Preparation and evaluation of bis(diallyl alkyl tertiary ammonium salt) polymer as a promising adsorbent for phosphorus removal

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ABSTRACT

Problems associated with water eutrophication due to high phosphorus concentrations and related environmentally safe solutions have attracted wide attention. A novel bis(diallyl alkyl tertiary ammonium salt) polymer, particularly poly(N¹,N¹,N⁶,N⁶-tetraallylhexane-1,6-diammonium dichloride) (PTAHADC), was synthesized and characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance, scanning electron microscopy, mercury intrusion method, and thermogravimetric analysis. The adsorption characteristics in phosphorus were evaluated in dilute solution, and the recycling properties of PTAHDADC were investigated. Results showed that PTAHDADC possessed macropores with a size distribution ranging from 30 to 130 μm in diameter and had 46.52% porosity, excellent thermal stability below 530 K, and insolubility. PTAHDADC could effectively remove phosphorus at pH = 7–11 and had a removal efficiency exceeding 98.4% at pH = 10–11. The adsorption equilibrium data of PTAHDADC for phosphorus accorded well with the Langmuir and pseudo-second-order kinetic models. Maximum adsorption capacity was 52.82 mg/g at 293 K. PTAHDADC adsorbed phosphorus rapidly and reached equilibrium within 90 min. Calculated activation energy Eₐ was 15.18 kJ/mol. PTAHDADC presented an excellent recyclability with only 8.23% loss of removal efficiency after five adsorption–desorption cycles. The morphology and structure of PTAHDADC slightly changed as evidenced by the pre- and post-adsorption of phosphorus, but the process was accompanied by the partial deprotonation of the (–CH₂)₃-NH⁺ group of PTAHDADC. The adsorption was a spontaneous exothermic process driven by entropy through physisorption, electrostatic attraction, and ion exchange. Survey results showed that PTAHDADC was a highly efficient and fast-adsorbing phosphorus-removal material prospective in treating wastewater.

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Introduction

Phosphorus, which is a main nutrient, is an important element of cells and biochemical functional components (Kumar et al., 2018; Zhang et al., 2011; Zhou et al., 2005). However, excessive phosphorus can cause water eutrophication, and such phenomenon has become a serious environmental problem worldwide (Ali and Khairy, 2016; Mahardika et al., 2018; Tu and You, 2014). Water eutrophication is accompanied by the rapid growth of algae, thereby causing the consumption of large amounts of dissolved oxygen in water and subsequently leading to the death of aquatic biology and the deterioration of water degradation (Hamoudi and Belkacemi, 2013; Novais et al., 2018). Therefore, excessive phosphorus should be decreased to prevent water eutrophication.

Various methods, such as chemical precipitation (Liu et al., 2011), biological treatment (Zou and Wang, 2016), and adsorption (Liu et al., 2018a; Mahardika et al., 2018), have been developed to remove phosphorus in the past few decades. Chemical precipitation, which is a mature and commonly used method, involves the addition of metal salts, such as Fe, Al, and Ca (Caravelli et al., 2012). Although chemical precipitation is widely used for industrial wastewater treatment, it can lead to large amounts of chemical sludge and related processing problems (Antunes et al., 2018; Pratt et al., 2012). In addition, chemical precipitation is affected by conditions of redox and potential of hydrogen, which cannot be directly controlled in the water treatment of lakes or rivers (Ko et al., 2016). Biological treatment, which is a method that uses microorganisms to remove phosphorus from liquids, has low operating costs and does not consume chemicals (Antunes et al., 2018). However, this method produces sludge, resultant microbes, and concentrated hazardous materials, which can cause safety and environmental risks; moreover, the method insufficiency absorbs phosphorus and thus cannot meet wastewater discharge standards (Zhou et al., 2017). Adsorption, which is a method that uses a functional adsorbent, has increasingly become popular in relation to the abovementioned two methods due to its high efficiency, easy operation, excellent safety and reliability, and wide application range; this method is especially suitable for low-concentration phosphorus-containing wastewater and its deep treatment (Qiu et al., 2018). However, the method has the disadvantages of weak anti-interference ability and dissolution loss for most adsorbents, poor regeneration, and phosphorus recovery. The treatment efficiency, cost, and sludge production of adsorption method are significantly dependent on the adsorbent properties. Although the widely used natural inorganic adsorption materials have wide sources and low price, they have low adsorption capacity and produce large amounts of sludge that cause secondary pollution (Moharami and Jalali, 2013; Jiang et al., 2013). Activated carbon and biochar developed in recent years are other adsorbents widely used in the treatment of phosphorus-containing wastewater, but they also have the problems of low adsorption capacity and large quantity of sludge (Mahardika et al., 2018; Yin et al., 2018). Moreover, these adsorbents are difficult to be modified. All these factors limit their applicability in phosphorus-containing wastewater treatment (Liu et al., 2017). Magnetic nano-iron oxide can separate adsorbents loaded with phosphorus after adsorption, but the resultant adsorbent aggregates and thus reduces adsorption capacity. Furthermore, the magnetic separation of nanoparticles smaller than 15 nm may be ineffective, and the remaining nanoparticles in the waste water may lead to new types of water contamination (Zhu et al., 2018). Recently, some novel composite adsorbents are being developed for the treatment of phosphorus-containing wastewater, such as Fe(III)-doped chitosan and crosslinked Fe(III)-chitosan (Zhang et al., 2018a) and lanthanum-loaded carbomethyl konjac glucomannan microspheres (Zhang et al., 2018b). However, these materials have low adsorption capacities, relatively complicated synthesis process, and high cost. Given that functional water-insoluble polymer adsorbent has function and structure that can be designed depending on the characteristics of adsorbate, it is the promising development direction of novel high-efficiency adsorbents for phosphorus-containing wastewater. However, to our best knowledge, except poly(p-phenylenediamine) for the removal of Cr(VI) (Mdlalose et al., 2017) and poly[(2-methacyloyloxy) ethyl] trimethylammonium chloride) for the removal of As(V) (Morales et al., 2016), synthesized functional polymer adsorben- ts for the treatment of phosphorus-containing wastewater have been rarely reported. With the increasingly strict emission standards and the increasingly scarce phosphorus resources, the removal efficiency of phosphorus from wastewater and the recovery of phosphorus should be improved (Qiu et al., 2018). Therefore, new adsorbing materials that are highly adsorbent, low cost, easy to recycle, and environmental friendly (e.g., cause minimal secondary pollution) should be energetically developed.

