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Adsorption of phosphate by cancrinite in red mud: a first-principles study

Zhou Xiaotian [1,2], Longjiang Li [1,2,3,✉], Qiu Yueqin [1,2,3] and Liu Wanshuang [1,2,3]

1 College of Mining, Guizhou University, Guiyang 550025, People’s Republic of China
2 Guizhou Key Laboratory of Comprehensive Utilization of Non-metallic Mineral Resources, Guizhou 550025, People’s Republic of China
3 National & Local Joint Laboratory of Engineering for Effective Utilization of Regional Mineral Resources from Karst Areas, Guizhou, Guizhou 550025, People’s Republic of China

✉ Author to whom any correspondence should be addressed.

E-mail: mnljiang@163.com

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Abstract

Cancrinite is the key substance that affects the adsorption effect of phosphate from red mud (RM). Therefore, cancrinite in RM was modified to improve its adsorption performance. Based on density functional theory (DTF), this paper optimized the structure of cancrinite, the main component of red mud, modified the cancrinite with sodium dodecyl benzene sulfonate, and studied the surface wettability changes of cancrinite before and after modification through dynamics relaxation. The effects of wetting modification on the adsorption properties of cancrinite were studied by molecular dynamics, simulation of radial distribution function, adsorption site, adsorption energy and mean square displacement. Research shows that modified cancrinite Surface wettability increased by 77%, also has more adsorption sites, adsorption energy is smaller, diffusion process is accelerated, so the adsorption capacity is stronger. This study lays a theoretical foundation for enhancing the adsorption of phosphate from wastewater by RM.

1. Introduction

Due to the recent rapid developments related to industrialisation, such as the chemical industry and mineral processing plants, a large amount of phosphorus-containing wastewater is discharged into the environment, causing serious deterioration of water resources. There are many methods of treating phosphorus-containing wastewater, such as chemical [1–5], biological [6–11] and adsorption [12–18] methods. Adsorption uses the adsorption affinity of some porous or large-surface solid materials (e.g., bentonite, zeolite, natural calcite and red mud (RM)) towards phosphate in wastewater for phosphorus removal [19]. However, RM alone as an adsorbent for phosphorus shows unsatisfactory adsorption performance. Studies have shown that the unmodified RM surface has a poor wetting effect, low activity and a small specific surface area. Moreover, the basic group on the RM surface results in more negative charges of RM under high-pH conditions, which enhances the repulsion of phosphate and thereby leads to unsatisfactory phosphorus adsorption performance of undisturbed RM [20].

However, RM can be used as the main material to adsorb phosphorus-containing wastewater. Many scholars have researched this. Hu et al. [21] used industrial residues, borax and RM to prepare adsorbents for phosphate adsorption under alkaline conditions. The phosphate (monopotassium phosphate) removal rate reached 93%. Li [22] modified RM by impregnating the cationic surfactant cetyltrimethylammonium bromide (CTMAB) to change the surface properties of RM and studied its adsorption performance towards phosphorus. The results showed that at a mass concentration 8 g l−1 of CTMAB in the impregnation solution, a roasting temperature of 500 °C, an initial concentration of 5 mg l−1 of the simulated phosphorus-containing wastewater, wastewater pH of 3 and a shaking time of 60 min, the phosphorus (monopotassium phosphate) removal rate by the modified adsorbent exceeds 90%. Due to significant improvements in computing power, molecular dynamics
(MD) simulation calculations can be used to explore the interaction between liquids and substances. Compared with traditional experiments, simulation calculations have overcome some objective limitations in experimental testing. Many calculations based on MD study the wetting characteristics of liquids on solid surfaces. Liu [23] performed MD simulations of the wettability of salt water drops with different mass fractions on the sandstone surface and found that the wetting angle increases with an increase in the brine mass fraction until the specific mass fraction is reached, and then there are no longer any changes. Li [24] studied the wetting process of water droplets on the smooth mineral surface.

