

Article

Adsorption of Hydrated Pr^{3+} and $\text{NH}_4^+/\text{Mg}^{2+}$ Ions onto the (001) Surface of Montmorillonite: A DFT Analysis with Experimental Verification

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Abstract: Montmorillonite is a major mineral present in ion-adsorption rare earth ores, and the microscopic adsorption states of rare earth ions on its surface are of a great significance for the efficient exploitation of ion-adsorption rare earth ores. In this article, density functional theory calculations were used to investigate the adsorption mechanisms and bonding characteristics of hydrated Pr, Mg and NH_4 ions on the (001) surface of montmorillonite. Pr^{3+} exhibited a directed tendency geometry with $\text{Pr}(\text{H}_2\text{O})_{10}^{3+}$, which was adsorbed onto montmorillonite by hydrogen bonding with an adsorption energy of -1182 kJ/mol, and one coordinated H_2O ligand was separated from the first hydration layer of Pr. Both hydrated Mg and NH_4 ions were adsorbed onto the montmorillonite surface through hydrogen bonds, and the adsorption energies were -206 and -188 kJ/mol, respectively, indicating that the adsorption stability of the hydrated Mg ion was slightly higher than that of the hydrated NH_4 ion, but both were lower than that of hydrated Pr (-1182 kJ/mol). Hence, higher concentrations of Mg and NH_4 ions than rare earth ions would be necessary in the leaching process of ion-adsorption rare earth ores. Additionally, desorption experiments revealed that the recovery of Pr^{3+} by Mg^{2+} with a concentration of 38 mmol/L is 80%, while it is only 65% with the same concentration of NH_4^+ , and the concentrations of Mg^{2+} and NH_4^+ were much higher than that of Pr^{3+} in lixivium, which is consistent with the DFT calculations.

Keywords: DFT; Pr^{3+} ; Mg^{2+} ; NH_4^+ ; montmorillonite; adsorption

1. Introduction

Rare earths elements (REEs) are known as industrial vitamins and are widely used in the fields of permanent magnet materials, petroleum catalysis, metal products and optical devices due to their unique 4f electronic layer structure [1–3]. Ion-adsorption rare earth (RE) ores, which are the main source of REEs in the world, have the characteristics of a complete distribution and low mining cost and have always attracted the attention of scholars. Ion-adsorption RE ores are unique ores that are formed by the following processes: first, RE original rocks (such as igneous rocks and granite) are gradually weathered in a warm and humid environment, and the RE ions in them are released into the solution. With

the continuous migration of rainwater, adsorption and desorption occur continuously on the surfaces of kaolinite, montmorillonite (Mt) and other clays during the migration process [4,5]. The occurrence forms of RE in ion-adsorption rare earth ores can be divided into four types, namely, the water-soluble phase, hydrated or hydroxyl-hydrated ionic phase, colloidal sedimentary phase and mineral phase, among which the hydrated or hydroxyl-hydrated ionic phase dominates [6], which can be desorbed by an ion exchange with highly active electrolytes (ammonium sulphate and magnesium sulphate) [7,8]. However, the use of ammonium sulphate would lead to the eutrophication of water around a mine lot.

Mt is a typical 2:1-type layered silicate mineral, which is composed of two silicon-oxygen tetrahedra mixed with an aluminium-oxygen octahedron in the middle [9]. Mt has a large number of negative charges due to the isomorphic substitution of silicon and aluminium by low-valence aluminium and magnesium, respectively, hence, Mt can adsorb positively charged metal cations [10]. Alshameri et al. [11] systematically studied and compared the adsorption/desorption of La^{3+} and Yb^{3+} by kaolinite, Mt, muscovite and illite and found that Mt has the highest adsorption capacity; they also found that the maximum adsorption capacity of Yb^{3+} is approximately 8.5 mg/g, which is slightly higher than that of La^{3+} , and that the desorption of the RE ions from Mt is more difficult than that from kaolinite or illite. In addition, Zhou et al. [12] investigated the adsorption of rare earth elements in sulfuric acid-modified Mt and found that the adsorption capacities of Mt for La^{3+} and Y^{3+} were significantly improved. The adsorption conformed to the kinetic second-order reaction model. Additionally, a chemical adsorption was observed, and the Arrhenius activation energies of La^{3+} and Y^{3+} were determined to be 14.259 kJ/mol and 22.845 kJ/mol, respectively. These studies mainly revealed the adsorption/desorption characteristics of RE in Mt through macroscopic test methods, while research on the adsorption of RE in Mt at the atomic and molecular scales has been rarely reported, especially regarding the comparison of RE ions and cations of the leaching agents.

With the development of computer technology, quantum chemical calculations have been gradually applied to scientific research [13,14], especially the density functional theory (DFT), which is an important method for supplementing experimental results and gaining new insights into chemistry-related problems [15,16]. Qiu et al. [17] studied the adsorption behaviour of hydroxyl-hydrated lutetium ions on the surface of kaolinite and found that on an ideal kaolinite (001) surface, the lutetium ions are mainly adsorbed through hydrogen bonding, which is called an outer-sphere adsorption, and the adsorption energy on the silicon-oxygen surface is lower than that on the surface of aluminium hydroxyl. In contrast, coordination bonds are formed between lutetium ions and the kaolinite surface if the surface is deprotonated, which is called an inner-sphere adsorption, and the adsorption energy is much lower than that of outer-sphere adsorption. In addition, Peng et al. [18] investigated the adsorption of $[\text{Y}(\text{OH})_2]^+$ onto the kaolinite (001) surface as a function of the pH value and found that $[\text{Y}(\text{OH})_2]^+$ ions are adsorbed onto the aluminium hydroxyl surface by coordination and electrostatic bonding, while the adsorption onto the silicon-oxygen surface is mainly through an electrostatic attraction. These works used computer simulation technology to investigate the adsorption behaviour of RE ions onto the surface of kaolinite at the atomic level and clarified the adsorption mechanism. Similar to kaolinite, Mt is a host mineral of RE ions in ion-adsorption RE ores. Therefore, it is of great significance to simulate the adsorption behaviours of RE ions and other cations onto the surface of Mt by the DFT.

