Fixed-bed column dynamics of ultrasound and Na-functionalized diatomite to remove phosphate from water

Junxiu Ye 1 · Min Yang 1 · Xuemei Ding 1 · Wei Tan 1 · Guizhen Li 1 · Shuju Fang 1 · Hongbin Wang 1

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Abstract
A continuous fixed-bed column study was used to evaluate phosphate adsorption performance of U-D-Na which was functionalized by the cheap NaCl reagent after simple ultrasonic purification of diatomite. In this work, various effect factors, including flow rate, initial phosphate concentration, and the bed height, on breakthrough performance of fixed column were investigated. Experimental results demonstrated that the breakthrough time declined with the increase of inlet phosphate concentration and feed rate, whereas the increase of bed height turned out to significantly extend the breakthrough time. The dynamic adsorption process could be well fitted by the Thomas model, with a correlation coefficient $R^2 > 0.9000$ under main operating conditions. A thrice loop of effective regeneration was achieved with 0.1 M hydrochloric acid eluent and deionized water. The maximum removal rate for phosphate was more than 95% in the column adsorption process. The results proved that U-D-Na could be used as a better alternative phosphate adsorbent for wastewater in a continuous column sorption process.

Keywords Removal of phosphate · Functionalized diatomite · Ultrasonic · Dynamic adsorption · Sewage treatment · Thomas model · Responsible Editor: Tito Roberto Cadaval Jr

Introduction
Eutrophication caused by the high content of nutrients such as phosphate in water is concerned in the field of water treatment (Si et al. 2000). It was reported that the inland river basins in many developed countries (e.g., the USA) and some developing countries (e.g., China) were suffering from water eutrophication. The trend of water deterioration is largely related to human activities, and the level of pollution in the river near densely populated areas was more serious (Bhagowati and Ahamad 2019, Bu and Xu 2013, Yi et al. 2011). According to the US Environmental Protection Agency (USEPA), the phosphate concentration in water exceeding 0.02 mg/L might lead to eutrophication. China’s “Pollutant Discharge Standard for Municipal Wastewater Treatment Plants” stipulates that the phosphate content in urban sewage discharge should be no more than 0.50 mg/L. In recent years, plenty of treatment methods, such as membrane filtration, adsorption, flocculation, precipitation, and crystallization, were carried out by many scholars to remove phosphate in sewage (Duan et al. 2013; Fan et al. 2017; Greenlee et al. 2009; Wen and Jian 2008; Wu et al. 2018). Among them, the adsorption technology was considered to be a potential alternative due to its simple operation, rapid adsorption performance, low cost, and high utilization rate of resources. This is of great significance in sewage treatment and environmental protection (Cong et al. 2014; Zhao et al. 2018).

The adsorption technology was widely applied in many water treatment plants for phosphate removal. It is an increasing tendency in fully utilizing effective adsorbent to remove target substances in sewage. Generally, the pollutions are attached to the surface of the adsorbent due to a certain unbalanced attractive force, such as electrostatic attraction, chemical bonding, and van der Waals force or physical sedimentation. The strength of the acting force that exists in the adsorbent would largely affect the sorption performance. Therefore, the selection and optimization of the adsorbent are key factors to technology in actual production. In the past few years, various adsorbents for phosphate removal had been explored (Chouyyok et al. 2010; Zhou et al. 2011). At present, the adsorbent based on diatomite to remove phosphate is under study.
The natural diatomite is an important silicate material evolving from seafloor diatoms. It has a large number of micropores in surface and interior, specific surface area, strong acid and alkali resistance, and a lot of striking chemical and physical properties of diatomite. The surface of diatomite is rich in silyl hydroxyl groups and hydrogen bonds (Xiao et al. 2010), which could be modified by different groups or functionalized particles by chemical reactions. Many adsorption mechanisms of diatomite are also based on these functional groups. Although a certain adsorption effect of raw diatomite can be also observed depending on its structural properties, the surface modification of diatomite is the main approach to improve its adsorption performance. The previous studies have been found that the functionalized diatomite showed a promising sorption performance for phosphate. For instance, Xu and Pang pointed out that the phosphate removal efficiency of the diatomite could be largely improved by increasing the specific surface area, void volume of diatomite, and removing surface moisture and organic matter (Xu and Pang 2009). The diatomite (Wu et al. 2018) modified by hydrated lanthanum chloride (La-diatomite) also showed effective adsorption capacity for phosphate, with a maximum adsorption capacity of 58.7 mg/g. Additionally, a sizable high dephosphorization efficiency (close to 100%) could be also achieved by diatomite functionalized with zeolite and aluminum metal modifier (Duan et al. 2013; Wu and Chen 2011). Numerous researchers had validated that the modified diatomite presented an excellent sorption capacity. Especially some information on thermodynamics, kinetics, and adsorption mechanism was obtained at the stage of static experiments. However, it is also extremely necessary to carry out fixed-bed experiments to evaluate the practical performance of the novel adsorbent.