It is found that cancrinite is not only the main component in RM, but also has stronger adsorption capacity for phosphate ions than other main components [25]. However, its adsorption mechanism is not clear. Therefore, this paper takes cancrinite as the research object. Through simulation calculations based on density functional theory (DFT) [26–28] and MD [29–31], we studied the adsorption mechanism of RM for phosphate removal from phosphorus-containing wastewater. Both wettability [32–34] and adsorption energy [35–37] provide strong evidence to explain adsorption. This study established the crystal structure of cancrinite and built a sodium dodecylbenzene sulfonate (SDBS) wetting layer on its surface. Then, we performed simulation calculations based on MD and performed comparative analysis of the adsorption process rule of phosphate-containing water clusters on the surface of cancrinite and wetting-modified cancrinite from the perspectives of adsorption equilibrium conformation, radial distribution function (RDF) and interaction energy. The process and mechanism of the phosphate water cluster–cancrinite interaction were analysed on the basis of wettability characteristics to determine the wettability of cancrinite and its adsorption of phosphate.

2. Method

2.1. Materials
Cancrinite, a common mineral found in alkaline rocks and related dikes, is formed by the hydrothermal alteration or weathering of nepheline or feldspar and has a hexagonal crystal structure [38]. RM was obtained from Guizhou Huajin Aluminum Co., Ltd (China). After drying at 50 °C for 12 h with a moisture content of 30%, the RM was ground using a planetary ball mill to a thickness of 0.075 mm and then sieved.

2.2. X-ray diffraction analysis
X-ray diffraction (XRD; PANalytical, X’Pert PRO, UK) was performed for qualitative and quantitative analyses of the phase and crystal structure of RM. The raw data were processed using jade software according to the Powder Diffraction File database, followed by peak fitting and mineral composition identification. A Cu target Kα ray source (λ = 0.154 nm) with a tube voltage of 40 kV and a tube current of 40 mA was used. Step scanning was adopted with a step size of 0.05, a scan speed of 0.5°/s and a scan range of 10°–70°.

2.3. Scanning electron microscopy–X-ray energy spectrum analysis
Scanning electron microscopy (SEM; ZEISS Merlin Compact, Germany) was performed to examine the surface structure of RM. X-ray energy spectroscopy (EDS; Oxford X-MAX–20 mm2, UK) was performed to determine the elemental composition distribution on the RM surface. The characteristic X-rays emitted by different elements have different frequencies, that is, different energies, and the elements can be determined only by the energy detection of different photons. The element content was determined by quantitative analysis without standard samples. The point analysis method of an X-ray energy spectrometer supports the simultaneous detection of multiple elements, with a fast analysis speed, a small analysis volume and high sensitivity [38], so it was used for rapid fixed-point or microarea element analysis of RM to determine the presence of cancrinite.

2.4. Model selection and calculation
The crystal unit cell of cancrinite (Na7.54(CO3)2(Si6Al6O24)) was determined by XRD, and models of PO43−, HPO42− and H2PO4− were plotted using Materials Studio simulation software. The constructed models were subjected to geometry optimisation to find the reasonable molecular structure of the system and the configuration under the state of minimum energy so that dynamics calculation could be performed.

The CASTEP module in Materials Studio was used for geometry optimisation of the models based on DFT. Local density approximation (LDA) and generalised gradient approximation (GGA) were selected for functional methods, including LDA–CA–PZ, GGA–RPBE, GGA–PBE, GGA–PW91 and GGA–WC. To calculate the exchange correlation functional, the fixed cut-off energy was set to 380 eV and the k-point in the Brillouin zone was set to 1 × 1 × 1.

The Amorphous Cell module was used to build an SDBS wetting layer, similar to the cancrinite unit cell lattice. Next, the Build Layers module was used to add the SDBS wetting layer on the cancrinite (1 0 0) surface to create a wetting modification cancrinite model.
In terms of the geometrically optimised configuration, the adsorption behaviour of phosphate-containing water clusters on the surface model of cancrinite and wetting-modified cancrinite was subjected to dynamics relaxation with the Forice module. The precision control was set to ultrafine, the canonical ensemble (NVT) was selected, the initial speed was set to random at a time step of 1 fs, the total calculation time was 50 ps, the temperature control function was Nose (by constant temperature calculation, the real NVT ensemble is achievable), and the ability field was a COMPASS force field.

The Fixed loading task in the Sorption module was used to fix 100 phosphate ions on the surface of cancrinite and wetting-modified cancrinite, with 100,000 maximum loading steps, 1,000,000 equilibration steps, 10,000,000 production steps and a fixed temperature of 298 K. The precision control was set to ultrafine, the method was Metropolis and the ability field was a COMPASS force field. Sampling was done at an interval of 25 steps.