In this article, the first-principles method based on the density functional theory was used to investigate the hydrated structure of Pr(III) ions in aqueous solution, and the adsorption energy, bonding mechanisms, Mulliken charge and density of the states of hydrated Pr(III) ions adsorbed onto the Mt (001) surface were studied. Based on the leaching agent used in the mining of ion-adsorption RE ores, the adsorption behaviours of hydrated magnesium ions and hydrated ammonium ions onto the (001) surface of Mt were also simulated using the DFT, which were compared with the adsorption behaviour of hydrated Pr(III) ions. In addition, to verify the accuracy of the calculation results, the

adsorption and desorption experiments of Pr(III) ions on Mt were studied. This study provides theoretical guidance for the leaching of RE ions from Mt and the selection of leaching agent cations.

2. Models and Experiments

2.1. DFT Model Methodology

First-principles calculations were performed in the framework of the DFT using the Cambridge Sequential Total Energy Package (CASTEP) (Cambridge, UK) [19–21]. The Perdew–Burke–Ernzerhof (PBE) generalised gradient approximation (GGA) was applied to analyse the exchange–correlation potentials [22]. The interactions between the nuclei and valence electrons were approximated with the Vanderbilt ultrasoft pseudopotential [23]. The cut-off energy of the plane-wave basis set was 360 eV. K-point grids ($3 \times 2 \times 1$) were used for the Mt crystal and surface models. The atomic positions were optimised using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm until the energy, atomic force and displacement converged to less than 5×10^{-6} eV/atom, 0.07 eV/Å and 0.005 Å, respectively. The system was optimised in a $15 \times 15 \times 15$ Å³ periodic box. When MS stated “Geometry optimization completed successfully”, that means the system is in equilibrium, and the “Final Enthalpy” was the energy of the system. The hydrated Pr^{3+} , NH_4^+ and Mg^{2+} complex in the centre of a silicate ring was used as the initial adsorption structure.

The stability of the hydrated species was evaluated in terms of the binding energy (E_{bind}), which is defined as follows (1):

$$E_{\text{binding}} = E_{\text{tol}} - E_{\text{Pr}} - nE_{\text{H}_2\text{O}} \quad (1)$$

where E_{binding} is the binding energy of hydrated Pr^{3+} , E_{tol} is the total energy of the hydrated Pr^{3+} system, E_{Pr} is the energy of Pr^{3+} , $E_{\text{H}_2\text{O}}$ represents the energy of H_2O and n is the number of H_2O molecules.

The feasibility of the adsorption was evaluated based on the adsorption energy (E_{ads}), which is defined as Equation (2):

$$E_{\text{ads}} = E_{\text{M/S}} - E_{\text{M}} - E_{\text{S}} \quad (2)$$

where E_{ads} represents the adsorption energy of the hydrated $\text{Pr}^{3+}/\text{NH}_4^+/\text{Mg}^{2+}$ complex, $E_{\text{M/S}}$ is the total energy of the hydrated $\text{Pr}^{3+}/\text{NH}_4^+/\text{Mg}^{2+}$ complex system after the adsorption and E_{M} and E_{S} denote the total energies of the hydrated $\text{Pr}^{3+}/\text{NH}_4^+/\text{Mg}^{2+}$ complex and Mt (001) surface, respectively.

2.2. Experimental Details

First, 5 g Mt and 125 mL of chloride praseodymium with a concentration of 2 g/L at pH 5 were mixed in a conical flask in a mechanical shaker at a speed of 180 r/min and a temperature of 25 °C for 240 min. The solution's pH was adjusted by sulfuric acid, and no other ions were added. Then, the adsorbent was separated by vacuum filtration with a sand core funnel and rinsed with deionised water several times. After that, the adsorbent was dissolved with nitric acid, hydrochloric acid, sulfuric acid and perchloric acid, and the concentration of Pr^{3+} was determined by inductively coupled plasma–optical emission spectrometry (ICP–OES). The equilibrium adsorption capacities (q_e) of the adsorbents were calculated by using the following equation:

$$q_e = \frac{m}{M} \quad (3)$$

where q_e is the adsorption capacity (mg/g) and m and M are the masses of the adsorbed Pr^{3+} and Mt, respectively.

The desorption efficiencies of Pr^{3+} from Mt by MgSO_4 and $(\text{NH}_4)_2\text{SO}_4$ were investigated with a solid/liquid ratio of 1:50 at a pH value of 2.5. In the desorption experiments, the molarity of the Mg ions was the same as that of the NH_4 ions in the range of 0.015

to 0.11 mol/L. When the desorption reached equilibrium after 240 min, the mixed liquid was vacuum filtrated with a sand core funnel, the supernatant was collected and the Pr^{3+} content was determined by ICP–OES. The desorption efficiencies were calculated by the following equation:

$$\text{Recovery (\%)} = \frac{CV}{m q_e} \times 100 \quad (4)$$

where C is the concentration of Pr^{3+} in the solution after desorption, V is the volume of the desorption solution and m and q_e are the mass and adsorption capacity, respectively, of Mt.