The column experiment is a continuous process of interaction between the target pollutant and the adsorbent. Many key factors such as initial concentration, feed rate, and bed depth that affect column efficiency need to be considered during the adsorption process. The large-scale sewage in industries was generally treated by fixed-bed adsorption. This process filled the gap that the static adsorption could only address small batches of solution (Singh et al. 2012). In the dynamic sorption test, the saturation layer continuously increased, while the height of the adsorption layer declined with large amounts of target ions in the solution continuously enter and leave the column. When the column reached the stage of complete saturation, we considered that the column reached the dynamic adsorption equilibrium. Parameters such as breakthrough time, equilibrium adsorption capacity, and regeneration capability in the dynamic system are vital to evaluate the performance of columns. These factors can be measured by the breakthrough curves at different conditions. Therefore, it is significant to investigate the influence of changes in experimental parameters on the dynamic adsorption performance of the adsorbent.

For those reasons, based on the study of static adsorption properties of U-D-Na recently conducted by our research team, various test conditions were carried out to further explore the phosphate removal ability in the fixed-bed column. Through the study of various influence factors on fixed-bed sorption performance, this paper intended to provide some basic proofs for the design and operation of the U-D-Na in a continuous sorption application.

**Materials and methods**

**Reagents and instruments**

Natural diatomite used as the adsorbent precursor in this study was collected from a local town, Xundian, Yunnan, which could be developed for phosphate removal in water after simple modification treatment. The other chemicals such as KH₂PO₄, NaCl, and HCl were analytical reagents and used as received. The solutions are prepared with secondary deionized water.

Electric heating blast drying oven DL402 and Ultrasonic cleaner AS10200AD were produced by Tianjin Experimental Instrument Factory. UV-vis spectrum was recorded by the anti-molybdenum antimony spectrophotometer 7200 (Uniko Shanghai Instrument). Dynamic sorption experiments were operated in a fixed-bed column with an inside diameter of 0.8 cm and a bed height of 35 cm. A constant flow rate was guaranteed by a commercial peristaltic pump.

**Experimental methods**

**Preparation of U-D-Na**

The U-D-Na was prepared according to the following method. Briefly, an appropriate amount of diatomite was crushed, sieved, and ultrasonically cleaned for 1 h, then dried at 110 °C, and stored in a dry container. The treated diatomite was added into 5% NaCl solution thoroughly for 2 h, then dried at 95 °C, and stored at 110 °C. Finally, diatomite was transferred into a muffle furnace calcining and heated at 400 °C for 2 h, and the adsorbent U-D-Na was prepared (detailed in the under-review article entitled “Study on sodium functionalized ultrasonic-diatomite and its performance for phosphorus removal”).

