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Porous Pr(OH)$_3$ nanowires as novel high-performance adsorbents for phosphate removal

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ABSTRACT:

Porous Pr(OH)$_3$ nanowires (NWs), which were synthesized via an electrodeposition approach, were utilized in phosphate removal for the first time. Our prepared porous Pr(OH)$_3$ NWs exhibited superior phosphate removal performances, due to their large surface area, unique porous structure, and abundant hydroxyl groups as active sites. Their phosphate adsorption equilibrium data were well described by utilizing the Langmuir isotherm model ($R^2 \geq 0.996$), with a maximum phosphate adsorption capacity of 128.96 mg P/g at 25 °C. The thermodynamic study showed that the phosphate adsorption of Pr(OH)$_3$ NWs was a spontaneous and exothermic process. On the other hand, the phosphate adsorption kinetics was well described with the use of the pseudo-second-order model, suggesting the adsorption process be chemisorption. In the pH range of 3.0 – 10.0, the high adsorption capacities of Pr(OH)$_3$ NWs were observed; whilst, the presence of Cl$^-$, HCO$_3^-$, or NO$_3^-$ did not dramatically affect the phosphate uptake. Our experimental results
strongly suggest that the use of porous Pr(OH)$_3$ NWs hold a great potential in achieving highly efficient phosphate removal in practical water treatment.

**Keywords:** Pr(OH)$_3$; Electrodeposition; Nanowires; Porous; Phosphate removal

1. **Introduction**

Phosphate has been considered as one of crucial nutrients to support the growth of many living species in ecosystems. However, an excessive amount of phosphate anions existing in aquatic environment causes a serious eutrophication problem and subsequently worsens water quality [1]. Therefore, there is a need to reduce the concentration of phosphate in wastewater before its discharge. So far, a great deal of research effort has been contributed to studying the removal of phosphate from water *via* different approaches [2], such as biological treatment, membrane separation and chemical coagulation/precipitation [3-5]. In particular, adsorption method has been most widely investigated, due to its easy operation, low cost, high removal rate and efficiency, and invulnerability to coexisting pollutants [6-10].

Rare earth oxides and hydroxides are a class of interesting materials. Because of the extraordinarily inherent properties, they have been selected for study in many of practical applications, e.g. optical displays, medical diagnostics, and chemical catalysis [11]. Recent studies have revealed their great potential as prominent materials to efficiently remove a number of pollutants from water, including phosphate anions [11-17]. For instance, our previous study found that La(OH)$_3$ particles exhibited a promising maximum phosphate adsorption capacity, which was 57.8 mg P/g [17]. Our recent work reported the preparation of La(OH)$_3$-doped exfoliated
vermiculite (La-EV); its phosphate uptake was approximately one order of magnitude greater than that of undoped natural exfoliated vermiculite [18]. When used in the secondary-treated wastewater, ~ 98% of the final adsorption capacity of La-EV reached within 10 min; especially after that the phosphate concentration was reduced to < 50 µg P/L [18]. Yang and co-workers synthesized La$_2$O$_3$-loaded SBA-15 mesoporous silica materials, which exhibited a maximum adsorption capacity of 45.6 mg P/g [19]; however, the pure parent SBA-15 material could hardly adsorb phosphate anions. Currently, the development of high-performance phosphate adsorbents consisting of rare earth oxides and/or hydroxides is continuously in progress.

In recent decades, the utilization of one dimensional (1D) nanomaterials, i.e. nanobelts, nanotubes, and nanowires (NWs), with porosity as adsorbents has become an increasing area of research, thanks to their highly accessible surface areas and unique porous structures [12, 20]. In particular, the successful development of electrochemical deposition is believed to make the fabrication of porous 1D nanomaterials to be scalable, cost-effective, and environmental friendly, as compared with other conventional synthetic methods, e.g. high-temperature hydrothermal reaction or hard-templating strategy [11-16, 20-24]. Moreover, this approach can easily and precisely tailor the morphology and structure of resulting materials by varying experimental parameters, i.e. current density, potential, electrolyte, disposition time, etc. [12, 16]. In 2012, Tong’s group reported the electrochemical synthesis of porous 1D rare earth hydroxide, Pr(OH)$_3$, nanomaterials and their application in removing Congo red dye from water [11,12]. The Congo red adsorption capacity of porous Pr(OH)$_3$ NWs was ~ 837 mg/g, which was dramatically greater than that of active carbon, ascribed to their unique structural and chemical properties, e.g. great surface area, special porous structure, and ample hydroxyl groups [12]. More importantly, the environmental
toxicity study on porous 1D Pr(OH)$_3$ NWs suggested they be environmentally friendly adsorbents for practical water treatment [12].