In this study, a novel bis(diallyl alkyl tertiary ammonium salt) polymer, particularly poly[N,N,N′,N′′,N′′′-tetraallylhexane-1,6-diammonium dichloride] (PTAHADC), was synthesized. Then, its structure was characterized through Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR) spectroscopy, scanning electron microscopy (SEM), mercury intrusion method, and thermogravimetric analysis. The adsorption behavior of PTAHADC toward phosphorus under different conditions, such as pH value, initial phosphorus concentration, contact time, and temperature, were systematically investigated. The related thermodynamic and kinetic parameters were obtained. The adsorption mechanism was evaluated through SEM, element mapping, FT-IR, and X-ray photoelectron spectroscopy (XPS). The results show that PTAHADC has excellent adsorption performance for phosphorus. Therefore, PTAHADC is a promising adsorbing material for treating phosphorus-containing effluent.

1. Experimental

1.1. Materials

Diallylamine, 1,6-dibromohexane, 2,2′-Azobis(2-methylpropionamide) dihydrochloride (AIBA), potassium carbonate, hydrochloric acid, sodium hydroxide, and potassium phosphate monobasic were obtained from commercial sources (Appendix A). All chemical reagents were of analytical grade and used directly as purchased without any further purification. Deionized water was used in the experiments.
1.2. Preparation of PTAHDADC

The synthetic route of PTAHDADC is shown in Fig. 1. In preparing the materials, diallylamine (49.57 g, 0.5 mol), 1,6-dibromohexane (49.78 g, 0.2 mol), and K₂CO₃ (42.31 g, 0.3 mol) were first added to deionized water (100 mL) and reacted at 33.15K for 6 hr under vigorous stirring. Then, the mixture was separated and the organic phase was distilled under −0.1 MPa. The fractions volatilized at 453.15–458.15K, namely, N₁,N₁,N₆,N₆-tetraallylhexane-1,6-diamine (TAHDA, 47.45 g, 0.17 mol, 85% yield), were collected. Subsequently, 8.0 mol/L HCl was added dropwise to the TAHDA until the pH was approximately equal to 6. After evaporation and concentration, the monomer solution of N₁,N₁,N₆,N₆-tetraallylhexane-1,6-diammonium dichloride was obtained (TAHDADC, 58.00 g, 99% yield). Thereafter, TAHDADC at a concentration of 3.6–4.5 mol/L was degassed with nitrogen for 30 min and initiated by AIBA (0.4–0.6 g) and polymerized for 6 hr at 33.15K. The final product (i.e., PTAHDADC) was acquired by washing three times with deionized water and drying to a constant weight under vacuum at 33.15K (57.40 g, 99% yield). The detailed procedures are shown in Preparation procedure of PTAHDADC in Appendix A.

1.3. Characterization

The FT-IR spectra of TAHDA, TAHDADC, PTAHDADC, and phosphorus-loaded PTAHDADC were recorded in a Nicolet 6700 FT-IR spectrophotometer (Thermo Fisher Co., America) using the KBr particle method. The ¹H NMR spectra of TAHDA, TAHDADC, and PTAHDADC were recorded using an AVANCE II superconductive NMR spectrometer (500 MHz, Bruker Co., Germany). The pore size distribution and porosity of PTAHDADC were measured by an AutoPore IV 9510 (Micromeritics Instrument Co., USA). Thermogravimetric analysis was conducted using a STA 449 F3 Jupiter thermal gravimetric analyzer (NETZSCH, Germany) at 10°C/min heating rate under N₂ atmosphere. The change in morphology of PTAHDADC corresponding to pre- and post-adsorption was observed using a SU8020 field-emission SEM (Hitachi Co., Japan). A SEM-mapping of PTAHDADC post-adsorption was performed to explore the adsorption behavior of phosphorus onto PTAHDADC, and the XPS spectra of PTAHDADC at pre- and post-adsorption were investigated by Thermo ESCALAB 250Xi XPS (Thermo Electron, USA) with C1s peak at 284.8 eV as a reference.