3. Results and Discussion

3.1. Geometries of $\text{Pr}(\text{H}_2\text{O})_n^{3+}$

Qiu et al. [17,24,25] studied the hydration numbers of hydrated La^{3+} , Y^{3+} and Lu^{3+} ions and found that the most stable hydrated structures of those RE ions have 9–10 H_2O ligands. Hence, Pr^{3+} coordination numbers larger than six were studied. Figure 1 shows the equilibrium geometric structure of $\text{Pr}(\text{H}_2\text{O})_{6-10}^{3+}$. It was found that Pr^{3+} is connected with H_2O molecules by covalent bonds. The hydrate maintains a high symmetry when the number of H_2O molecules is six, whereas the space around Pr^{3+} becomes more crowded with the increase in the number of H_2O ligands.

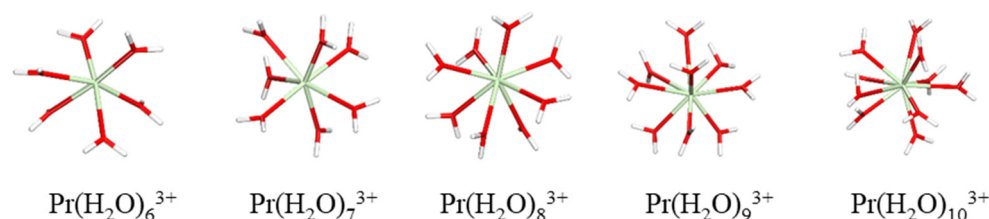


Figure 1. The equilibrium geometries of $[\text{Pr}(\text{H}_2\text{O})_{6-10}]^{3+}$ from periodic DFT calculations.

The equilibrium geometric parameters and binding energy of $[\text{Pr}(\text{H}_2\text{O})_{6-10}]^{3+}$ are shown in Table 1. The average bond length (R_{mean}) of the Pr–O bond increases with the increasing number of H_2O ligands. Because there is a steric hindrance between the H_2O ligands, which is not conducive to the subsequent coordination of H_2O and Pr^{3+} , the average bond length increases. Additionally, the bond length between one H_2O molecule and Pr^{3+} was found to be 3.03 Å when the coordination number was 10, indicating that H_2O escapes the first hydration layer of Pr^{3+} when the coordination number of H_2O is higher than 10. More H_2O ligands provide electrons to Pr^{3+} with an increasing coordination number, resulting in decreases in the charge and ionicity of the Pr^{3+} , making it more stable. In addition, the binding energy of hydrated $[\text{Pr}(\text{H}_2\text{O})_{6-10}]^{3+}$ was found to decrease with an increasing number of H_2O ligands, indicating that it becomes more stable. It was found that $[\text{Pr}(\text{H}_2\text{O})_{10}]^{3+}$ is the most stable structure with the lowest binding energy of -2680 kJ/mol, which was used as the initial structure of hydrated Pr^{3+} adsorbed on the Mt (001) surface.

Table 1. The equilibrium geometries parameters and binding energy of $[\text{Pr}(\text{H}_2\text{O})_{6-10}]^{3+}$.

n	$R(\text{Pr}-\text{O}_w)^a/\text{\AA}$	$R(\text{Pr}-\text{O}_w)_{\text{max}}/\text{\AA}$	$R(\text{Pr}-\text{O}_w)_{\text{avg}}^b/\text{\AA}$	$E_{\text{binding}}/\text{kJ}\cdot\text{mol}^{-1}$	Pr Charge/e
6	2.43	2.46	2.44	−2187	2.08
7	2.44	2.53	2.49	−2394	2.05
8	2.40	2.66	2.53	−2511	2.05
9	2.49	2.79	2.58	−2486	2.06
10	2.45	3.03	2.68	−2680	2.04

^a Distance of Pr to oxygen centre of H_2O ligands. ^b Average distance of Pr to oxygen centre of H_2O ligands.

The Mulliken charge population and difference charge density of $[\text{Pr}(\text{H}_2\text{O})_{10}]^{3+}$ are shown in Table 2 and Figure 2. Compared with a $\text{Pr}(\text{III})$ ion, the charge of hydrated Pr

decreases from +3 to +2.13, that is, Pr loses a total of 2.13 electrons; specifically, the 2s, 2p, 5d and 4f orbitals obtain 0.13 and lose 0.29, 0.17 and 1.81 electrons, respectively. As a result, the coordinated O of H₂O gains electrons overall, with a charge between −0.92 and 0.99, that maybe due to the electron density lowering of the adjacent H atoms and Pr atom. Figure 2 shows the difference charge density of [Pr(H₂O)₁₀]³⁺; the red area represents the gain of the electrons, and the blue area represents the loss of the electrons. It is obvious that the H atoms are surrounded by blue areas because they are attracted by the electronegative O atom; hence, the O atom is surrounded by a red area. There is also a blue area in the periphery of Pr, which is consistent with the results in Table 2.

Table 2. The Mulliken charge population of Pr and O in [Pr(H₂O)₁₀]³⁺.