**Dynamic adsorption experiment**

The simple diagram of the fixed-bed column in the experiment is shown in Fig. 1. The peristaltic pump was used to transport the liquid and controlled the injection flow rate. A tank was located at the outlet of the separation column to collect the tail...
In order to facilitate the connection between the column and peristaltic pump and prevent the U-D-Na from floating, the steel sieve of the bottom of the column was plugged with absorbent cotton, and the top of the column was sealed with a ground-glass piston.

Dynamic adsorption experiment was carried out in a fixed-bed column with the height of 35 cm and the inner diameter of 0.8 cm. To begin with, an amount of U-D-Na was packed in the column to the desired bed height of 1, 3, and 5 cm (equivalent to 1, 3, and 5 g of U-D-Na), and then various concentrations of phosphate solution (15.00, 20.00, and 25.00 mg/L) were pumped into the column at the flow rate of 1, 2, and 3 mL/min, respectively. The effluent sample concentrations were measured at the exit of the column by molybdenum antimony spectrophotometry at a regular interval.

Calculation of breakthrough curve parameters

The adsorption performance of the column was evaluated by the breakthrough curve and the sorption capacity (Rout et al. 2017). The breakthrough curve was a function defined by the ratio of the outflow concentration \( C_t \) and the inlet concentration \( C_0 \) against time \( T \). The breakthrough time \( t_b \) was determined as the time when the outlet phosphate concentration \( C_t \) reached 10% of the inlet phosphate concentration \( C_t/C_0 = 0.1 \). Similarly, the exhaustion time \( t_e \) was determined as the time when the outlet phosphate concentration \( C_t \) reached 90% of the inlet phosphate concentration \( C_t/C_0 = 0.9 \).

Calculation of total adsorption capacity:

\[
q_{\text{total}} = \frac{Q}{1000} \int_{t=0}^{t=t_{\text{total}}} C_{\text{ad}} dt
\]

where \( q_{\text{total}} \) is the total amount of adsorbed phosphate onto U-D-Na column, mg; \( Q \) is the volumetric flow rate, mL/min; \( C_{\text{ad}} \) is the difference in the phosphate concentration at the initial time and the \( t \) time, mg/L; and \( t_{\text{total}} \) is the total time when the adsorption equilibrium of column reached saturation, min.

Calculation formula of equilibrium adsorption capacity:

\[
q_e = \frac{q_{\text{total}}}{M}
\]

where \( q_e \) is the equilibrium uptake capacity, mg/g, which is derived as the quantity adsorbed \( q_{\text{total}} \) per weight of adsorbent \( (M \) is the amount of U-D-Na packed in the column, g).

Calculation formula of removal rate:

\[
R(\%) = \frac{C_0-C_t}{C_0} \times 100\%
\]

Theoretical model

Mathematical models of breakthrough performance of fixed-bed systems are essential for the successful design and optimization of the adsorption process of packed columns. In actual operation, the concentration of the column outlet and bed height could be evaluated and predicted by an appropriate mathematical model, which was convenient and necessary for expanding the experimental scale. Meanwhile, a suitable mathematical model could be also helpful for practitioners to understand and explain the affinity, surface properties, and adsorption process between adsorbents and adsorbate (Foo et al. 2013). In the present research, the Thomas and Yoon-Nelson models were used to fit the continuous adsorption process of U-D-Na.

Successive cycles of sorption and desorption by column

The experimental procedures of adsorption/desorption were conducted to assess the reusability of U-D-Na. For the first cycle, the phosphate solution (25.00 mg/L) was first passed through the fixed bed with 3 g of U-D-Na at a constant flow rate (2 mL/min) at room temperature until the column saturated. Then the saturated column was rinsed several times with 7% HCl solution and deionized water in turn. Tail samples were collected and measured at different time intervals. Until the exit phosphate concentration was nearly equal to zero, the column then finished its regeneration and could be used for subsequent adsorption/desorption cycle experiments. All the test process was repeated three times. Then, the regeneration capacity was evaluated by the breakthrough curves.