Adsorption energy is the energy generated during adsorption. Adsorption is a process in which the molecule moves from fast to slow speed and finally stays on the adsorption medium surface. When the speed decreases, a part of energy is released. This part of energy is known as adsorption energy [39]. When interacting with the same mineral surface, different kinds of substances exhibit different surface adsorption energies. The adsorption strength of phosphate-containing water clusters and the cancrinite (100) surface can be determined through the size of adsorption energy [40]. The adsorption energy can be calculated by formula (1).
where \( E_{\text{adsorption}} \) is the phosphate-containing adsorption energy, \( E_{\text{total}} \) is the total energy of the system, \( E_{\text{surface}} \) is the surface energy and \( E_{\text{polymer}} \) is the energy of the phosphate-containing water cluster.

Geometry Optimization, Anneal calculations, NVT dynamics simulation relaxation structure and NVE molecular dynamics calculations were performed for the configurations of cancrinite and wetted modified cancrinite to adsorb \( \text{PO}_4^{3-} \), \( \text{HPO}_4^{2-} \) and \( \text{H}_2\text{PO}_4^- \). Then calculate. Mean square displacement of \( \text{PO}_4^{3-} \), \( \text{HPO}_4^{2-} \) and \( \text{H}_2\text{PO}_4^- \) on the surface of cancrinite and wetting modified cancrinite.

### 3. Results and discussion

#### 3.1. XRD analysis results of RM

As shown in figure 1, the minerals from top to bottom were katoite, calcite, hematite, cancrinite, diaspore, anatase, kaolinite, chlorite and mica. The cancrinite content was 26.05%, and the lattice constants were \( a = b = 13.051 \text{ Å}, c = 5.310 \text{ Å}, \alpha = \beta = 90^\circ \) and \( \gamma = 120^\circ \) (space group \( P6_3/m \)).

#### 3.2. Scanning electron microscopy and X-ray energy spectrum analysis results of red mud

Figure 2(a) is an enlarged view of the RM surface, and figure 2(b) is the EDS spectrum at the box in figure 2(a). Figure 2(a) shows that the RM surface had an irregular shape, a loose structure and large interparticle voids.
Figure 4. Sodium dodecylbenzene sulfonate wetting-modified cancrinite (space group P63/m) surface.

Figure 5. Total energy change of phosphate-containing water clusters on the surface of cancrinite (space group P63/m) (a) and wetting-modified cancrinite (b).
Figure 2(b) shows that the scanning point contained five elements (C, O, Na, Al and Si), which is consistent with the main elements in the molecular formula of cancrinite (Na$_{7.54}$\((\text{CO}_3)\)(Si$_6$Al$_6$O$_{24}$)).

3.3. Geometry optimisation of the adsorption structure

Before dynamics relaxation, the geometry optimisation of different cross-linking functionals was performed on cancrinite. The total energy of the system is shown in table 1. The smaller the total energy of the system, the more stable the crystal structure [41, 42]. When cancrinite adopted the exchange correlation functional GGA-PW91, the system energy was the lowest, that is, the crystal structure was in the most stable state. Analysis of the most stable configuration of cancrinite shows that the valence electron orbital for optimisation of Al and O atoms in cancrinite is 3s$^2$3p$^1$. Figure 3(a) shows the cancrinite structure before geometry optimisation, in which the Al–O$_1$, Al–O$_2$, Al–O$_3$, and Al–O$_4$ bond lengths are 1.768, 1.586, 1.757 and 1.763 Å, respectively.

Figure 3(b) shows the calcium structure after geometry optimisation, in which the Al–O$_1$, Al–O$_2$, Al–O$_3$, and Al–O$_4$ bond lengths are 1.682, 1.492, 1.650 and 1.655 Å, respectively. The Al–O bonds in the optimised structure were all smaller after optimisation, indicating that the optimised cancrinite surface possesses stronger electronegativity [43, 44]. To illustrate in detail the electronic structure on the cancrinite surface, the density of states (DOS) and the partial density of states (PDOS) were compared. As shown in figure 3(b1), the electronic energy levels of cancrinite were mainly distributed between –52 eV and 3 eV. According to the distribution characteristics of valence electrons and the number of atoms in the unit cell, the number of theoretical Al atoms of cancrinite was 6 before optimisation. The number of valence electrons was 26.982 before optimisation and 27 after optimisation. The two were basically the same, indicating balanced distribution of electrons in the overall system. As shown in figure 3(b2), a new peak appeared in the...
partial-wave-state density of O atoms near the Fermi level. Thus, O atoms have higher electronegativity in the cancrinite system.