Atom	N	S	P	D	F	Total	Charge/e
O	1	1.86	5.09	0	0	6.95	−0.95
O	2	1.86	5.07	0	0	6.93	−0.93
O	3	1.84	5.08	0	0	6.92	−0.92
O	4	1.85	5.08	0	0	6.93	−0.93
O	5	1.85	5.08	0	0	6.93	−0.93
O	6	1.85	5.08	0	0	6.93	−0.93
O	7	1.86	5.09	0	0	6.95	−0.95
O	8	1.86	5.08	0	0	6.94	−0.94
O	9	1.86	5.08	0	0	6.94	−0.94
O	10	1.85	5.14	0	0	6.99	−0.99
Pr	1	2.13	5.71	0.83	2.19	10.87	2.13

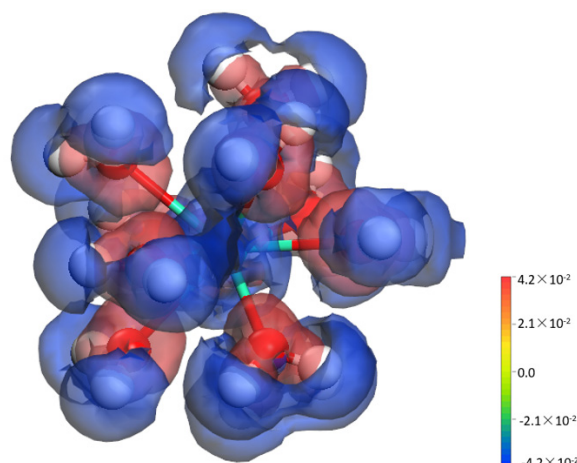


Figure 2. The difference charge density of [Pr(H₂O)₁₀]³⁺.

3.2. [Pr(H₂O)_n]³⁺ Adsorbed on the (001) Surface of Mt

The (001) surface of Mt is rich in oxygen atoms, which can form hydrogen bonds with the H₂O ligands of [Pr(H₂O)₁₀]³⁺ as this ion approaches the (001) surface. Figure 3 shows the equilibrium geometry of [Pr(H₂O)₁₀]³⁺ adsorbed on the (001) surface. Mt has a strong attraction to the positively charged [Pr(H₂O)₁₀]³⁺ due to the large number of negative charges on the surface of Mt, hence, [Pr(H₂O)₁₀]³⁺ is relatively close to the surface. As a result, four hydrogen bonds were observed between the H atom in the H₂O ligand and the surface O atom, with distances of 2.397, 1.534, 1.772 and 2.424 Å, two of which are close to the range of chemical bonds, indicating a strong interaction between [Pr(H₂O)₁₀]³⁺ and the surface. Due to the steric hindrance effect on the surface of Mt, the coordinating H₂O molecules are squeezed to varying degrees when [Pr(H₂O)₁₀]³⁺ approaches the surface; consequently, a coordinating H₂O molecule with a weak connection to the Pr atom moves away from the first hydration layer and becomes a free H₂O molecule.

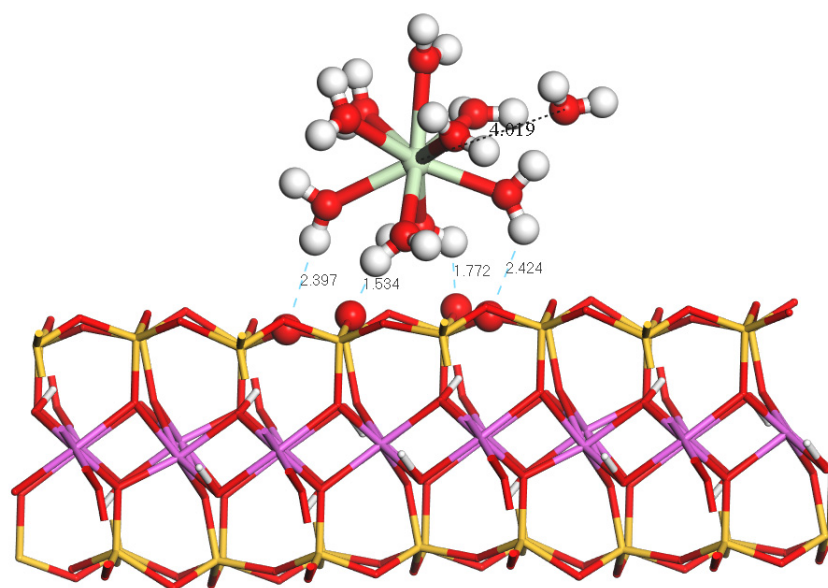


Figure 3. Equilibrium geometry of $[\text{Pr}(\text{H}_2\text{O})_{10}]^{3+}$ adsorbed on the (001) surface of Mt.

The adsorption energy and structural parameters of $[\text{Pr}(\text{H}_2\text{O})_{10}]^{3+}$ adsorbed on the (001) surface are listed in Table 3. The number of H_2O ligands of the Pr atom is reduced from 10 to 9, and the average length of the Pr–O bond is reduced from 2.78 Å to 2.59 Å after the adsorption. The adsorption energy is -1182 kJ/mol, indicating that the adsorption of $[\text{Pr}(\text{H}_2\text{O})_{10}]^{3+}$ on the (001) surface of Mt is a spontaneous exothermic process. The adsorption energy is significantly lower than the values reported by other scholars on the Si–O surface of kaolinite (-473.37 kJ/mol) [24], suggesting that the adsorption stability of RE ions on the surface of Mt is significantly higher than that on kaolinite. This is consistent with a previous study [12], showing that it is more difficult to desorb RE ions from Mt than from kaolinite.

Table 3. Adsorption energy and structural parameters of $[\text{Pr}(\text{H}_2\text{O})_{10}]^{3+}$ adsorbed on the (001) surface of Mt.

