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Investigation of Adsorption of Nd(III) on Boron Nitride Nanosheets in Water

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ABSTRACT

In this paper, boron nitride materials were prepared by a two-step synthesis method, and this material's adsorption property for neodymium ions was explored. The experimental results show that the adsorption capacity of boron nitride is closely related to pH. When the pH is 6.0, the adsorption performance of the material is the best; the kinetic data show that the adsorption equilibrium can be reached in about 150 min, and the adsorption capacity at equilibrium is 207.3 $mg.g^{-1}$. In addition, the Freundlich and Langmuir models were used to fitting the thermodynamic results. It was found that the adsorption process of boron nitride on Nd(III) involved both monolayer adsorption and multi-layer adsorption. These data indicate that boron nitride has a good adsorption effect on Nd(III) in water and is a promising material for environmental remediation.

INTRODUCTION

In recent years, with the rapid development of science and technology, the demand for rare earth elements continues to increase. Neodymium is a rare earth element often used to prepare Nd-Fe-B permanent magnet materials (Kamimoto et al. 2017) for energy storage and constant magnetic field generation. In addition, neodymium is also commonly used in the doping modification of materials (Wojcieszak et al. 2012) and in tracking isotopic elements (Wilson et al. 2012). Although Nd(III) plays a key role in many fields, such as permanent magnet materials, we must face the harm caused by Nd(III) pollution. Industrial sewage containing rare earth elements has caused serious environmental pollution (Zhao et al. 2021). Rare earth elements can induce human respiratory, cardiovascular, and nervous diseases (Shin et al. 2019). Therefore, how to remove neodymium from the environment has caused extensive research. At present, methods for removing Nd from wastewater have been widely reported. Among these methods, adsorption is feasible due to its high removal rate and simple operation. The core of the adsorption method lies in the adsorbent. The common materials used for adsorption are carbon, zeolite, clay, polymeric materials, etc. At the same time, new adsorption materials are constantly being developed and applied.

Boron nitride (BN) has great development potential because of its excellent properties, such as high mechanical strength, good electrical insulation, oxidation resistance, etc. (Kim et al. 2018). Due to its special properties, the application field of BN has gradually expanded in recent years. Researchers such as Lale have explored the hydrogen storage capacity of BN (Lale et al. 2018). An's research group prepared graphene/boron nitride composite aerogels (An et al. 2017), and BN is even used as a nanocarrier for anticancer drugs (Emanet et al. 2017). BN is also often used in adsorption and to adsorb heavy metal ions and organic dyes (Yu et al. 2017). Song studied the removal performance of BN materials for antibiotic pollutants in water (Song et al. 2017). Li et al. used BN materials to study the adsorption of metal ions such as Cr^{3+}, Co^{2+}, and Ni^{2+} and organic pollutants such as tetracycline, methyl orange, and Congo red (Li et al. 2013). In summary, this paper uses BN materials to conduct adsorption experiments on Nd to explore the effect of different adsorption conditions on the adsorption performance of BN.

This paper investigated the adsorption capacity of BN on Nd(III) ions in wastewater. SEM, TEM, XRD, and FT-IR analyzed the morphology and structure of BN material. Subsequently, the kinetic and thermodynamic experimental data were fitted to propose a possible adsorption mechanism.

MATERIALS AND METHODS

Experimental Materials and Preparation of BN

The chemical reagents used in this experiment were all

analytical reagent grade without further purification. This experiment used a two-step synthesis method to prepare BN adsorbents (Li et al. 2020). The melamine and boric acid are mixed uniformly according to the molar ratio of 1:2 and calcined in a muffle furnace for 1 hour, the temperature is constant at 1373K, and the product is obtained by natural cooling. All reagents used in the experiments were prepared with deionized water.

Characterization

In this study, the scanning electron microscope (SEM) of Japan Electronics (JEOL) and JSM-6360LV were used to characterize the surface morphology of BN materials. Transmission electron microscopy (TEM) can be used to observe the finer structure of the sample and the microstructure inside the material. After uniformly dispersing the samples, our team used the JEM-101 transmission electron microscope of Japan Electronics Corporation for TEM characterization. The X-ray energy dispersive spectrometer (XRD), manufactured in Panaco, Netherlands, with the model Empyrean, is used to determine the crystal form of BN materials. The Fourier infrared spectrometer (NICOLET6700) of Thermoelectric Technology Company of the United States determined the molecular structure and chemical composition of BN samples, such as functional groups. The spectra ranged from 400 to 4000 cm^{-1}, and the resolution was better than 4 cm^{-1}.