Results and discussions

The morphology analysis of U-D-Na

The characterization of U-D-Na was based on the static experiment; some necessary data are listed in Table 1. The morphology and elementary composition of U-D-Na were
characterized by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and Fourier transform infrared (FTIR) spectroscopy. It could be seen from SEM that the surface micropores of U-D-Na were loosely arranged and ordered smoothly, and the sodium chloride flat attached diatomaceous earth surface and matched with the results on EDS. Several necessary parameters are listed in Table 3. The CH\textsubscript{3} stretching vibration absorption peak (1400 cm\textsuperscript{-1}) disappeared, and the carbon dioxide absorption peak (2352.83 cm\textsuperscript{-1}) appeared in U-D-Na according to the FTIR analysis, but overall the structure of diatomite before and after modification remained basically unchanged. This result could also be verified by EDS and the appearance of 26–27 (°) in XRD, which is the characteristic peak of silica skeleton. According to the EDS, there was a slight increase in the content of iron and aluminum in the modified diatomite, mainly because some insoluble impurities and volatile organic matter will reduce after ultrasonic and calcination. Especially, the decrease in oxygen of U-D-Na was also observed in EDS, which could be ascribed to the removal of volatile organic matters due to the synergistic effect of high prepared temperature and ultrasonic treatment and could be evidenced by the disappearance of 32 (°) in XRD. Furthermore, Amaniampong et al. (2018, 2019) and Thang et al. (2018) provided a constructive and theoretical explanation about this phenomenon, the appearance of oxygen vacancy resulted from the implosion of the cavitation bubble, and some ultrasonic-caused H\textsuperscript{+} combined with the lattice oxygen in crystal components of diatomite.

### Study on dynamic adsorption using fixed-bed column

#### Effect of flow rate

Figure 2 illustrates the breakthrough curves of the column packed with U-D-Na at various flow rates with an initial phosphate concentration of 25.00 mg/L and bed height of 3 cm. As can be seen from Fig. 2, the breakthrough time and the exhaustion time decreased with the increasing flow rates. Specifically, the breakthrough time (at \(C_t/C_0 , 10\%\)) decreases from 50 to 20 min with the flow rate increase from 1 to 3 mL/min, respectively. Because a large flow rate could result in a faster sorption rate and weaken the interaction between the adsorbate molecules and adsorbent (Dwivedi et al. 2008), the active sites of U-D-Na were quickly occupied by massive phosphate ions available. Therefore, the sorption process was speeded up. A similar tendency was also reported in a previous article about phosphate removal (Singh et al. 2012; Zhang et al. 2014). The sorption capacity at different flow rates (Table 2) showed a decrease with the uprising of flow rates. The equilibrium adsorption capacity \(q_e\) declined from 1.43 to 1.13 mg/L with the flow rate increased from 1 to 3 mL/min. Excessive flow rate is not conducive to the retention of phosphate by the column. The more residence time of the phosphate ions in the column, the more effective sorption interaction is between phosphate and column (Bulgariu and Bulgariu 2013). With the consideration of the breakthrough time (Fig. 2) and sorption performance (Table 2), a flow rate of 2 mL/min was selected in the subsequent experiment.

#### Effect of bed height

The breakthrough curves with various bed depths of 1, 3, and 5 cm were investigated at a constant concentration of 25.00 mg/L and a flow rate of 2 mL/min as shown in Fig. 3. The amount of U-D-Na in the column was approximately 1, 3, and 5 g, respectively. As can be seen from Fig. 3, the breakthrough time increased with the increasing bed height. The time of reaching the saturation point of phosphate was concomitantly increased with the growing bed height (amount of U-D-Na). The exhaustion time increased from 95 to 280 min with the bed heights raised from 1 to 5 cm (Table 2), respectively. The fact is that a higher bed height could lead to a lengthier mass transfer zone (Jain et al. 2013) and enhance the axial dispersion phenomenon (Saha et al. 2012; Vijayaraghavan et al. 2004). Additionally, the total phosphate uptake capacity \(q_{\text{total}}\) was proportional to bed height, and the \(q_{\text{total}}\) values were

| Material | Natural diatomite | U-D-Na |
|----------|------------------|--------|
| EDS      | Si (%) 47.95     | 47.07  |
|          | O (%) 39.27      | 36.90  |
|          | Na (%) -         | 0.77   |
| XRD      | 32 (°) Existed   | Disappeared |
|          | 26–27 (°) Existed | Existed |
| Removal rate (%) | 14.64 | 97.14 |