1.4. Adsorption experiments

Batch experiments were performed to evaluate the performance of PTAHDADC toward phosphorus. The stock phosphorus solution (1000 mg/L) was prepared by dissolving anhydrous KH₂PO₄ in deionized water and diluted to a pre-determined concentration before utilization. After 50 mL of a certain amount concentration of phosphorus solution was added to a series of 100 mL conical flasks, the initial pH of each phosphorus solution was adjusted to the desired value by using a 1 mol/L HCl or NaOH solution. Then, an amount of PTAHDADC was added to the flasks and shaken for a certain time under specific conditions. Thereafter, the adsorption solution was filtered using a membrane filter (0.45 μm, Shanghai Peninsula Industrial Co., China). The concentration of residual phosphate in the filter liquor was analyzed by ammonium molybdate spectrophotometry. The average of three adsorption experiments was used for experimental analysis. The detailed test methods and procedures are shown in Adsorption experimental details in Appendix A.

1.5. Regeneration investigation

The regenerability of PTAHDADC was conducted following consecutive adsorption cycles. In each cycle, 250 mL of 10 mg/
L simulated phosphorus solution was adsorbed by PTAHDADC for 4 hr at pH = 10 and 293K. Then, the PTAHDADC was separated using a membrane filter, eluted in 0.1 mol/L NaOH for 6 hr, and regenerated in 0.1 mol/L HCl for another 6 hr. The adsorbing materials were washed and dried at 60°C and reused as the adsorbent for phosphorus adsorption for another four cycles under the same experimental conditions (Regeneration experimental details, Appendix A).

2. Results and discussion

2.1. Characterization of PTAHDADC

The FT-IR spectra of TAHDA, TAHDADC, and PTAHDADC are shown in Fig. 2.

Fig. 2a shows that the weak absorption peak at 3076 cm$^{-1}$ can be ascribed to the stretching vibration of C=C=H in TAHDADC, and the corresponding in-plane and out-of-plane bending vibrations are apparent at 1417, 995, and 920 cm$^{-1}$ (El-hoshoudy, 2018; Gao et al., 2018; Qiao et al., 2012; Wang et al., 2019). The peaks near 2780–2520 cm$^{-1}$ (A) and 660–520 cm$^{-1}$ (B), which can be attributed to the stretching vibration and out-of-plane bending vibration of N–N of (–CH$_2$)$_2$N–H in TAHDADC, thereby leading to easy adsorption of water. Thus, a broad absorption peak presents at 3433 cm$^{-1}$, which can be attributed to the stretching vibration of the –N–H group of TAHDADC and the O–H group of water. Simultaneously, two wide peaks appear near 2780–2520 cm$^{-1}$ (A) and 660–520 cm$^{-1}$ (B), which can be attributed to the stretching vibration and out-of-plane bending vibration of N–H of (–CH$_2$)$_2$N–H (El-hoshoudy, 2018; Gao et al., 2018; Wang et al., 2019), respectively. Correspondingly, the peak at 1642 cm$^{-1}$ assigned to the bending vibration of O–H of water in tested samples and that at 1446 cm$^{-1}$ assigned to the bending vibration of –CH$_2$– in H–N$^+$–CH$_2$–CH$_2$ have enhanced. The enhancement of peak at 1642 cm$^{-1}$ is due to its easy adsorption of water after protonation, and the enhancement of peak at 1446 cm$^{-1}$ may be attributed to the induction effect that enhances the polarity of the groups. After the polymerization of TAHDADC (PTAHDADC, Fig. 2c), the peaks near 3079, 1702, 1420, and 1000–910 cm$^{-1}$, which represent the infrared vibration of –CH=CH$_2$ in TAHDADC, have disappeared. This phenomenon indicates that TAHDADC has been polymerized. The wide peaks near 2780–2520 cm$^{-1}$ (A) remain apparent in Fig. 2c, and those at 660–520 cm$^{-1}$ (B in Fig. 2b) become distinct at 619 and 581 cm$^{-1}$ (B in Fig. 2c). These findings can be explained by the presence of the (–CH$_2$)$_2$N–H group in PTAHDADC. Therefore, PTAHDADC has been successfully synthesized.

The $^1$H NMR spectra of TAHDADC, TAHDADC, and PTAHDADC are shown in Fig. 3A. As shown in Fig. 3A(1) (CDCl$_3$ as solvent), the characteristic peaks (δ, ppm) of TAHDADC are attributed to the following: 1.233–1.332 (m, 4H, N–CH$_2$–CH$_2$–, a), 1.387–1.495 (m, 4H, N–CH$_2$–CH$_2$–, b), 2.365–2.423 (t, 4H, N–CH$_2$–CH$_2$–CH$_2$–, c), 3.045–3.102 (d, 8H, N–CH$_2$–CH$_2$–, d), 5.075–5.204 (m, 8H, =CH$_2$, f). Fig. 3A(2) (TAHDADC, D$_2$O as solvent) shows that, after the protonation of TAHDADC to PTAHDADC, the peaks of NH$^+$–CH$_2$–CH$_2$–NH$^+$ (Figure 3A(1)) remain distinct at 5.407–5.204 ppm (2H, =CH$_2$). The peaks at 1.332 (m, 4H, N–CH$_2$–CH$_2$–) and 3.045–3.102 (d, 8H, N–CH$_2$–CH$_2$–) keep the same. In addition, the peak of NH$^+$–CH$_2$–CH$_2$–NH$^+$ (Figure 3A(1)) has evidently shifted to low field (b$'$, c$'$, d$'$ in Fig. 3A(2)), the closer the groups get, the more significant the chemical shift is. These phenomena may be due to the induction effect of –NH$^+$ after protonation. Similarly, the peaks of =CH$_2$ (5.407–5.552, m, 8H) have evidently shifted to low field (e$'$ in Fig. 3A(2)), which may be attributed to the strong attraction to the π-electron cloud of C=C. Nevertheless, the peaks of NH$^+$–CH$_2$–CH$_2$–CH$_2$–NH$^+$ (5.723–5.885, m, 4H, f) keep the same. The reason may be attributed to that the induction effect of –NH$^+$ reduces the electron cloud of –CH$_2$–, whereas the strong attraction to the π-electron cloud of C=C increases the electron cloud of –CH=CH$_2$. As a result, the electron cloud of –CH$_2$– keeps the same. In addition, the peak of –NH$^+$ has presented at 7.049–7.157 (s, 2H, g$'$) due to the protonation of (–CH$_2$)$_2$N. As shown in Fig. 3A(3) (PTAHDADC, DMSO-d$_6$ as solvent), the characteristic peaks of PTAHDADC have changed.

