm, S.; Luangkachao, J.; Tantirungrotechai, J.; Tangboriboonrat, P. Titania-functionalized graphene oxide for an efficient adsorptive removal of phosphate ions. J. Environ. Manage. 2016, 167, 99–104.
(55) Nohde, H. R.; Sereshti, H.; Ahsarian, E. Z.; Nouri, N. Enhanced removal of phosphate and nitrate ions from aqueous media using nanosized lanthanum hydrous doped on magnetic graphene nano-composite. J. Environ. Manage. 2017, 197, 265–274.
(56) Lin, J.; Zhan, Y.; Wang, H.; Chu, M.; Wang, C.; He, Y.; Wang, X. Effect of calcium ion on phosphate adsorption onto hydrous zirconium oxide. Chem. Eng. J. 2017, 309, 118–129.
(57) Xue, Y.; Hou, H.; Zhu, S. Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag. J. Hazard. Mater. 2009, 162, 973–980.
(58) Zhang, G.; Liu, H.; Liu, R.; Qi, J. Removal of phosphate from water by a Fe-Mn binary oxide adsorbent. J. Colloid Interface Sci. 2009, 335, 168–174.
(59) Yao, Y.; Gao, B.; Inyang, M.; Zimmerman, A. R.; Cao, X.; Pulimmanapalli, P.; Yang, L. Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. J. Hazard. Mater. 2011, 190, 501–507.
(60) Zhou, J.; Yang, S.; Yu, J. Facile fabrication of mesoporous MgO microspheres and their enhanced adsorption performance for phosphate from aqueous solutions. Colloids Surf, A 2011, 379, 102–108.
(61) Xie, Q.; Li, Y.; Lv, Z.; Zhou, H.; Yang, X.; Chen, J.; Guo, H. Effective adsorption and removal of phosphate from aqueous solutions and eutrophic water by Fe-based MOFs of MIL-101. Sci. Rep. 2017, 7, 3316.
(62) Almasri, D. A.; Saleh, N. B.; Atieh, M. A.; McKay, G.; Ahzi, S. Adsorption of phosphate on iron oxide doped halloysite nanotubes. Sci. Rep. 2019, 9, 3232.
(63) Marañón, E.; Ulmanu, M.; Fernández, Y.; Anger, I.; Castrillón, L. Removal of ammonium from ammonium solutions with volcanic tuff. J. Hazard. Mater. 2006, 137, 1402–1409.
(64) Kizito, S.; Wu, S.; Kipkemoi Kirui, W.; Lei, M.; Lu, Q.; Bah, H.; Dong, R. Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry. Sci. Total Environ. 2015, 505, 102–112.
(65) Vassileva, P.; Tzvetkova, P.; Nickolov, R. Removal of ammonium ions from aqueous solutions with coal-based activated carbons modified by oxidation. Fuel 2009, 88, 387–390.
(66) Thornton, A.; Pearce, P.; Parsons, S. A. Ammonium removal from solution using ion exchange on to MesoLate, an equilibrium study. J. Hazard. Mater. 2007, 147, 883–889.
(67) Karadag, D.; Akgül, E.; Tok, S.; Erturk, F.; Kaya, M. A.; Turan, M. Basic and reactive dye removal using natural and modified zeolites. J. Chem. Eng. Data 2007, 52, 2436–2441.
(68) Sun, Z.; Qu, X.; Wang, G.; Zheng, S.; Frost, R. L. Removal characteristics of ammonium nitrogen from wastewater by modified Ca-bentonites. Appl. Clay Sci. 2015, 107, 46–51.
(69) Halim, A. A.; Aziz, H. A.; Johari, M. A. M.; Ariffin, K. S.; Hung, Y. T. Removal of ammonical nitrogen and COD from semi-aerobic landfill leachate using low-cost activated carbon zeolite. Int. J. Environ Waste Manage. 2009, 4, 399.
(70) Xu, K.; Lin, F.; Dou, X.; Zheng, M.; Tan, W.; Wang, C. Recovery of ammonium and phosphate from urine as value-added fertilizer using wood waste biochar loaded with magnesium oxides. J. Clean. Prod. 2018, 187, 205–214.
(71) Bhardwaj, D.; Sharma, M.; Sharma, P.; Tomar, R. Synthesis and surfactant modification of clinoptilolite and montmorillonite for the removal of nitrate and preparation of slow release nitrogen fertilizer. J. Hazard. Mater. 2012, 227–228, 292–300.
(72) Khosravi, A.; Esfemosseini, M.; Khezri, S. Removal of ammonium ion from aqueous solutions using natural zeolite: kinetic, equilibrium
and thermodynamic studies. *Res. Chem. Intermed.* 2014, 40, 2905–2917.

(73) You, X.; Valderrama, C.; Querol, X.; Cortina, J. L. Recovery of ammonium by powder synthetic zeolites from wastewater effluents: optimization of the regeneration step. *Water, Air, Soil Pollut.* 2017, 228, 396.

(74) Wang, X.; Liu, S.; Gao, C.; Xu, X.; Zhang, X.; Bai, X.; Liu, M.; Wu, L. Highly efficient adsorption of ammonium onto palygorskite nanocomposite and evaluation of its recovery as a multifunctional slow-release fertilizer. *Chem. Eng. J.* 2014, 252, 404–414.