Structure	N	Pr–O/Å	Pr–O _m /Å	E _{ads} /kJ·mol ^{−1}
Before	10	2.67, 3.83, 2.67, 2.67, 2.67 2.67, 2.67, 2.67, 2.67, 2.67	2.78	−1182
After	9	2.58, 2.55, 2.59, 2.51 2.69, 2.55, 2.67, 2.62, 2.58	2.59	

The partial densities of states (PDOSs) of Pr and the (001) surface before and after adsorption are shown in Figure 4. The 4f orbital of Pr is sharp and thin near the Fermi level before the adsorption, indicating that the 4f orbital is very active because 4f belongs to the valence electron orbital of Pr, which easily gains and loses electrons. However, the 5d and 6p orbitals are in the inner layer, and the activity is lower, hence, their PDOS is far from the Fermi level. Similarly, the 2p orbital of the (001) surface is also near the Fermi level before the adsorption. Notable changes occur after the adsorption, with the 4f orbital of the Pr atom shifting towards a higher energy, which is far from the Fermi level, while the energy of the (001) surface decreases to maintain the stability of the system. Additionally, the energy scope of the Pr 4f orbital expands to 11.2–14 eV, implying that the non-locality of the Pr 4f orbital is increased, which may be beneficial for bonding. According to the Mulliken charge of Pr (Table 4), following the adsorption, the Pr 4f orbital loses 0.15 e, while the 6s and 5d orbitals lose 0.02 e and 0.06 e, respectively. The total charge of Pr increases obviously from 2.28 to 2.52. A large number of electron transfers lead to the peak shape of the density of states of the Pr atoms to change significantly.

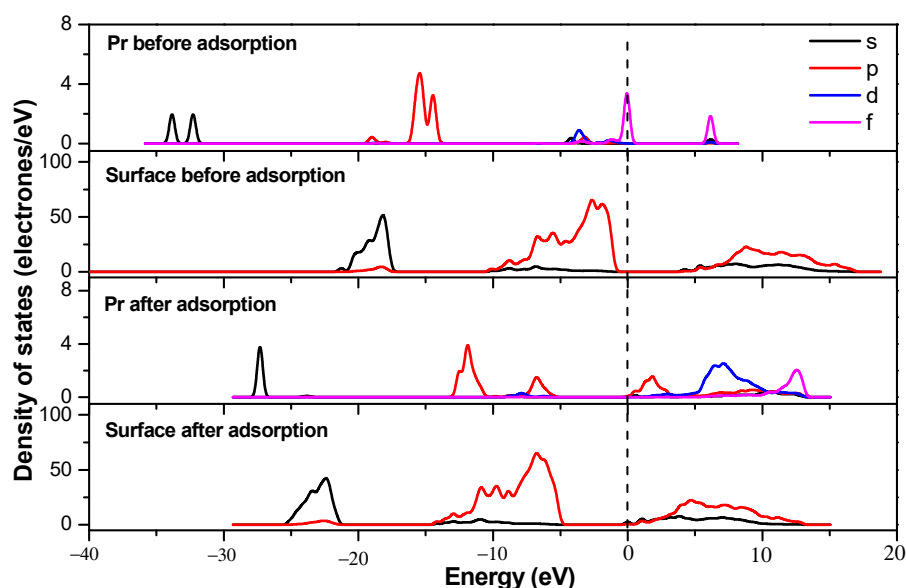


Figure 4. PDOS of Pr and (001) surface of Mt before and after adsorption.

Table 4. Mulliken charges of Pr adsorbed on the (001) surface of Mt.

Element	S	P	D	F	Total	Charge/e
Pr before	2.13	5.64	0.78	2.16	10.71	2.28
Pr after	2.11	5.64	0.72	2.01	10.48	2.52

3.3. $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ Adsorbed on the (001) Surface of Mt

A previous work [26] revealed that the most stable structure of hydrated Mg^{2+} is $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, which was used as the initial adsorption structure in this article. Table 5 shows the equilibrium geometry of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ after the adsorption on the montmorillonite (001) surface, which is similar to the adsorption of hydrated Pr ions. As shown in Figure 5, two hydrogen bonds form between the hydrogen of H_2O ligands and oxygen of the surface, with lengths of 2.016 and 2.375 Å, respectively, so that the hydrated Mg complex can be stably adsorbed on the (001) surface of Mt. According to the structural parameters and adsorption energy of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ before and after the adsorption (Table 5), the bond length of $\text{Pr}-\text{O}_w$ increases from 2.26 Å before the adsorption to 2.40 Å due to the steric hindrance. Because of the lower number of H_2O ligands in $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ than in $[\text{Pr}(\text{H}_2\text{O})_9]^{3+}$, no H_2O ligands escape from the first hydration layer of Mg^{2+} ions after the adsorption.

The calculation results show that the adsorption energy of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ on the (001) surface of Mt is -206 kJ/mol, which is much lower than that of $[\text{Pr}(\text{H}_2\text{O})_{10}]^{3+}$ (-1182 kJ/mol), indicating that it is difficult to thermodynamically desorb Pr^{3+} ions from Mt by Mg^{2+} ions; thus, dynamic approaches should attract more attention, such as enhancing the concentration of the leaching agent, which may be beneficial for the desorption. Additionally, the calculation results also show that Pr^{3+} is prone to a reverse adsorption if the concentration of Mg^{2+} ions is the same as that of Pr^{3+} ions. Hence, it is necessary to maintain the concentration of the leaching agent in a high range to prevent the reverse adsorption of rare earth ions.

Figure 6 shows the PDOSs of Mg^{2+} and the (001) surface before and after adsorption. The 2s and 2p orbitals of the Mg^{2+} ion were far from the Fermi level before adsorption because the ionic radius of Mg^{2+} is short and it has difficulty gaining and losing electrons. After the adsorption, the 2p orbital of the Mg^{2+} ion obviously moved in the lower energy direction away from the Fermi level. Additionally, the 2s and 2p orbitals of the (00) surface also moved away from the Fermi level in the lower energy direction, and the intensity was obviously weakened, indicating that the energy of the system decreased, and it became more stable after the adsorption. The Mulliken charges of Mg^{2+} are listed in Table 6. The 2s

and 2p orbitals of the Mg^{2+} ion lost 0.04 e and 0.06 e, respectively, and the charge increased from 1.68 to 1.78.