Fig. 2 – FT-IR spectra of (a) TAHDADC, (b) TAHDADC, (c) PTAHDADC, and (d) phosphorous-loaded PTAHDADC.
substantially after TAHDADC polymerization. The peaks at 1.020–1.093 (m, 8H) and 2.044–2.106 (s, 4H) are assigned to –CH–CH2– (a”) and –CH–CH2– (d”) protons of the main chain of PTAHDADC, respectively. The peaks at 1.193–1.363 (m, 4H), 1.475–1.789 (m, 4H), and 3.175–3.523 (s, 4H) are assigned to N(CH2)3CH2–CH2–CH2–CH2–C= (b’), N(CH2)3CH2–CH2–CH2–C= (c’), and N(CH2)3CH2–CH2–CH2–C= (e”) protons of the side chain of N(CH2)3CH2–CH2–CH2–CH2–N+, respectively. The –CH2– of pyrrole ring is close to the N+–H group the same as the –CH2– of the side chain N(CH2)3CH2–CH2–CH2–CH2–N+. Thus, the peaks of them appear nearly at the same position as that of N(CH2)3CH2–CH2–CH2–CH2–N+. Hence, the peaks at nearly 41.35 (d”) are attributed to the C atom of the –CH2– of the side chain N(CH2)3CH2–CH2–CH2–CH2–N+. The 13C spectrum of PTAHDADC was not obtained through solid NMR was used to measure its 13C spectrum, as shown in Fig. 3B(3). The peaks at approximately 24.45 can be assigned to the C atom of the main chain of –CH2–CH2– (a”) and the C atoms of the side chain of NH–CH2–CH2–CH2– (b” and c”); the peaks at nearly 41.35 (d”) are attributed to the C Atom of –CH2– (d”). Moreover, the peak of N+–H appears at 7.111–7.199 (s, 2H, f”). Compared with the peaks in Fig. 3A(2), the peaks near 5.000–5.000 ppm that represent CH2 = CH have disappeared after TAHDADC polymerization, and the positions and shapes of the other peaks have changed significantly, which indicates that TAHDADC has been completely polymerized.

Fig. 3B shows the 13C NMR spectra of TAHDA, TAHDADC, and PTAHDADC. As shown in Fig. 3B(1) (CDCl3 as solvent), the characteristic peaks (δ, ppm) of TAHDA are attributed to the following: 26.741–26.859 (N–CH2–CH2–CH2–, a), 27.355–27.455 (N–CH2–CH2–CH2–, b), 53.185–53.316 (N–CH2–CH2–CH2–, c), 56.705–56.903 (N–CH2–CH2–, d), 117.206–117.435 (=CH2, e), and 136.642–136.835 (N–CH2–CH2–CH2–, f). As shown in Fig. 3B(2) (TAHDADC, D2O as solvent), the characteristic peaks are shifted to different degrees after TAHDADC is protonated to TAHDADC: the peaks assigned to the C of NH–CH2–CH2–CH2– (a”) shift to 23.056–23.124, those assigned to the C of NH–CH2–CH2–CH2– shift to 25.106–25.255 (b’), those due to the C of NH–CH2–CH2–CH2– shift to 31.764–31.866 (c’), and those attributed to the C of NH–CH2–CH2–CH2– shift to 54.555–54.802 (d’). These peaks have shifted to high field. This result may be due to that the local electric field generated by the protonated tertiary amine groups (–CH2)3N+–H causes the polarization of the adjacent C–H bond (i.e., electric field effect), which increases the density of the electron cloud outside the nucleus of the corresponding C atom. As a result, the chemical shift is decreased and shifted to high field. Unlike the above-mentioned results, the peaks assigned to the C of NH–CH2–CH2–CH2– (e”) shift to low field to 125.456–125.651. By contrast, those assigned to NH–CH2–CH2–CH2– (f”) shift to high field to 126.406–126.566. This result is mainly due to that the induction effect generated by the protonated tertiary amine groups (–CH2)3N+–H drifts the π-electron of C=C to the C atom of –CH=CH2 and away from the C atom of –CH=CH2. This phenomenon decreases the electron cloud of the C atom of –CH=CH2 and increases that of –CH=CH2. Moreover, the chemical shift of C atom becomes evident because the increases of electron cloud density of the C atom of –CH=CH2 caused by the induction effect and electric field effect are superimposed.