LDA, local density approximation; GGA, generalised gradient approximation.

3.4. Dynamics relaxation

As shown in figure 4, an SDBS wetting layer a was added to the cancrinite surface b to form a new wetting-modified cancrinite system c, and then dynamics relaxation was performed.

As the adsorption in the system progresses, the system energy fluctuation gradually stabilises, so it can be used to judge the system balance [45, 46]. Figure 5 shows the change in system energy with time during dynamics relaxation. The total energy of the three phosphate-containing water clusters stabilised after 5 ps, that is, the system reached equilibrium at 5 ps. In addition, among the three water clusters, the HPO$_4^{2-}$-containing water cluster possessed the smallest energy when it reached a stable state, followed by the H$_2$PO$_4^{-}$-containing water cluster and then the PO$_4^{3-}$-containing water cluster.

During the dynamics relaxation of the system, the three water clusters interacted on the surface of cancrinite and wetting-modified cancrinite, and the system configuration changed dynamically, as shown in figure 6. The three water clusters showed a similar reaction process on the surface of cancrinite and wetting-modified cancrinite. In the initial state, the PO$_4^{3-}$, HPO$_4^{2-}$ and H$_2$PO$_4^{-}$-containing water clusters in a1, b1 and c1 were all on the cancrinite surface, while those in d1, e1 and f1 were all on the wetting-modified cancrinite surface. After the reaction, the configuration of water molecules and phosphate in the system changed to downward O atoms. For instance, the PO$_4^{3-}$, HPO$_4^{2-}$ and H$_2$PO$_4^{-}$-containing water clusters in a2, b2, c2, d2, e2 and f2 migrated towards the cancrinite surface and the wetting-modified cancrinite surface and then adsorbed to the crystal.

Figure 7. Radial distribution function of PO$_4^{3-}$-containing water clusters: cancrinite (space group P63/m) (a) and wetting-modified cancrinite (b).

Figure 8. Radial distribution function of HPO$_4^{2-}$-containing water clusters: cancrinite (space group P63/m) (a) and wetting-modified cancrinite (b).
surface. Finally, the wetting film on the surface of the phosphate-containing water cluster was broken and the number of hydrogen bonds in the cluster decreased, so the water molecules and phosphate adsorbed to the cancrinite surface. Comparison of the PO$_4^{3-}$-, HPO$_4^{2-}$- and H$_2$PO$_4^-\$-containing water clusters in a$_2$, d$_2$, b$_2$, e$_2$, c$_2$ and f$_2$ showed that the water clusters completely spread on and adsorbed to the wetting-modified cancrinite.

**Figure 9.** Radial distribution function of H$_2$PO$_4^-$-containing water clusters: cancrinite (space group P63/m) (a) and wetting-modified cancrinite (b).

**Figure 10.** Stable adsorption sites of phosphate on the surface of cancrinite (space group P63/m) (a) and wetting-modified cancrinite (b): (a1, b1) PO$_4^{3-}$, (a2, b2) HPO$_4^{2-}$ and (a3, b3) H$_2$PO$_4^-\$. 
surface, while new small clusters formed and adsorbed to the cancrinite surface. The measured contact angles of \( \text{PO}_4^{3-} \), \( \text{HPO}_4^{2-} \) and \( \text{H}_2\text{PO}_4^{-} \) containing water clusters on the surface of cancrinite are 17.8°, 17.8°, and 17.6°, respectively, and the contact angles on the surface of modified cancrinite are 4.2°, 4.0°, 4.1°, indicating that the wetting-modified cancrinite surface has significantly improved adsorption [47, 48].

Table 2. Adsorption energy of three phosphate-containing (space group P63/m) water clusters (eV).

| Name               | Cancrinite (eV) | Wetting-modified cancrinite (eV) |
|--------------------|----------------|----------------------------------|
| \( \text{PO}_4^{3-} + \text{H}_2\text{O} \) | −758.8775        | −942.9294                        |
| \( \text{HPO}_4^{2-} + \text{H}_2\text{O} \) | −801.6099        | −1014.4586                       |
| \( \text{H}_2\text{PO}_4^{-} + \text{H}_2\text{O} \) | −914.8535        | −1064.3895                       |