Motivated by our previous work in the field of phosphate adsorption [18, 25-27], we reported the phosphate removal with the utilization of porous 1D Pr(OH)$_3$ NWs, which were fabricated via electrochemical deposition, for the first time herein. Their phosphate adsorption isotherms and kinetics were investigated in detail. Moreover, systematic studies were carried out to investigate the impact of several factors, including contact time, adsorbent dosage, temperature, solution pH and coexisting ion, on their phosphate adsorption performances.

2. Materials and methods

2.1. Preparation of porous Pr(OH)$_3$ nanowires

Our phosphate adsorbents, porous Pr(OH)$_3$ nanowires (NWs), were prepared based on the literature [11, 12]. Typically, the electrodeposition was carried out by utilizing a home-made DJS-292B potential static apparatus in a three-electrode cell, in which a Cu foil, graphite rod and saturated Ag/AgCl electrode were selected as the working, counter and reference electrodes, respectively. Before the electrodeposition, the surface of Cu foil was firstly cleaned by ultrasonication in order of distilled water, ethanol, acetone, and distilled water. Afterwards, it was immersed in a solution, which was consisting of 0.01 M Pr(NO$_3$)$_3$.6H$_2$O (Sinopharm Chemical Reagent Co. Ltd.) and 0.02 M CH$_3$COONH$_4$ (Sinopharm Chemical Reagent Co. Ltd.). The electrodeposition of porous Pr(OH)$_3$ NWs on the Cu foil was completed at the current density and the temperature of 4 mA/cm$^2$ and 70 °C, respectively, in 2 h. Finally, the formed thin film of Pr(OH)$_3$ NWs was scarped from the Cu foil substrate, grinded, and utilized as the adsorbents in
phosphate adsorption studies.

2.2. Material characterization

The morphology and structure of our porous Pr(OH)$_3$ NWs depositing on the Cu foil substrate were examined with the use of field emission scanning electron microscopy (FE-SEM, JSM-6330F) and X-ray powder diffraction (XRD) pattern (Cu K$_\alpha$ radiation, Bruker D8 Advance diffractometer). Meanwhile, the thin film of Pr(OH)$_3$ NWs was scarped from the Cu foil substrate and grinded into fine powders; which were used in the investigations of transmission electron microscopy (TEM, JEM 2010-HR), high-resolution transmission electron microscopy (HRTEM, JEOL SM-6330F), and nitrogen adsorption-desorption measurement (77 K, ASAP 2010, Micromeritics Inc.). Before the nitrogen adsorption-desorption analysis, the powders of porous Pr(OH)$_3$NWs were degassed at 120 °C under vacuum for 12 h.

2.3. Phosphate adsorption studies

In the series of batch phosphate adsorption tests, the fine powders of Pr(OH)$_3$ NWs, scraped from the Cu foil substrate after the electrodeposition, were utilized as the adsorbents. In equilibrium experiments, 0.005 g of as-prepared Pr(OH)$_3$ NWs were added into 50.0 mL of phosphate solution (K$_2$HPO$_4$, Sinopharm Chemical Reagent Co., Ltd) with concentrations varying from 10.0 mg P/L to 100.0 mg P/L. After the sealed polypropylene bottles were then shaken in water bath for 24 h, the solution was filtered through a syringe nylon-membrane filter (pore size of 0.45 µm, Shanghai Minglie Science Technology Co., Ltd.); the phosphate concentration in the filtrate was measured by Optima 2000 DV (Perkin Elmer Inc.).