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Fig 2 Effect of flow rate on the breakthrough curve of phosphate adsorption onto U-D-Na (natural pH, initial phosphate concentration of 25.00 mg/L, bed height of 3 cm)
found to be 2.15, 2.78, and 6.63 g for the bed heights of 1, 3, and 5 cm (Table 2). However, the equilibrium adsorption capacity \( q_e \) showed a slight decrease with the increase of bed height. This is mainly because the retention efficiency for phosphate was reduced due to the underutilization of active sites of per unit mass of U-D-Na at a higher bed height (Kumar et al. 2011; Singh et al. 2012). Therefore, a bed height of 3 cm was used in this work.

**Effect of influent phosphate concentration**

The influence of inlet phosphate concentrations on the breakthrough curves is depicted in Fig. 4. The result indicated that the breakthrough time was reversely related to the influent phosphate concentration at a given flow rate of 2 mL/min and bed depth of 3 cm. The breakthrough time was found to be 70, 60, and 30 min for phosphate concentration of 15.00, 20.00, and 25.00 mg/L, respectively. A similar trend for exhaustion time (280, 190, and 110 min) was observed compared to breakthrough time under the above-mentioned conditions (Table 2). One of the facts is that the larger the concentration gradient, the stronger the mass transfer force, resulting in a longer MTZ at a higher initial phosphate concentration. A higher concentration gradient was favorable for mass transfer coefficient or diffusion (Zhang et al. 2011). Additionally, the steeper the curves, the higher the sorption capacity for the column (Cruz-Olivares et al. 2013). And the steepest slope was observed at the concentration of 25.00 mg/L. Therefore, the phosphate concentration of 25.00 mg/L was considered as an excellent concentration point to study the dynamic sorption capacity of the column.

**Breakthrough curve model**

**Thomas model**

The Thomas model was widely used to evaluate column performance and predict the phosphate adsorption breakthrough curve (Foo et al. 2013). It was dependent on two assumptions: (1) the adsorption interface is not affected by chemical reaction with an absence of axial dispersion, and (2) data fits Langmuir isotherm and the second-order reversible reaction kinetics. The Thomas model is suitable for describing the entire process of dynamic adsorption \( \frac{C_t}{C_0} = 0.0-1.0 \). The equation of the Thomas model is shown as below:

![Fig. 3 Effect of bed height on the breakthrough curve of phosphate adsorption onto U-D-Na (natural pH, flow rate of 2 mL/min, initial phosphate concentration of 25.00 mg/L)](image1)

![Fig. 4 Effect of influent phosphate concentration on the breakthrough curve of phosphate adsorption onto U-D-Na (natural pH, flow rate of 2 mL/min, bed height of 3 cm)](image2)

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**Table 2** Fixed-bed adsorption parameters for the adsorption of phosphate onto U-D-Na at room temperature

| \( F \) (mL/min) | \( IC \) (mg/L) | \( H \) (cm) | \( T_b \) (min) | \( T_e \) (min) | \( q_{total} \) (mg) | \( q_e \) (mg/g) | Maximum removal rate (%) |
|-----------------|----------------|-------------|----------------|--------------|-----------------|------------------|--------------------------|
| 1.00            | 25.00          | 3.00        | 50             | 320          | 4.29            | 1.43             | 98.14                    |
| 2.00            | 25.00          | 3.00        | 30             | 110          | 2.78            | 0.93             | 98.14                    |
| 3.00            | 25.00          | 3.00        | 20             | 90           | 3.40            | 1.13             | 98.14                    |
| 2.00            | 25.00          | 1.00        | 25             | 95           | 2.15            | 2.15             | 98.14                    |
| 2.00            | 25.00          | 5.00        | 90             | 280          | 6.63            | 1.33             | 98.14                    |
| 2.00            | 15.00          | 3.00        | 70             | 280          | 4.52            | 1.51             | 97.14                    |
| 2.00            | 20.00          | 3.00        | 60             | 190          | 4.03            | 1.34             | 98.20                    |