3.5. Radial distribution function

We thoroughly studied the adsorption distribution characteristics of the three phosphate-containing water clusters on the cancrinite surface. Figures 7–9 reveal the RDFs of O atoms and \( \text{H}_2\text{O} \) on the cancrinite surface in different phosphate-containing water clusters adsorbed by cancrinite, as well as O atoms and \( \text{PO}_4^{3-} \), \( \text{HPO}_4^{2-} \) and \( \text{H}_2\text{PO}_4^{-} \). Figures 8(a), (b) and 9(a),(b) show that among the three systems in which cancrinite and wetting-modified cancrinite adsorb phosphate-containing water clusters, two obvious peaks appeared in O-HPO_4^{2-} and O-H_2PO_4^{-}. Comparison of figures 7(a), (b), 8(a), (b) and 9(a), (b) showed that in the three systems in which cancrinite and wetting-modified cancrinite adsorbed phosphate-containing water clusters, adsorption to
wetting-modified cancrinite had higher peaks of O-H2O, O-PO4^3−, −HPO4^2− and O−H2PO4^− than adsorption to cancrinite. This suggested that the wetting-modified cancrinite surface has more adsorption sites than the cancrinite surface and that more HPO4^2− and H2PO4^− are adsorbed around O atoms compared with PO4^3− [49−51]. This also confirmed that in geometry optimisation, O atoms on the cancrinite surface possess higher electronegativity [52−54].

3.6. Adsorption site
To further explore the mechanism underlying adsorption of the three phosphate ions to cancrinite and wetting-modified cancrinite, the Sorption module was used to determine the stable adsorption sites of PO4^3−, HPO4^2− and H2PO4^− on the crystal structure surface of each component on the basis of the geometrically optimised configuration of its crystal structure. As shown in figure 10, when cancrinite and wetting-modified cancrinite adsorbed phosphate, each phosphate ion type had different adsorption sites. PO4^3− and H2PO4^− are adsorbed as bilayer on the surface of cancrinite and wetting-modified cancrinite, while HPO4^2− is adsorbed as monolayer.

3.7. Adsorption energy
Table 2 shows that the adsorption energy of wetting-modified cancrinite for phosphate-containing water clusters was far lower than that of cancrinite, indicating that the wetting-modified cancrinite surface has greater adsorption strength than the cancrinite surface for phosphate-containing water clusters. As a result, after the wetting film on the water cluster surface is broken, the wetting-modified cancrinite surface can absorb more water molecules and phosphate in closer arrangement, which illustrates why a modified cancrinite surface has higher wettability than a cancrinite surface.

3.8. Mean square diffusion
As shown in figure 11, the mean square displacement curve shows that the motion state of phosphate is relatively stable, and the linear relationship is good. Po4^3− and h2po4^− move and oscillate slightly on the surface of cancrinite and modified cancrinite. The mean square displacement curves of PO4^3−, HPO4^2− and H2PO4^− were calculated by the Einstein [53] relational method, and the diffusion coefficients on the surface of cancrinite and modified cancrinite were obtained as: a = 0.0026 cm^2 s ^−1, b = 0.0412 cm^2 s ^−1, respectively, c = 0.0581 cm^2 s ^−1, d = 0.0136 cm^2 s ^−1, e = 0.0583 cm^2 s ^−1, f = 0.2802 cm^2 s ^−1. Among them, the diffusion coefficient of HPO4^2− is doubled, while the diffusion coefficient of PO4^3− and H2PO4^− is five times that before modification. The diffusion coefficients on the surface of modified cancrinite are all better than those on the surface of cancrinite, indicating that the modified cancrinite has better adsorption.

4. Conclusion
In summary, using simulation calculations based on DFT and MD, we examined the wetting adsorption characteristics of three water clusters (PO4^3−, HPO4^2− and H2PO4^−) on the surface of cancrinite and wetting-modified cancrinite. The main conclusions are as follows:

(1) The optimised cancrinite surface is more wettable than the undisturbed cancrinite surface, the surface wettability is improved by 77%.

(2) Good wettability helps the cancrinite surface better adsorb phosphate. The adsorption energies of the modified cancrinite surface are smaller than those before the modification, and the adsorption sites are obviously more than those before the modification.

(3) The wettability of RM as an adsorbent can be adjusted to increase the adsorption of phosphate by RM. Provides a new modification idea for RM as an adsorption material to protect the environment.

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Data availability statement
The data that support the findings of this study are available upon reasonable request from the authors.
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ORCID iDs

Zhou Xiaotian https://orcid.org/0000-0002-8265-5953
Longjiang Li https://orcid.org/0000-0002-9222-986X
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