The amount of phosphate adsorbed on Pr(OH)$_3$ NWs at the equilibrium ($q_e$) was calculated based on Eq. (1),
\[ q_e = \frac{(C_0 - C_e) \times V}{m} \]  \hspace{1cm} (1)

where \( C_0 \) is the initial phosphate concentration in solution (mg P/L); \( C_e \) is the equilibrium phosphate concentration in solution (mg P/L); \( m \) is the mass of the adsorbent added (g); and \( V \) is the volume of phosphate solution (L).

The equilibrium data of phosphate adsorption were explored by using the Langmuir and Freundlich isotherm models, as seen in Eqs. (2) and (3), respectively [28, 29]:

**Langmuir model:**

\[ \frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0} \]  \hspace{1cm} (2)

**Freundlich model:**

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  \hspace{1cm} (3)

where \( C_e \) is the phosphate concentration at equilibrium (mg P/L); \( q_e \) is the corresponding adsorption capacity (mg P/g); \( q_0 \) (mg P/g) and \( K_L \) (L/mg P) are the constants in the Langmuir isotherm model, associated with the capacity and energy of adsorption, respectively; \( K_F \) (L/g) and \( n \) are the constants in the Freundlich isotherm model, associated with the adsorption capacity and intensity, respectively.

In order to examine the thermodynamic nature of the adsorption, three fundamental thermodynamic parameters, e.g. \( \Delta G^\circ \), \( \Delta H^\circ \) and \( \Delta S^\circ \), were calculated. \( \Delta G^\circ \) was estimated based on Eq. (4):

\[ \Delta G^\circ = -RT \ln K_d \]  \hspace{1cm} (4)

where \( R \) is the gas constant, 8.314 J/mol K; \( T \) is the temperature in Kelvin (K); and \( K_d \) is the thermodynamic equilibrium constant of the adsorption. \( K_d \) was determined by plotting \( \ln(q_e/C_e) \) versus \( q_e \) and extrapolating \( q_e \) to zero [30]. \( \Delta H^\circ \) and \( \Delta S^\circ \) were evaluated by using the Van’t Hoff equation, Eq. (5) [31]:
\[
\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (5)
\]

The slope and intercept of the linear plot of \(\ln K_d\) versus \(1/T\) were used to determine the values of \(\Delta H^0\) and \(\Delta S^0\).

In kinetic experiments, 0.005 g of as-prepared Pr(OH)\(_3\) NWs were added in 50.0 mL of 10.0 mg P/L phosphate solution. The sealed polypropylene bottle was then shaken in water bath for 24 h. During that, 1.0 mL of the suspension was withdrawn over a given period of time, which was then filtered through a syringe nylon-membrane filter. The phosphate concentration in the filtrate was measured by using Optima 2000 DV (Perkin Elmer Inc.).

In order to analyze the kinetic mechanism of adsorption, the experimental kinetic data were fitted in the pseudo-first-order and pseudo-second-order models, in Eqs. (6) and (7) [32-36]:

Pseudo-first-order model: \[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)
\]

Pseudo-second-order model: \[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)
\]

where \(q_t\) is the amount of phosphate adsorbed at a given period of time (mg P/g); \(q_e\) is the amount of phosphate adsorbed at equilibrium (mg P/g), respectively; \(t\) is the time interval (min); \(k_1\) is the first-order adsorption rate constant (1/min); and \(k_2\) is the second-order adsorption rate constant (g/mg P/min).

The effects of adsorbent dosage, pH and coexisting ion on the phosphate adsorption of as-prepared Pr(OH)\(_3\) NWs were studied in detail herein. The impact of adsorbent dosage, ranged from 0.02 g/L, 0.06 g/L, 0.10 g/L, 0.14 g/L to 0.18 g/L, was examined in 10.0 mg P/L phosphate solution. In the study on the pH effect, 0.005 g of Pr(OH)\(_3\) NWs were added in 50.0 mL of the phosphate solution, in which the pH was tailored from 2.0 to 12.0 by using 1.0 M NaOH or/and 1.0 M HCl solution.
To study the effect of coexisting anions, 0.005 g of Pr(OH)$_3$ NWs were added in 50.0 mL of 10.0 mg P/L phosphate solution, in which 0.005 M NaCl, NaNO$_3$, Na$_2$SO$_4$, Na$_2$CO$_3$ or NaHCO$_3$ salt was dissolved, respectively.