The 13C spectrum of PT AHDADC was not obtained through liquid NMR due to its small solubility in DMSO-d6. Thus, the solid NMR was used to measure its 13C spectrum, as shown in Fig. 3B(3). The figure shows that the peak position, intensity, and shape have changed greatly. The spectrum peaks are greatly broadened due to the existence of multiple interactions in solid NMR. The peaks at approximately 24.45 can be assigned to the C atom of the main chain of –CH2–CH2– (a”) and the C atoms of the side chain of NH–CH2–CH2–CH2– (b” and c”); the peaks at nearly 41.35 (d”) are attributed to the C Atom of –CH2– (d”). Moreover, the peak of N+–H appears at 7.111–7.199 (s, 2H, f”). Compared with the peaks in Fig. 3B(2), the peaks at 120–130 assigned to the C atoms of –CH=CH2 have disappeared, which further confirms the complete polymerization of TAHDADC.
The morphology of the as-prepared PTAHDADC is shown in Fig. 4a. The PTAHDADC appears with coral-like morphological features and a rough and irregular surface, which enables the phosphorous ions to undergo adsorption. Although PTAHDADC shows porous morphology, its specific surface area and pore size distribution could not be determined through the BET and BJH methods using N2 (77K), Ar (87K), and CO2 (273K) as adsorptive gas. The reason may be that the pore size is beyond the range of measurement. Therefore, the mercury intrusion method was applied to determine the pore size distribution of PTAHDADC, and the results are shown in Fig. 4b. The figure shows that the pores in PTAHDADC mainly belong to macropores. The pore size distribution is relatively centralized and ranges from 30 to 130 μm and concentrates at 63 μm in diameter. The total pore volume and porosity of PTAHDADC are 0.7452 cm3/g and 46.52%, respectively. The abundant macropores and high porosity provide abundant active sites for adsorption.

The thermogravimetric curve of PTAHDADC is shown in Fig. 4c. The total weight loss of PTAHDADC is approximately 8.36% between 323 and 530K, which may be attributed to the release of adsorbed water and impurities. Although the temperature is between 530 and 750K, the weight loss increases rapidly to 73.43%, which may be due to the thermal decomposition of PTAHDADC. When the temperature is above 750K, the weight is the same, thereby indicating the complete thermolysis of PTAHDADC. This result indicates that PTAHDADC is very stable below 530K, which is sufficient for the adsorption of phosphorus in aqueous solution.

PTAHDADC is found to be insoluble in water or any other acidic/alkaline solution, thereby indicating that it has low solubility and good chemical stability and is suitable for phosphorus adsorption in various environments.

2.2. Adsorption performance of PTAHDADC toward phosphorus ion

2.2.1. Effect of PTAHDADC dosage on the removal efficiency
The effect of PTAHDADC dosage on the removal efficiency (R) of the phosphorus ions is shown in Fig. 5. In the figure, R increases rapidly with the increase in PTAHDADC dosage at amounts below 1000 mg/L. After the dosage reaches 1200 mg/L, R stabilizes and slowly rises with the continuous increase in dosage. Consequently, the appropriate dosage of PTAHDADC is 1200 mg/L, and the removal efficiency can reach 89.09%.

2.2.2. Effect of initial pH on the removal efficiency
The species of phosphorus ion, the surface charge of the adsorbent, and the degree of protonation are affected significantly by the initial pH; thus, the initial pH is regarded as an important factor in the adsorption process (Chen et al., 2012; Zhang et al., 2018a; Li et al., 2019). The initial pH of the tested phosphorus solution was controlled at the range of 1.0–13.0 with 1 mol/L HCl or NaOH solution to investigate the effect of pH on removal efficiency, and the PTAHDADC dosage was 1200 mg/L. The result is shown in Fig. 6.

The removal efficiency (R) of the phosphorus ions is closely related to the initial pH of the tested solution. The R value of phosphorous is less than 56% in the pH range of 1–3 and is abruptly increased from 55.72% to 81.21% in the pH range of 3–4. Subsequently, R slowly increases from 81.21% to 98.72% with the increase in pH from 4 to 11. However, R abruptly decreases from 98.72% to 54.23% between the pH values of 11 and 13. Notably, R exceeds 98% when the pH is between 10 and 11. In general, the adsorption of charged adsorbent toward ion
species is primarily caused by their electrostatic attraction (Li et al., 2019; Qiao et al., 2019). In PTAHDADC-phosphorus adsorption systems, PTAHDADC has high positive charge density due to its positive charge at every six –CH₂ (or –CH₃) units (Fig. 1). The electrostatic attraction between the positively charged protonated tertiary amine groups of PTAHDADC and the negatively charged phosphorus ions plays a vital role in the adsorption process (Zhang et al., 2018a, 2018b). Therefore, the above-mentioned results may be explained by the effects of pH on phosphorus ion species and protonation degree and surface charge of PTAHDADC (Liu et al., 2012).