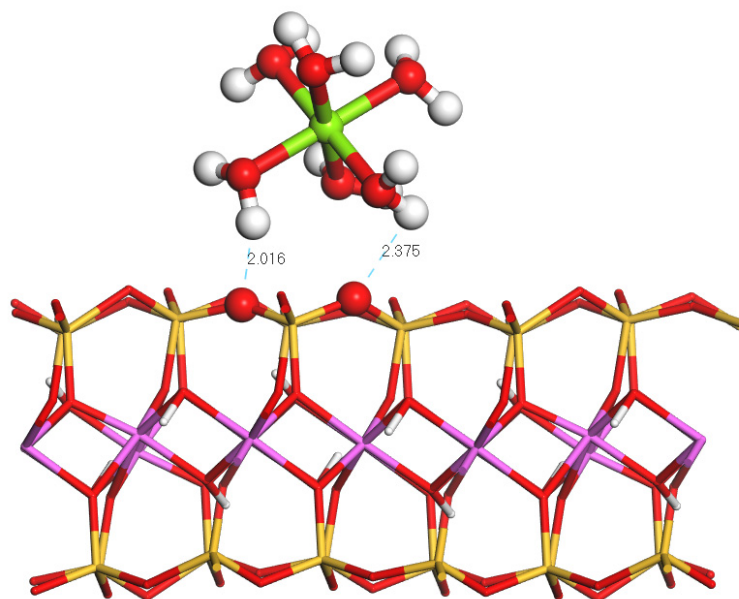


Figure 5. Equilibrium geometry of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ adsorbed on the (001) surface of Mt.

Table 5. Adsorption energy and structural parameters of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ adsorbed on the (001) surface of Mt.

Structure	N	Mg-O/Å	Mg-O _m /Å	E _{ads} /kJ·mol ^{−1}
Before	6	2.26, 2.26, 2.26 2.26, 2.26, 2.26	2.26	−206
After	6	2.31, 2.41, 2.42 2.47, 2.46, 2.33	2.40	

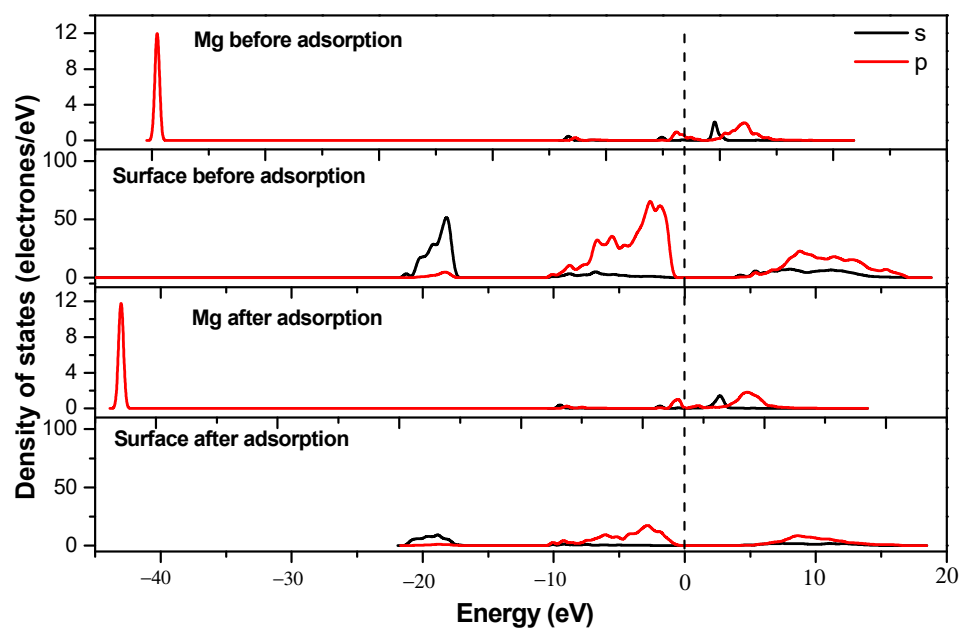


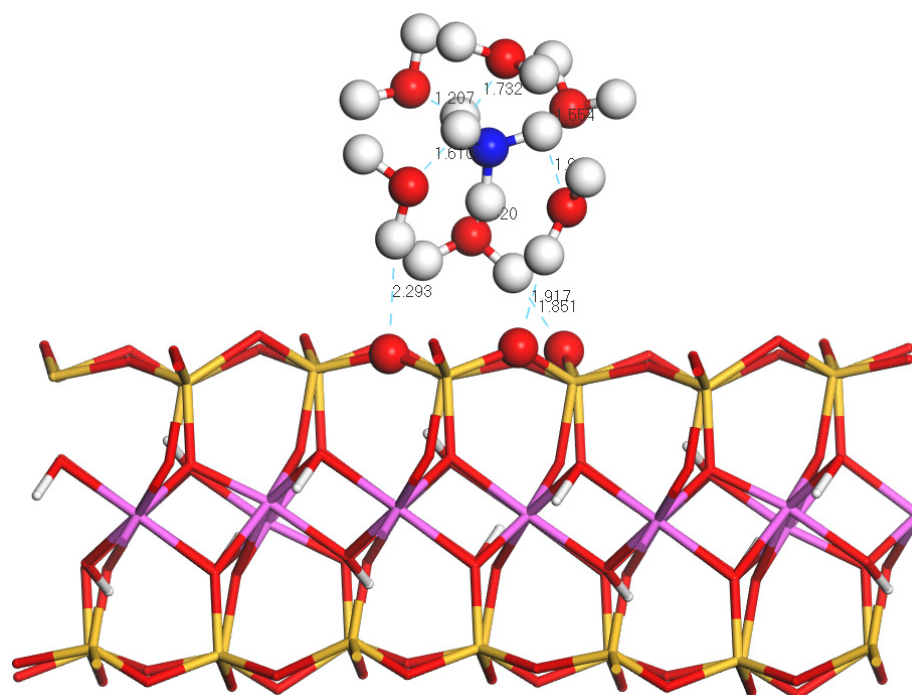
Figure 6. PDOS of Mg and (001) surface of Mt before and after adsorption.