3. Results and discussion

3.1. Pr(OH)$_3$ characterization

The morphology and structure of as-prepared Pr(OH)$_3$ NWs are studied in the XRD pattern (Fig. 1a), SEM image (Fig. 1b), TEM image (Fig. 1c), HR-TEM image (Fig. 1d), as well as nitrogen adsorption-desorption analysis (Fig. 2a and b), respectively. All of those observations agree well with the works published by Tong’s group [11, 12]. As seen in the XRD pattern (Fig. 1a), the characteristic diffraction peaks can be indexed to (100), (110), (101), (201), (211) and (220) planes (JCPDF card 45-0086), corresponding to the hexagonal phase of Pr(OH)$_3$, with lattice constants of $a = 0.652$ nm and $c = 0.378$ nm. Furthermore, there are no other characteristic diffraction peaks of impurity recorded in Fig. 1a; this strongly suggests the Pr(OH)$_3$ sample be pure. The SEM image (Fig. 1b) shows that the Pr(OH)$_3$ nanowires deposited on the Cu foil substrate after the electrodeposition are disordered and loosely interlaced with others to form a three-dimensional reticulation. In the TEM image (Fig. 1c), these porous nanowires have an average diameter ranging from 30 nm to 50 nm. In particular, the unique porous structure is observed in our prepared Pr(OH)$_3$ NWs; that a number of pores with a wide range of diameters are distributed unevenly across the nanowires. The SAED pattern of Pr(OH)$_3$ NWs, shown in the inset of Fig. 1c, further confirms the crystallinity of as-prepared powders. In the HRTEM photo (Fig. 1d) of selected area (highlighted in red in Fig. 1c), the distance of the lattice fringes is 0.31 nm; this is in
accordance with the (101) plane in the hexagonal phase of Pr(OH)₃. Fig. 2 depicts the N₂ adsorption-desorption isotherm (a) and the corresponding pore size distribution (b) of Pr(OH)₃ NWs. The BET specific surface area, average pore diameter and total pore volume are 100.2 m²/g, 14.4 nm and 0.41 cm³/g, respectively. These results are consistent with our TEM observation in Fig. 1c, proving the existence of pores with a wide range of sizes in the Pr(OH)₃ nanowires.

3.2 Phosphate adsorption

3.2.1 Adsorption isotherms

Fig. 3 shows the fittings of phosphate adsorption data of Pr(OH)₃ NWs at different temperatures into the Langmuir and Freundlich adsorption isotherms, respectively; Table 1 summarizes the relevant values of parameters. The data show a good agreement with the Langmuir isotherm model ($R^2 \geq 0.996$), as compared with the use of the Freundlich model ($R^2 = 0.865 \sim 0.945$). This implies that the observed sorption feature of Pr(OH)₃ NWs be caused by monolayer adsorption. The maximum adsorption capacities ($q_0$) estimated by the Langmuir models are 128.956 mg P/g, 120.244 mg P/g, and 113.849 mg P/g at 25°C, 35 °C, and 45 °C, respectively. On the other side, the adsorption capacity reduces when elevating temperature; this reveals the phosphate adsorption onto Pr(OH)₃ NWs to be exothermic [18].

Table 2 presents the comparison of adsorption capacity of Pr(OH)₃ NWs with other adsorbents consisting of metal oxides or hydroxides in literature. Even though the selected initial P concentrations and testing pH differ, our adsorbents, Pr(OH)₃ NWs, exhibit a superior phosphate adsorption capacity of approximately 129.0 mg P/g. This may be due to the presence of ample hydroxyl groups on the surfaces of Pr(OH)₃ NWs [12], working as active sites to effectively
attract phosphate anions from solution. Furthermore, the unique porous structure and high surface area of Pr(OH)$_3$ NWs are capable to offer a large number of pathways and active sites to greatly enhance the phosphate transportation and adsorption, leading to the observed outstanding phosphate uptake.