The oxygen-containing anions of phosphorus exist as different species, as in the case of PO₄³⁻, HPO₄²⁻, H₂PO₄⁻ and H₃PO₄ with dissimilar pH values. The transformation of species can be described using Eqs. (1)–(3) (Xia et al., 2017; Zhang et al., 2011; Zhou et al., 2005) and Fig. 7.

\[
\begin{align*}
H_3PO_4 & \rightleftharpoons H^+ + H_2PO_3^- \quad K_1 = 2.15 \\
H_2PO_3^- & \rightleftharpoons H^+ + HPO_2^- \quad K_2 = 7.20 \\
HPO_2^- & \rightleftharpoons H^+ + PO_3^- \quad K_3 = 12.33
\end{align*}
\]

The major species of phosphorus is H₂PO₃⁻ in the pH range of 3–7, and it transforms into HPO₄²⁻ as pH varies from 7 to 11. When pH is >11, the major species gradually transform into PO₄³⁻ (Rodrigues and Silva, 2010; Kilpimaa et al., 2015; Li et al., 2019). In addition, the protonation degree and the surface charge of PTAHDADC vary with the change in pH. Several studies have verified that the positively charged protonated tertiary amine groups can stably exist at pH below 9.7 (Hernández-Olivares et al., 2017; Kozmai et al., 2018; Yao et al., 2015). Therefore, the surface of PTAHDADC is positive when pH is <9.7 mainly because of strong electrostatic attraction to phosphorus anions. When pH is <2, the electrostatic attraction between phosphorus and PTAHDADC is weak because the main species take the form of neutral H₃PO₄ (Zhang et al., 2018b), thereby resulting in low adsorption capacity. When pH is increased from 2 to 9.7, the phosphorus species gradually transform into negatively charged H₂PO₄⁻ and HPO₄²⁻ (Chen et al., 2012). This phenomenon increases the electrostatic attraction between PTAHDADC and negatively charged phosphorus ions, and thus increases adsorption capacity. When pH is increased from 9.7 to 11, the protonated tertiary amine groups of PTAHDADC gradually and partially lose H⁺ (Kozmai et al., 2018; Yao et al., 2015), but the H₂PO₄⁻ converts into HPO₄²⁻. This phenomenon results in strong electrostatic attraction between PTAHDADC and negatively charged phosphorus ions, and adsorption capacity reaches the maximum at rates higher than 98%. When pH is >11, the protonated tertiary amine groups rapidly lose H⁺ until they become neutral at pH = 12 (Yao et al., 2015), but the phosphorus ion species transform into negatively charged PO₄³⁻. Then, electrostatic attraction abruptly decreases, which leads to the sharp decrease in adsorption capacity from 98.72% to 58.91%. The R value of the phosphorus ions at pH = 13 (54.23%) approximates that at pH = 2 (52.54%), as shown in Fig. 6. This similarity indicates that the adsorption of phosphorus ions is attributed to the same mechanism. Comparison of the existing species of phosphorus ions and the ionization states of PTAHDADC at pH = 2 and pH = 12 reveals the absence of electrostatic attraction between PTAHDADC and phosphorus species at the two pH conditions. In such scenarios, the adsorption mainly originates from the physisorption caused by the surface residual force field of PTAHDADC due to its high porosity (Fig. 4b). The existing species of phosphorus ions, the ionization state of PTAHDADC, and the adsorption between PTAHDADC and phosphorus ions at different pH values are shown in Fig. 8.

2.2.3. Adsorption isotherms

The adsorption isotherms of PTAHDADC toward phosphorus ions at 293, 303, 313, and 323K are shown in Fig. 9a. The optimized PTAHDADC dosage of 1200 mg/L was added to phosphorus-simulated solutions with the pH values adjusted to 10, and the contact time was 4 hr.
Fig. 9a shows that, at the same temperature, the amount of phosphorus adsorbed on PTAHDADC increases rapidly with increase in initial concentration when phosphorus concentration is less than 100 mg/L (fifth experimental point). Then, the amount stabilizes when the concentration exceeds 100 mg/L. Moreover, the adsorption isotherm decreases with the increase in temperature. This condition indicates the prevalence of exothermic adsorption.

The Langmuir and Freundlich models were used to fit the experimental data in Fig. 9a. The fitting parameters are presented in Appendix A Table S1. The correlation coefficients ($R^2$) fitted to the Freundlich model are significantly lower than those fitted to the Langmuir model, which indicates that the adsorption process complies more effectively with the latter. The maximum adsorption capacity of PTAHDADC toward phosphorus in the Langmuir adsorption model is 52.82 mg/g at 293K, which approximates the experimental value ($q_{m,exp}$) but is considerably higher than those of common adsorbents reported in literature (Table 1). In addition, the values of fitting parameter $n$ in the Freundlich model are all >1, which indicate that the adsorption of PTAHDADC toward phosphorus is a favorable adsorption process (Chitrakar et al., 2006). The nature of adsorption described above indicates that the cationic group of $\text{(-CH}_2\text{)}_3\text{N}^+\text{H}$ acts as an important adsorption active site for the binding of negatively charged phosphorus ions through electrostatic interaction. In particular, the phosphorus ions adsorbed on PTAHDADC inevitably exchange with the

Fig. 8 – Ionization state of PTAHDADC and phosphorus ion in the solution with various pH values and corresponding electrostatic attraction and adsorption.

Fig. 9 – (a) Adsorption isotherms of PTAHDADC toward phosphorus; (b) $\ln K_P$ versus $1/T$ for phosphorus adsorption on PTAHDADC.
counterion Cl\(^{-}\) of PTAHDADC. Therefore, the adsorption process also involves ion exchange.