Batch Adsorption Experiments

Herein, neodymium nitrate hexahydrate was used as Nd(III) source to prepare Nd(III) stock solution. Test solutions of different concentrations needed to be obtained by diluting the stock solution. To adjust the acidity and alkalinity of the solution and explore the effect of the best acidity and alkalinity environment on the adsorbent's performance, it is necessary to add a small amount of HCl and NaOH to adjust the pH of the solution. After adjusting the pH of the solution, a certain amount of BN adsorbent was added, and it was fully shaken at 303.0 K for 12 h to ensure that the adsorption equilibrium was reached. Finally, the solution was separated through a 0.22-μm polyethersulfone membrane filter. In the adsorption kinetics of BN on Nd(III), the pH of the solution was adjusted to 6, and the test solution was taken out at certain intervals. To obtain the adsorption isotherm, the temperature was set at 303.0 K and 313.0 K in the experiment, the solution was obtained by subsequent separation, and the concentration of neodymium ions was determined by spectrophotometry at 632 nm. The performance of BN is reflected by the amount of Nd(III) adsorbed on the adsorbent per unit weight (adsorption capacity, q). The adsorption capacity at any time t and the adsorption capacity at equilibrium are denoted by q_t and q_e($mg.g^{-1}$), respectively. C_0 is the initial concentration of the solution, the concentration at time t and the concentration at equilibrium time are C_t and C_e, respectively, V(L) is the volume of the solution, and m (g) is the amount of adsorbent. The calculation formula for the relevant parameters is as follows:

$$q_t = \frac{C_0 - C_t}{m} V \quad \ldots(1)$$

$$q_e = \frac{C_0 - C_e}{m} V \quad \ldots(2)$$

RESULTS AND DISCUSSION

Adsorption

To explore the effect of the initial pH of the neodymium stock solution on the BN adsorption performance, we adopted a batch experiment, adding 10 mg BN adsorbent to 100 ml of 50 $mg.L^{-1}$ Nd(III) solutions with different initial pH. The results are shown in the figure. Fig. 1A shows that as the pH of the solution increases, the adsorption effect is significantly improved. Still, Fig. 1B shows that, without adding adsorbent, when the pH is greater than 7, the solution's residual Nd(III) content will also be greatly reduced. This is because when the hydrogen ion concentration in the solution is low, Nd(III) will form precipitation, which greatly interferes with the adsorption. Considering the above two situations, we believe that pH 6 is the most suitable, and we set the initial pH of the subsequent experiments to 6.

Fig. 2A shows the change curve of the adsorption amount of BN on Nd(III) with contact time. It can be seen that the adsorption amount of BN increases rapidly before 60 min, and the adsorption amount increases more rapidly in the range of 60-150 min. Slowly, the adsorption equilibrium was reached at about 150 min, and the maximum adsorption capacity was 207.3 $mg.g^{-1}$. Through the adsorption process, the adsorption results can be predicted and verified according to the change of the adsorption amount with contact time. Herein, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models are used to fit the experimental data. They can be expressed as linearized formulas (3-5) (Ho & McKay 1999, Ho 2006).

$$ln\,(q_e - q_t) = lnq_e - k_1 t \quad \ldots(3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \ldots(4)$$

$$q_t = K_d \times t^{1/2} + I \quad \ldots(5)$$

Herein, K_1(min^{-1}) and K_2($g\ mg^{-1}min^{-1}$) are the rates of first, and second-order adsorption constants and K_d($g\ mg^{-1}min^{-1/2}$) is the rate constant of intraparticle