3.2.2 Thermodynamic analysis

Fig. 4 shows the Van’t Hoff plot of ln$K_d$ versus $1/T$, which is linear with $R^2 = 0.998$. Table 3 summarizes the values of $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$, which are obtained by using the thermodynamic analysis. The negative values of $\Delta G^\circ$ increase when the temperature is elevated from 25 °C to 45 °C; that reveals the nature of adsorption is spontaneous and the spontaneity is reduced at higher temperatures [18, 26]. The negative value of $\Delta H^\circ$ confirms the phosphate adsorption on Pr(OH)$_3$ NWs is an exothermic process [44]. This conclusion is consistent with the aforementioned isotherm results; that the adsorption capacities decline by increasing temperatures. The negative $\Delta S^\circ$ suggests the reduction in randomness during phosphate adsorption [18, 26].

3.2.3 Kinetic study

In order to further investigate the phosphate adsorption of Pr(OH)$_3$ NWs [46], we carried out the kinetic study in the phosphate solution with an initial concentration of 10.0 mg P/L. In Fig. 5a, the phosphate adsorption onto Pr(OH)$_3$ NWs rapidly increases to 60.93 mg P/g in the first 5 min. Afterwards, the whole adsorption process reaches the equilibrium in 6 h, with a phosphate adsorption of 99.88 mg P/g.

Both of the pseudo-first-order and pseudo-second-order models are used to evaluate the kinetic data. Our results are found to better match the pseudo-second-order model ($R^2 = 0.966$) (Fig. 5b
and Table 4), as compared with the pseudo-first-order model ($R^2 = 0.921$; Table 4); that suggests the adsorption of Pr(OH)$_3$ NWs be chemisorption [46]. Moreover, the experimental $q_e$ value (99.880 mg P/g) is close to the calculated $q_e$ (95.606 mg P/g), further implying the better suitability of the pseudo-second-order model in describing the phosphate adsorption of Pr(OH)$_3$ NWs.

### 3.2.4 Effect of dosage

Fig. 6 shows the phosphate removal (%) by varying the dosage of Pr(OH)$_3$ NWs in the solution. The phosphate adsorption capacities at the equilibrium are 171.65 mg P/g, 121.08 mg P/g, 100.00 mg P/g, 71.42 mg P/g, and 55.56 mg P/g, by adding 0.02 g/L, 0.06 g/L, 0.10 g/L, 0.14 g/L to 0.18 g/L adsorbent, respectively. In particular, the phosphate removal rates keep almost constant at ~100%, when the dosage of Pr(OH)$_3$ NWs is greater than 0.10 g/L. By considering the high addition of adsorbent may result in a sludge treatment and disposal problem, 0.10 g/L is suggested as an optimal dosage and has been adopted in all our experiments herein.

### 3.2.5 Effect of pH

Fig. 7a shows the impact of pH, ranging from 2 to 11, on the phosphate adsorption of Pr(OH)$_3$ NWs. At the pH of 2.0, the adsorption capacity of Pr(OH)$_3$ NWs is as low as 4.25 mg P/g. When the pH is 3.0, the adsorption capacity is dramatically increased to 99.41 mg P/g; and then fluctuates at a level of ~100 mg P/g within the pH range of 3.0 and 6.0. As the pH is further raised from 7.0 to 11.0, the adsorption capacity is reduced moderately to 76.75 mg P/g. Those observed changes may be elucidated by two mechanisms: electrostatic attraction and inner-sphere ligand exchange; both of which have been widely adopted in literature [39, 47-50].
As known, phosphate anions are present in different forms of ionic species, e.g. $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{2-}$, and $\text{PO}_4^{3-}$, greatly depending on the solution pH [25, 51]. At the pH ranging from 2.13 to 7.20, the main species in solution is monovalent ion, $\text{H}_2\text{PO}_4^-$; whilst in the pH range of 7.20 and 11.0, $\text{HPO}_4^{2-}$ is the predominant species of phosphate.