Table 6. Mulliken charges of Mg adsorbed on the (001) surface of Mt.

Element	S	P	D	F	Total	Charge/e
Mg before	0.33	5.99	0	0	6.32	1.68
Mg after	0.29	5.93	0	0	6.22	1.78

3.4. Hydrated NH_4^+ Adsorbed on the (001) Surface of Mt

Different from Mg^{2+} , NH_4^+ interacts with H_2O ligands through hydrogen bonds; in simulations, the coordination number of NH_4^+ was found to be approximately five [27,28], whereas the experiments indicated that the coordination number is larger [29]. Hence, the coordination number of NH_4^+ was chosen to be six, which is beneficial for a comparison with Mg^{2+} . The equilibrium geometry of hydrated NH_4^+ after the adsorption is shown in Figure 7. Although there were no coordination bonds between the NH_4^+ ion and H_2O , several hydrogen bonds formed. The hydrogen bonds were very short, with lengths ranging from 1.207 Å to 1.943 Å, indicating a strong interaction between the NH_4^+ ion and H_2O ligands. In addition, three hydrogen bonds formed between the H_2O ligands and surface O, with an adsorption energy of -188 kJ/mol. This adsorption energy is more positive than that of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, indicating that the adsorption stability of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ is higher than that of the hydrated NH_4^+ ion, that is, the desorption efficiency of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ for RE ions is stronger than that of the hydrated NH_4^+ ion. Similar to $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, the adsorption energy of the hydrated NH_4^+ ion is much lower than that of $[\text{Pr}(\text{H}_2\text{O})_{10}]^{3+}$ (-1182 kJ/mol). Hence, it is difficult to thermodynamically desorb Pr^{3+} ions from Mt by NH_4^+ ions.

**Figure 7.** Equilibrium geometry of hydrated NH_4^+ adsorbed on the (001) surface of Mt.

The PDOSs of NH_4^+ and the (001) surface before and after the adsorption are shown in Figure 8. Since there were no coordination bonds between the NH_4^+ ion and H_2O , the PDOS of the NH_4^+ ion showed almost no change after the adsorption. In contrast, the PDOS of the surface shifted towards the lower energy direction, and its 2s and 2p orbitals were obviously far away from the Fermi level. The change in PDOS indicated that the system became more stable after the adsorption. The Mulliken charge of N is listed in Table 7. Similar to the slight change in the PDOS, the electron transfer of the N atom was

very low, and its 2s and 2p orbitals only obtained 0.01 e and 0.05 e, respectively. The N atom obtained 0.06 e, and the charge decreased from -0.79 to -0.81 after the adsorption.

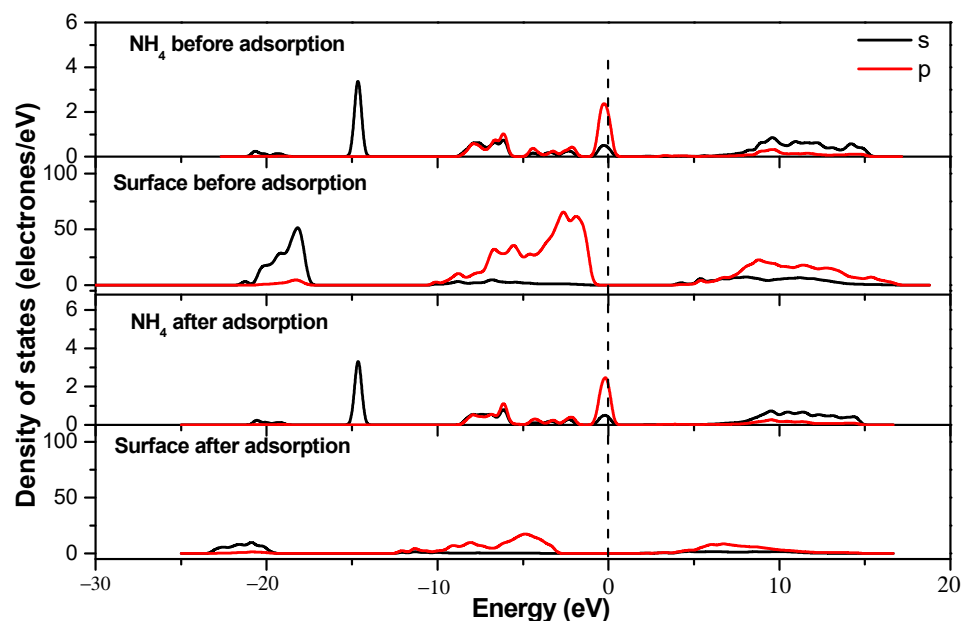


Figure 8. PDOS of NH_4 and (001) surface of Mt before and after adsorption.

Table 7. Mulliken charges of NH_4 adsorbed on the (001) surface of Mt.