---
where \( C_0 \) and \( C_t \) are the initial inlet and effluent phosphate concentrations, \( m/g \); \( q_0 \) is the equilibrium adsorption capacity, \( m/g \); \( m \) is the mass of adsorbent, \( g \); \( K_{TH} \) is the kinetic constant, \( mL/min \cdot mg \); and \( Q_0 \) is the fed flow rate, \( mL/min \). The \( q_0 \) and \( K_{TH} \) were obtained by intercept and slope from the linear regression equation of \( ln \left( \frac{C_0}{C_t-1} \right) \) against \( t \), respectively.

The characteristic parameters of the Thomas model at different experimental conditions are listed in Table 3. It was clear that the Thomas rate constant \( K_{TH} \) had a positive relationship with feed rate and initial phosphate concentration. The \( K_{TH} \) value increased from 0.70 to 1.90 \( mL/min \cdot mg \) with the increase in feed rate from 1 to 3 \( mL/min \), respectively, while the \( K_{TH} \) was inversely proportional to the bed height. These can be ascribed to the fact that a high concentration gradient and feed rate could result in a strong driving force, and increasing bed height led to higher steric hindrance (Paudyal et al. 2013). According to Table 3, the Thomas model was found to fit well the dynamic sorption process of U-D-Na with a correlation coefficient of \( R^2 >0.9000 \) for most of the parameters (5/7). The values of \( q_e \) (1.53, 1.19, and 1.34 \( mg/g \)) calculated by the Thomas model were in good agreement with the experimental data (1.43, 0.93, and 1.13) at an uprising flow rate (1, 2, and 3 \( mL/min \)). Those results validated that the Thomas model is suitable for representing the dynamic sorption process. Therefore, a reliable \( q_e \) value could be obtained at a given test condition by the model. It could also be inferred that neither the internal nor the external diffusions of the adsorbent surface were the rate control step of the process (Chen et al. 2012).

### Yoon-Nelson model

The Yoon-Nelson model, developed by Yoon and Nelson in 1981, is the simplest mathematical and semiempirical expression with fewer parameters. This model need not consider the property of adsorbent and physical characters of the column. Similar to the Thomas model, it is suitable for describing the whole process of dynamic adsorption. This mathematical model depends on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule was proportional to the probability of adsorbate and the probability of adsorbate breakthrough on the adsorbent (Yoon and Nelson 1984). The linear expression of the Yoon-Nelson model is given by the following equation:

\[
ln \left( \frac{C_0}{C_0-C_t} \right) = K_{YN}t-\tau_{YN}
\]

where \( K_{YN} \) is the Yoon-Nelson rate constant \( (min^{-1}) \) and \( \tau \) is the time required for 50% phosphate breakthrough \( (min) \). The \( K_{YN} \) and \( \tau \) could be calculated from the linear plot of \( ln \left( \frac{C_0}{C_0-C_t} \right) \) against \( t \).

The data obtained from the Yoon-Nelson model are listed in Table 3. It was found that the \( K_{YN} \) increased and \( \tau \) decreased with the increase of flow rate \( (1 \times 3 \times mL/min) \) and initial concentration \( (15.00 \times 25.00 \times mg/L) \). At a high flow rate and initial concentration, the time of 50% phosphate breakthrough \( (\tau) \) was reached fast. According to the assumption of the Yoon-Nelson model, it could be inferred that the probability of phosphate passing through the column was enhanced at a high flow rate (Yuan et al. 2020). Nevertheless, increase of bed depth \( (1 \times 5 \times cm) \) resulted in a rise of \( \tau \) \( (30.00 \times 120.00 \times min) \) and a fall of \( K_{YN} \) \( (0.0808 \times 0.0230 \times min^{-1}) \); the reason for \( \tau \) rise is similar to the explanation of breakthrough time.