Subsequently, the distribution coefficients (\(K_p\)) of the phosphorus ions in the PTAHDADC-adsorbed phosphorus ion system at different temperatures were calculated using Appendix A Eq. (S5). Then, the \(\ln K_p - (1/T)\) diagram was plotted and linearly fitted (Fig. 9b). Given the intercept and slope of the fitting line, the adsorption thermodynamic parameters of \(\Delta S\), \(\Delta H\), and \(\Delta G\) were calculated using Appendix A Eqs. (S6)–(S7). The negative \(\Delta H\) (–12.377 kJ/mol) and positive \(\Delta S\) (6.991 J/(mol·K)) values indicate that the adsorption is an exothermic process with naturally increasing entropy. The \(\Delta G\) values are all negative at 293K (–14.409 kJ/mol), 303K (–14.517 kJ/mol), 313K (–14.593 kJ/mol), and 323K (–14.608 kJ/mol), which indicate a spontaneous adsorption process. Therefore, the adsorption process of PTAHDADC toward phosphorus ions is exothermic and has increasing entropy and spontaneous characteristics.

2.2.4. Adsorption kinetics

Fig. 10a shows the change in adsorption amount \(q_t\) of PTAHDADC toward phosphorus with contact time \(t\). The experimental data in Fig. 10a were fitted using the pseudo-first-order and pseudo-second-order models. The kinetic fitting parameters are presented in Appendix A Table S2.

As shown in Fig. 10a, the adsorption amounts \(q_t\) rapidly increase within 40 min after the addition of PTAHDADC, moderately increase in the range of 40–60 min, and stabilize beyond 90 min. Therefore, the equilibrium time is 90 min. All the correlation coefficients (\(R^2\)) fitted by the pseudo-second-order kinetic model exceed 0.988, which are remarkably higher than those by the pseudo-first-order kinetic model. In addition, the fitted values are extremely close to the experimental ones \(q_{e,exp}\) (Fig. 10a and Appendix A Table S2). These findings indicate that the adsorption of PTAHDADC toward phosphorus complies well with the pseudo-second-order kinetic model. The short time for adsorption equilibrium indicates that the adsorption of phosphorus by PTAHDADC is rapid, which is valuable in practical applications.

The logarithm of the secondary adsorption rate constant (\(\ln k\)) (Appendix A Table S2) is plotted against the reciprocal of temperature 1/T, as shown in Fig. 10b. The values of \(\ln k\) at different temperatures linearly respond to 1/T, which indicates that the effect of temperature on adsorption rate agrees with
well with the Arrhenius equation (Appendix A Eq. (S11)). The activation energy \( E_a \) of the adsorption process is calculated as 15.18 kJ/mol from the slope of the fitted curve on the basis of Appendix A Eq. (S11). The negative value of \( E_a \) indicates that low temperatures favor phosphorus ion removal by adsorption onto PTAHDADC, and the adsorption process is exothermic in nature.

### 2.3. Regenerability of PTAHDADC

Table 2 shows that the removal efficiency \( R \) of phosphorus by PTAHDADC gradually decreases as the number of reuse cycles increase. The removal efficiency of phosphorus by PTAHDADC is still up to 89.12% after five adsorption–desorption cycles with a decrease of only 8.23%, which demonstrates that PTAHDADC has excellent elution and regeneration performance. The elution and regeneration of PTAHDADC involve the deprotonation and protonation of the active groups of \((-\text{CH}_{2})_3\text{N}^+-\text{H}\). Elution of phosphorus ion is realized by deprotonation to remove electrostatic attraction between the active groups and phosphorus ion, and the adsorption ability can be recovered by protonation of \((-\text{CH}_{2})_3\text{N}\). The results indicate that PTAHDADC has promising application in the treatment of phosphorus-containing wastewater.

### 2.4. Adsorption mechanism

SEM, SEM-mapping, FT-IR, and XPS analysis were performed to investigate the adsorption mechanism.

#### 2.4.1. SEM and SEM-mapping

The surface morphology of PTAHDADC after adsorption is shown in Fig. 11a, whereas the particularized SEM-mappings are shown in Figs. 11b–e. The surface of PTAHDADC is evidently smoother after the adsorption of phosphorus ions compared with those shown in Fig. 4a. However, the basic shape and size of PTAHDADC change slightly only, which indicates that the basic structure of PTAHDADC is relatively stable. The SEM-mappings show that the main elements of PTAHDADC after adsorption are C, O, N, Cl, and P, which imply that the phosphorus in the solution has been transferred to PTAHDADC. The P mapping is closely related to the C, O, and N mappings, and the P elements are denser than those of C and N. Therefore, considerable phosphorus species has been immobilized on PTAHDADC.

#### 2.4.2. FT-IR analysis

The FT-IR spectra of the phosphorus-loaded PTAHDADC are shown in Fig. 2d. Compared with those in Fig. 2c, the peaks of the phosphorus-loaded PTAHDADC near 3430, 2932, 2860, 1644, 1461, 1386, 937, and 730 cm\(^{-1}\) and at the range of 650–560 cm\(^{-1}\) (B\(^{\text{v}}\)) are nearly identical except for the small changes in peak position or intensity. After loading with phosphorus, the peaks at the range of 1000–1300 cm\(^{-1}\) have changed significantly. The peaks of C–N shift near 1121, 1222, and 1252 cm\(^{-1}\), particularly the new wide and strong peaks present at 1054 cm\(^{-1}\). Moreover, the wide peaks at 2780–2520 cm\(^{-1}\) (A\(^{\text{v}}\)) have disappeared. These changes may be ascribed to the interaction of the phosphorus species with the functional group \((-\text{CH}_{2})_3\text{N}^+-\text{H}\) of PTAHDADC. Meanwhile, the peaks at 1054 and 524 cm\(^{-1}\) can be attributed to the antisymmetric stretching of PO\(^4^+\) and the P–O bending vibration of PO\(^3^-\), respectively, which indicate that phosphate has been adsorbed on PTAHDADC (Novais et al., 2018; Yan et al., 2017; Zhao et al., 2019; Zhou et al., 2018).