In order to further reveal the adsorption mechanism of $\text{Pr(OH)}_3$ NWs, Fig. 7b shows the impact of pH on their zeta potential; in which the isoelectric point (pH\text{pzc}) is 6.7. When the pH is varied from 3 to 6, the surfaces of $\text{Pr(OH)}_3$ NWs are protonated, as seen in Eq. 9. Those protonated active sites can electrostatically attract phosphate species, e.g. $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$, which are shown in the Eqs. (10) and (11):

\begin{align}
\equiv \text{Pr} - \text{OH} & \rightleftharpoons \equiv \text{Pr} - \text{O}^- + \text{H}^+ \quad (8) \\
\equiv \text{Pr} - \text{OH} + \text{H}^+ & \rightarrow \equiv \text{Pr} - \text{OH}_2^+ \quad (9) \\
\equiv \text{Pr} - \text{OH}_2^+ + \text{HPO}_4^{2-} & \rightleftharpoons \equiv \text{Pr} - (\text{OH}_2^+)(\text{HPO}_4^{2-}) \quad (10) \\
\equiv \text{Pr} - \text{OH}_2^+ + \text{H}_2\text{PO}_4^- & \rightleftharpoons \equiv \text{Pr} - (\text{OH}_2^+)(\text{H}_2\text{PO}_4^-) \quad (11)
\end{align}

In addition, at low pH, the presence of $\text{H}^+$ ions in solution may greatly promote the inner-sphere ligand exchange (in Eqs. 12 and 13). Therefore, the adsorption capacities of $\text{Pr(OH)}_3$ NWs are relatively high within the pH range of 3.0 – 6.0.

\begin{align}
\equiv \text{Pr} - \text{OH} + \text{H}_2\text{PO}_4^- & \rightleftharpoons \equiv \text{Pr} - (\text{H}_2\text{PO}_4^-) + \text{OH}^- \quad (12) \\
\equiv 2(\text{Pr} - \text{OH}) + \text{HPO}_4^{2-} & \rightleftharpoons \equiv \text{Pr}_2^2 - (\text{HPO}_4^-) + 2\text{OH}^- \quad (13)
\end{align}

However, when the pH of solution is increased from 7.0 to 11.0, the active sites on $\text{Pr(OH)}_3$ are deprotonated (Eq. 8); and subsequently negative charges are formed on the adsorbent surfaces. As a result, the electrostatic repulsion takes place between the negatively charged phosphate species.
and the negatively charged adsorbent surfaces. Moreover, as shown in Eqs. (12) and (13), the high concentration of hydroxide in solution hinders the occurrence of ligand exchange. Consequently, the adsorption capacities are reduced at the pH varying from 7.0 to 11.0. Nevertheless, at pH = 7.0 – 10.0, the adsorption capacities are overall higher than ~ 90 mg P/L; suggesting the promising applicability of our adsorbent Pr(OH)$_3$NWs within a wide pH range.

It is noted that the lowest phosphate uptake of Pr(OH)$_3$ occurs at the pH of 2. Under that condition, the dominant phosphate species in the solution is H$_3$PO$_4$; which is hardly adsorbed onto the protonated surfaces of Pr(OH)$_3$ NWs. Moreover, at a such low pH, a large amount of H$^+$ existing in solution may make Pr(OH)$_3$ unstable [50]. However, the extremely low pH, e.g. pH ≤ 2, is rare in natural water environment or municipal wastewater treatment plant [50]. In other words, our prepared Pr(OH)$_3$ NWs can be directly used as the phosphate adsorbents in actual water treatment.

3.2.6 Effect of coexisting ion

As known, various inorganic anions are present in natural water bodies or wastewater, which may compete with phosphate anions for active sites on the adsorbent and in turn affect its phosphate removal [18, 26]. Fig. 8 shows the effect of coexisting ions on the phosphate adsorption performances of Pr(OH)$_3$ NWs. In the absence of foreign anions, the phosphate adsorption capacity of Pr(OH)$_3$ NWs is as high as 99.88 mg P/g. A slight reduction in the phosphate removal is observed when chloride, bicarbonate or nitrate anions are introduced; that signifies the presence of such competitive anions hardly interferes with the strong phosphate adsorption of Pr(OH)$_3$ NWs. One the other side, the phosphate adsorption of Pr(OH)$_3$ NWs is significantly reduced to only ~ 70 mg P/g, in the presence of sulfate or carbonate anions. This may be explained on the basis of the
ion exchange mechanism [52]. As aforementioned, phosphate ions are adsorbed onto the surfaces of Pr(OH)$_3$ NWs, which possess abundant hydroxyl groups. When foreign anions are introduced, they may compete with phosphate anions and replace those adsorbed on Pr(OH)$_3$ NWs, thus more or less deteriorating the final phosphate adsorption capacities. Moreover, the affinity between the adsorbent surfaces and competitive anions may differ, which could contribute to the observed order of changes in adsorption capacities when varying types of coexisting ions in solution [52].