### Table 3 Thomas and Yoon-Nelson model constants for the phosphate adsorption by U-D-Na packed column

| Parameters | Thomas model | Yoon-Nelson model |
|------------|--------------|-------------------|
| \( F \) \( C_0 \) \( H \) | \( K_{TH} \) \( q_{0cal} \) \( q_{0exp} \) \( R^2 \) | \( K_{YN} \) \( \tau_{cal} \) \( \tau_{exp} \) \( R^2 \) |
| 1.00 25.00 3.00 | 0.708 1.53 1.43 0.9480 | 1.75 184.58 140.00 0.9519 |
| 2.00 25.00 3.00 | 1.224 1.19 0.93 0.8747 | 2.98 71.07 52.00 0.8851 |
| 3.00 25.00 1.00 | 1.900 1.34 1.13 0.9225 | 4.26 52.31 50.00 0.9201 |
| 4.00 25.00 1.00 | 3.23 2.11 2.15 0.9312 | 8.08 42.25 30.00 0.9312 |
| 5.00 25.00 1.00 | 0.92 1.76 1.33 0.9494 | 2.30 176.39 120.00 0.9494 |
| 6.00 25.00 1.00 | 0.796 2.65 1.51 0.9019 | 1.99 158.67 101.00 0.9019 |
| 7.00 25.00 1.00 | 0.936 2.05 1.34 0.8842 | 2.34 123.00 76.00 0.8842 |

Notation: \( F \), flow rate \( (mL/min) \); \( C_0 \), initial phosphate concentration \( (mg/L) \); \( H \), bed depth \( (cm) \); \( K_{TH} \), the Thomas model rate constant \( (mL/min \cdot mg) \); \( q_{0exp} \), equilibrium phosphate sorption capacity calculated by the Thomas model \( (mg/g) \); \( q_{0cal} \), equilibrium phosphate sorption capacity obtained from experiment \( (mg/g) \); \( K_{YN} \), the Yoon-Nelson model rate constant \( (min^{-1} \cdot *10^{-2}) \); \( \tau_{cal} \), the time required for 50% breakthrough calculated by the Yoon-Nelson model \( (min) \); \( \tau_{exp} \), the time required for 50% breakthrough obtained from experiment \( (min) \)
Additionally, the correlation coefficient, $R^2$, obtained from the Yoon-Nelson model ranged from 0.8428 to 0.9519 (Table 3). And the $\tau$ values calculated by the Yoon-Nelson model do not completely agree with the experimental values. The $\tau$ values were found to be 140.00, 52.00, and 50.00 min, and experimental values were 184.58, 71.07, and 52.32 at the flow rate of 1, 2, and 3 mL/min, respectively. Therefore, it could be concluded that the Yoon-Nelson model was not suitable for the sorption system of neglect axial dispersion. The Thomas model is more suitable to represent the sorption process of phosphate-U-D-Na system in this experiment.

**Comparison of the performance of various adsorbents**

There are many studies focused on the modification of diatomite using zirconium, lanthanum, and other alkaline-earth metals and the static adsorption experiment of phosphate. The performance of U-D-Na used for removal of phosphate was compared with other adsorbents at different ranges of phosphate concentrations as listed in Table 4. The adsorption capacity and removal rate were compared. It can be seen that the prepared U-D-Na for phosphate removal exhibited good removal rate or comparable sorption performance. U-D-Na was prepared simple, low cost, and high removal rate, providing a promising application for phosphate removal in real pollution water.