#### 2.4.3. XPS analysis

The XPS spectra of bare PTAHDADC and phosphorus-loaded PTAHDADC were analyzed to gain additional insights into the adsorption process and mechanism of phosphorus toward PTAHDADC. The full-range values of bare PTAHDADC and phosphorus-loaded PTAHDADC are shown in Fig. 12a. The results show that carbon (Cls at 284.8 eV), oxygen (O1s at 531.43 eV), nitrogen (N1 s at 400.95 eV), phosphorus (P2p at 133.89 eV), and chlorine (Cl2p at 197.5 eV) exist in the broad-scan spectra of bare PTAHDADC and phosphorus-loaded PTAHDADC. The high-resolution spectra collected from the main regions of N1 s and P2p are shown in Figs. 12b–d. After phosphorus is adsorbed, the P2p region of PTAHDADC shows two peaks at 133.5 and 132.7 eV, which correspond to P=O and P–O of pentavalent P, respectively (Novais et al., 2018; Zhao et al., 2019; Zhou et al., 2018). This finding indicates that phosphorus exists on the surface of PTAHDADC. The BE values corresponding to –C–NH\(^+\) and –C–N are 401.1 and 398.8 eV, respectively (Wang et al., 2016; Zhang et al., 2018b). Compared with the ratio of N species at pre- and post-adsorption, –NH\(^+\) decreases from 84.23% to 63.92% and –C–N increases from 15.77% to 36.08%. This phenomena indicate that the protonated tertiary amine groups \((-\text{CH}_{2})_3\text{N}^+-\text{H}\) of PTAHDADC have been deprotonated with the loading of phosphorus on PTAHDADC to a certain extent under adsorption conditions.

#### 2.4.4. Proposed removal mechanism for phosphorus

The results of analysis show that the removal mechanism of PTAHDADC for phosphorus can be expressed as follows. (1) The suspended PTAHDADC involves natural adsorption to a certain extent for the phosphorus species in the solution, that is, physisorption is due to the residual force field and the several surface ions diffused in the solution. (2) The negatively charged species, such as H\(^+\)PO\(_4\)\(^2^-\), HPO\(_4\)\(^3^-\), and PO\(_4\)\(^4^-\), are attracted to the positively charged groups \((-\text{CH}_{2})_3\text{N}^+-\text{H}\) of PTAHDADC through electrostatic interaction. (3) The attracted negatively charged species are exchanged with the counterion Cl\(^-\) of PTAHDADC and appear to be affixed onto the surface of PTAHDADC. This phenomenon indicates the occurrence of ion exchange adsorption. HPO\(_4\)\(^3^-\) species were taken as an example for the removal process and mechanism of PTAHDADC for phosphorus (Fig. 13).

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Regeneration of PTAHDADC from phosphorus adsorption.</th>
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<tr>
<td>Items</td>
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<tr>
<td></td>
<td>0</td>
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<tr>
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<td>Decreasing percent (%)</td>
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Fig. 11 – (a) SEM spectra of phosphorous-loaded PTAHADC; (b) SEM image of phosphorous-loaded PTAHADC and its mapping results for (c) C, (d) O, (e) N, (f) Cl, and (g) P.
Fig. 12 – XPS spectra: (a) full range; (b) P2p; (c) N1 s of PTAHDADC; (d) N1 s of phosphorus-loaded PTAHDADC.

Fig. 13 – Possible process and mechanism of phosphorus removal based on analyses.
3. Conclusions

A novel coral-like adsorbing material (i.e., PTAHDADC) was successfully prepared from diallylamine, 1,6-dibromohexane, potassium carbonate, hydrochloric acid, and AIBA. PTAHDADC possessed macropores with a pore size distribution ranging from 30 to 130 μm concentrating at 63 μm in diameter. The total pore volume and porosity of PTAHDADC were 0.7452 cm³/g and 46.52%, respectively. In addition, PTAHDADC presented excellent thermal stability below 530K and insolubility.

PTAHDADC showed excellent adsorption performance for phosphorus species at the wide pH range of 7–11, especially at pH = 10–11, and the removal efficiency for phosphorus exceeded 98.4%. The data on the isothermal adsorption equilibrium of PTAHDADC for phosphorus were in good agreement with the Langmuir model. The maximum adsorption capacity derived from the Langmuir model was 52.82 mg/g at 293K. The adsorption of PTAHDADC toward phosphorus rapidly reached adsorption equilibrium within 90 min, the adsorption kinetics process agreed well the pseudo-second-order kinetic model, and activation energy E_a was calculated to be 15.18 kJ/mol. PTAHDADC possessed excellent recyclability with only 8.23% loss of removal efficiency.

The basic morphology and structure of PTAHDADC slightly changed before and after phosphorus adsorption. However, the adsorption process was accompanied by the partial deprotonation of the (–CH₂)₃NH⁺ group of PTAHDADC. The adsorption of PTAHDADC toward phosphorus species was exothermic, and entropy increased. The process was spontaneous and involved physisorption, electrostatic interaction, and ion exchange. Overall, PTAHDADC is a highly efficient and a rapidly adsorbing material and has wide application potential in the removal of phosphorus in wastewater.

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Appendix A. Supplementary data

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References