4. Conclusions

In summary, we synthesized porous Pr(OH)$_3$ nanowires (NWs) via the electrodeposition method and used them in phosphate removal for the first time. Our prepared Pr(OH)$_3$ NWs, exhibiting unique structural properties, could greatly adsorb phosphate anions from solution. The equilibrium data of Pr(OH)$_3$ NWs were fitted better by using the Langmuir isotherm model, as compared with the Freundlich isotherm model. The maximum adsorption capacity was 128.96 mg P/g at 25 °C; this outperformed those of phosphate adsorbents consisting of metal oxides or hydroxides in literature. The negative values of free energy ($\Delta G^\circ$) and enthalpy ($\Delta H^\circ$) reveal the spontaneous and exothermic nature of phosphate adsorption onto Pr(OH)$_3$ NWs. The use of Pr(OH)$_3$ NWs could reach over 70% of the final adsorption capacity within 30 min and the equilibrium after 6 h. The phosphate adsorption kinetics was better described by the pseudo-second-order model, indicating the adsorption process was chemisorption. The high adsorption capacities of Pr(OH)$_3$ NWs were observed within a wide pH range of 3.0 – 10.0; whilst the coexistence of Cl$^-$, HCO$_3^-$, or NO$_3^-$ anions did not significantly affect the final phosphate uptake. Herein, on the basis of excellent phosphate removal capacity, the porous 1D Pr(OH)$_3$ nanomaterials, which were
synthesized by a facile electrodeposition strategy, are suggested as promising phosphate adsorbents in water treatment. Our study is believed to open up a new avenue for developing prominent phosphate adsorbents in practical use.

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Figures

**Fig. 1.** XRD pattern (a), FE-SEM image (b), TEM image (c), and HRTEM image (d) of Pr(OH)$_3$ NWs; the inset in (c) is the SAED pattern.

**Fig. 2.** (a) Nitrogen adsorption-desorption isotherm and (b) pore size distribution of Pr(OH)$_3$ NWs.

**Fig. 3.** Langmuir and Freundlich isotherm fitting plots of the phosphate adsorption onto Pr(OH)$_3$ NWs at 25°C, 35°C, and 45°C, respectively.

**Fig. 4.** Van't Hoff plot for the phosphate adsorption on Pr(OH)$_3$ NWs.

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**Fig. 6.** Effect of adsorbent dosage on the phosphate removal (%) of Pr(OH)$_3$ NWs.

**Fig. 7.** Effect of pH on the phosphate adsorption capacity (a) and zeta potential (b) of Pr(OH)$_3$ NWs.

**Fig. 8.** Effect of coexisting anions on the phosphate adsorption capacity of Pr(OH)$_3$ NWs.
Tables

**Table 1.** Langmuir and Freundlich adsorption isotherm parameters for the phosphate adsorption onto Pr(OH)$_3$ NWs at 25 °C, 35 °C, and 45 °C, respectively.

**Table 2.** Comparison of the phosphate adsorption capacities between Pr(OH)$_3$ NWs and other adsorbents consisting of metal oxide/hydroxide in literature.

**Table 3.** Thermodynamic parameters for the phosphate adsorption onto Pr(OH)$_3$ NWs at different temperatures.

**Table 4.** Comparison of parameters in the pseudo-first-order and pseudo-second-order fitting plots of the phosphate adsorption onto Pr(OH)$_3$ NWs.
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Fig. 3
Fig. 4
Fig. 5
Fig. 6

Phosphate removal (%) vs. Dosage (g/L)
Fig. 7
Fig. 8
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Table 1