**Successive adsorption-desorption cycles**

**Regeneration of U-D-Na adsorbed phosphate**

In order to investigate the practical application ability of U-D-Na, the elution experiment of a saturated bed was carried out with 7.0% HCl solution at a constant flow rate of 2 mL/min. The plot between the outlet concentration and the elution time is depicted in Fig. 5. It could be clearly seen from Fig. 5 that the outlet phosphate concentration in the eluent presented a declination with continuous addition of the eluent. A sharp drop occurred in 60 min indicating a high elution rate in this period. The outlet phosphate concentration was found to be 94.06 mg/L after passing 7.0% HCl solution in column for 10 min and was near four times more than that of the initial concentration (25.00 mg/L), which indicated that the HCl solution could be a candidate as a highly effective eluent for phosphate in the batch system. The concentration of eluent could be reduced below 10% of the initial elution concentration in 100 min. A less regeneration time of the U-D-Na was achieved. Besides, phosphate attached on the column was cleaned off almost within 180 min.

**Breakthrough curves of the column after three time cycles**

Figure 6 depicts the breakthrough curves that the column of U-D-Na regenerated with HCl solution undergone three consecutive phosphate adsorption cycles to evaluate its reusability. It is clear that the breakthrough time did not change too much after being regenerated three times in the experiments. As depicted in Fig. 6, along with the increase in cycle times (1, 2, and 3 cycles) of regeneration, the breakthrough time (30, 20, and 20 min) decreased slightly. However, the removal efficiency was almost unchanged, and high adsorption efficiency was remained for phosphate compared to the first and

![Graph showing breakthrough curves](image)

**Table 4** Comparison of the dynamic adsorption parameters for phosphate of various adsorbents

| Adsorbents    | $C_0$ (mg/L) | $q_e$ (mg/g) | Average removal rate (%) | Reference       |
|---------------|--------------|--------------|--------------------------|-----------------|
| Zeolite       | 0.00–50.00   | 0.13         | <30                      | Jia et al. (2011) |
| GAC           | 0.00–50.00   | 0.33         | 33                       | Jia et al. (2011) |
| Steel slag    | 2.50–5.00    | 0.61         | Average of 24%           | Wang et al. (2020) |
| Zr-CBt        | 2.00–4.00    | 0.85         | -                        | Xu et al. (2021)  |
| PMC-Fe/C-B    | 5.00–20.00   | -            | 78                       | Li (2018)        |
| Ca-B          | 4.00–8.00    | <0.60        | -                        | Qian et al. (2018) |
| Fe/C composite| 5.00–30.00   | 3.70         | -                        | Liu et al. (2018) |
| U-D-Na        | 10.00–20.00  | 1.55         | 50                       | Present study    |
two times. A declination of breakthrough time might be ascribed to the damage of binding sites in column regeneration process due to physical or chemical interaction. According to the result of the breakthrough performance shown in Fig. 6, the U-D-Na was expected to be applied as an adsorbent for effective phosphate removal due to low-cost operation and resource-saving.

**Conclusion**

U-D-Na was found to be a promising candidate adsorbent for successive phosphate removal in this study. The results showed that the breakthrough time was positively correlated with the bed height but inversely correlated with the initial concentration and flow rate. Under the optimum experimental condition, the equilibrium sorption capacity ($q_e$) and the removal rate of U-D-Na for phosphate could reach 1.19 mg/g and 98.14%, respectively. The phosphate-U-D-Na sorption system was found well to be fitted by the Thomas model, with correlation coefficients, $R^2 >0.9000$, under the majority of conditions (5/7), and the surface sorption is the main rate-controlling step. Considerable removal efficiency after three desorption-adsorption cycles could reach nearly 98%. The effectiveness of continuous operations was evidenced successfully by the effective removal of phosphate from water, implying that U-D-Na is an economical and environmentally friendly adsorbent for water treatment.

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**Availability of data and materials** The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

**Declarations**

**Ethics approval and consent to participate** Not applicable.

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