Element	S	P	D	F	Total	Charge/e
N before	1.63	4.15	0	0	5.79	-0.79
N after	1.64	4.17	0	0	5.81	-0.81

3.5. Desorption Efficiencies of Mg^{2+} and NH_4^+

A series of desorption experiments were carried out to verify the DFT calculation result that the desorption efficiencies of Mg^{2+} are higher than those of NH_4^+ . Raw Mt was mixed with a chloride praseodymium solution to obtain Pr-Mt, which was used in the desorption process. Figure 9 shows the recovery of Pr^{3+} from Mt as a function of the $\text{NH}_4^+/\text{Mg}^{2+}$ concentration. The recoveries of Pr^{3+} were 55% and 80%, while the concentrations of Mg^{2+} were 15 mmol/L and 38 mmol/L, respectively, which were much higher than those of NH_4^+ (23% and 65%), whereas the desorption efficiencies of NH_4^+ and Mg^{2+} were equal under high concentrations. The concentrations of NH_4^+ , Mg^{2+} and Pr^{3+} in lixivium are listed in Table 8. The concentration of Pr^{3+} was only 1.64 mmol/L (with a recovery of 55%), while the concentration of Mg^{2+} was 15 mmol/L, which was nearly ten times larger than that of Pr^{3+} . Additionally, the concentration of NH_4^+ was forty times larger than that of Pr^{3+} , while the recovery was 95%. These results imply that the desorption efficiency of Mg^{2+} is higher than that of NH_4^+ and that the concentration of $\text{NH}_4^+/\text{Mg}^{2+}$ should be much higher than that of Pr^{3+} in the desorption process, which is consistent with the DFT calculation result that the adsorption stability of hydrated magnesium ions is higher than that of hydrated NH_4^+ , which is lower than that of Pr^{3+} .

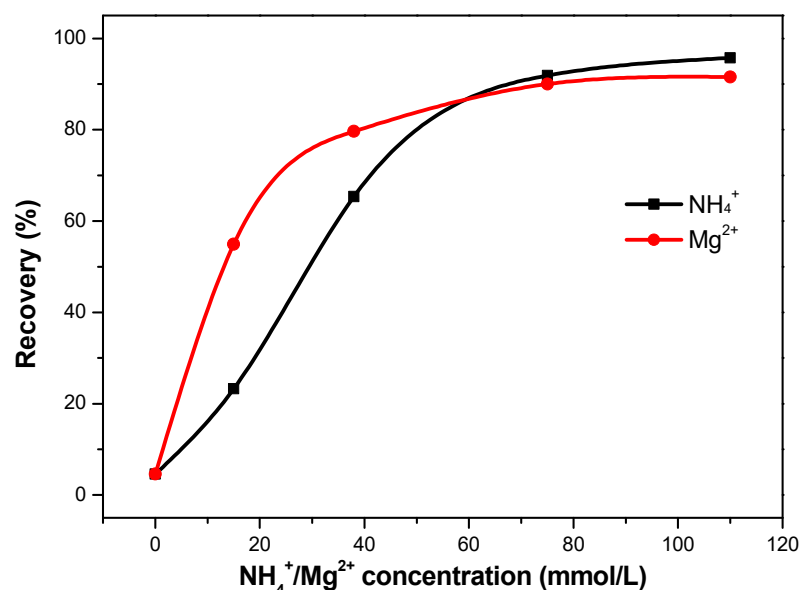


Figure 9. Influence of $\text{NH}_4^+/\text{Mg}^{2+}$ concentration on the recovery of Pr^{3+} from Mt.

Table 8. Concentration of NH_4^+ , Mg^{2+} and Pr^{3+} in desorption solution.

$\text{NH}_4^+/\text{Mg}^{2+}$ (mmol/L)	0	15	38	75	110
Pr^{3+} desorbed by NH_4^+ (mmol/L)	0.03	0.69	1.95	2.74	2.85
Pr^{3+} desorbed by Mg^{2+} (mmol/L)	0.03	1.64	2.37	2.68	2.73

4. Conclusions

The first-principles method based on the plane-wave pseudopotential DFT was applied to investigate the adsorption of hydrated Pr^{3+} , Mg^{2+} and NH_4^+ ions onto Mt. The DFT calculations showed that Pr^{3+} ions tend to coordinate with ten H_2O molecules with a binding energy of -2680 kJ/mol in aqueous systems. $[\text{Pr}(\text{H}_2\text{O})_{10}]^{3+}$ was adsorbed on the Mt (001) surface through four hydrogen bonds, with a negative adsorption energy of -1182 kJ/mol. One H_2O ligand escaped from the first hydration layer of the Pr ion after the adsorption. Similarly, $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ and the hydrated NH_4^+ ion were also adsorbed onto the Mt (001) surface through hydrogen bonds, and the adsorption energies were -206 and -188 kJ/mol, respectively, implying that the adsorption stability of $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ was slightly higher than that of the hydrated NH_4^+ ion, while both were lower than that of $[\text{Pr}(\text{H}_2\text{O})_{10}]^{3+}$ (-1182 kJ/mol), indicating that the desorption of Pr^{3+} from Mt by Mg^{2+} and NH_4^+ ions was thermodynamically difficult and that much higher concentrations of Mg^{2+} and NH_4^+ ions were necessary. These DFT conclusions have also been confirmed by desorption experiments: the desorption efficiency of Mg^{2+} is higher than that of NH_4^+ , and the concentration of $\text{NH}_4^+/\text{Mg}^{2+}$ should be much higher than that of Pr^{3+} in the desorption process.

However, the theoretical investigation of RE ions desorbed from the surface of clays would be improved in the future research work, while a molecule dynamic simulation, which is a supplement for the DFT, would be an important method.

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