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Langmuir</th>
<th></th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q₀ (mg P/g)</td>
<td>Kᵥ (L/mg P)</td>
<td>R²</td>
</tr>
<tr>
<td>25</td>
<td>128.956</td>
<td>59.077</td>
<td>0.998</td>
</tr>
<tr>
<td>35</td>
<td>120.244</td>
<td>120.632</td>
<td>0.996</td>
</tr>
<tr>
<td>45</td>
<td>113.849</td>
<td>227.131</td>
<td>0.999</td>
</tr>
<tr>
<td>Sample</td>
<td>Initial P concentration (mg P/L)</td>
<td>Solution pH</td>
<td>Adsorption capacity (mg P/g)</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>---------------------------------</td>
<td>-------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Pr(OH)$_3$ NWs</td>
<td>10 ~ 100</td>
<td>6.0</td>
<td>129.0</td>
</tr>
<tr>
<td>Lanthanum hydroxide</td>
<td>20 ~ 120</td>
<td>/</td>
<td>57.8</td>
</tr>
<tr>
<td>Tantalum hydroxide</td>
<td>7 ~ 65</td>
<td>2.0</td>
<td>25.6</td>
</tr>
<tr>
<td>Hydrous iron oxide</td>
<td>/</td>
<td>3.5</td>
<td>29.5</td>
</tr>
<tr>
<td>Fe/Cr hydroxide</td>
<td>3 ~ 13</td>
<td>4</td>
<td>2.1</td>
</tr>
<tr>
<td>Fe-Zr oxide</td>
<td>2 ~ 40</td>
<td>5.5</td>
<td>33.4</td>
</tr>
<tr>
<td>Mesoporous ZrO$_2$</td>
<td>0 ~ 300</td>
<td>6.7-6.9</td>
<td>29.7</td>
</tr>
<tr>
<td>Amorphous ZrO$_2$</td>
<td>2 ~ 16</td>
<td>6.2</td>
<td>32.3</td>
</tr>
<tr>
<td>La(OH)$_3$-modified exfoliated vermiculites</td>
<td>1 ~ 100</td>
<td>5</td>
<td>79.6</td>
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<tr>
<td>La$_2$O$_3$-modified macroporous ordered silica foams</td>
<td>1 ~ 100</td>
<td>/</td>
<td>70.4</td>
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<tr>
<td>La$_2$O$_3$-modified SBA-15</td>
<td>10 ~ 80</td>
<td>/</td>
<td>45.6</td>
</tr>
</tbody>
</table>
Table 3

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Kd</th>
<th>ΔG°(kJ/mol)</th>
<th>ΔS°(J/mol K)</th>
<th>ΔH°(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>46.673</td>
<td>-9.552</td>
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<tr>
<td>35</td>
<td>40.357</td>
<td>-9.469</td>
<td>-3.147</td>
<td>-10.440</td>
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<td>45</td>
<td>35.407</td>
<td>-9.430</td>
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<tr>
<td></td>
<td>Pseudo-first-order model</td>
<td>Pseudo-second-order model</td>
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<td></td>
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<tr>
<td>---------------------</td>
<td>--------------------------</td>
<td>---------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_e$ (mg P/g)</td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$R^2$</td>
<td></td>
<td></td>
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<tr>
<td>92.382</td>
<td>0.183</td>
<td>0.921</td>
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<td></td>
</tr>
<tr>
<td>$q_e$ (mg P/g)</td>
<td>$k_2$ (g/mg P/min)</td>
<td>$R^2$</td>
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<td></td>
</tr>
<tr>
<td>95.606</td>
<td>0.003</td>
<td>0.966</td>
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</tr>
</tbody>
</table>
Equations:

\[ q_e = \frac{(C_o-C_e) \times V}{m} \quad (1) \]

\[ \frac{C_e}{q_e} = \frac{1}{q_o K_L} + \frac{C_e}{q_o} \quad (2) \]

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3) \]

\[ \Delta G^0 = -RT \ln K_d \quad (4) \]

\[ \ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (5) \]

\[ \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6) \]

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7) \]
Highlights

- Porous Pr(OH)$_3$ nanowires were utilized in phosphate removal for the first time.
- The adsorption capacity estimated by Langmuir model was 129.0 mg P/g at 25 °C.
- The adsorption was chemisorption; and it was spontaneous and exothermic.
- The presence of Cl$^-$, HCO$_3^-$, or NO$_3^-$ had negligible effects on P adsorption.
- The adsorbent could work efficiently in a wide pH range of 3-10.