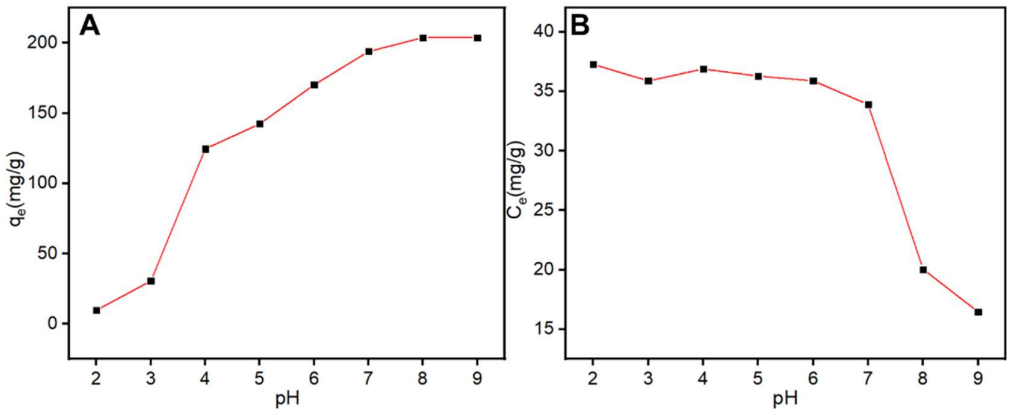

Fig. 1: Effect of initial pH value on BN adsorption capacity (q_e) (A), the residual concentration (C_e) of Nd(III) solution under different pH conditions (B).

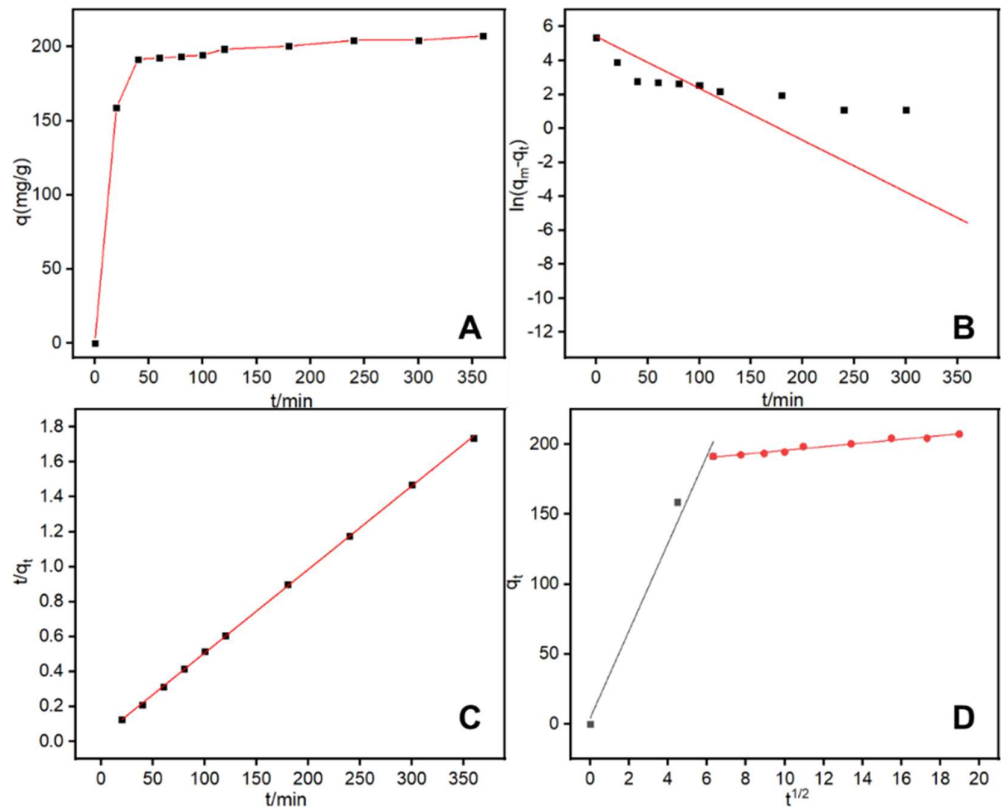

Fig. 2: Adsorption time curve of BN on Nd(III) solution (A), pseudo first order model (B), pseudo Second Order Model (C), intraparticle Diffusion Model (D), experimental conditions: initial pH is 6, C=40 mg L^{-1}, m=20 mg, V=100 mL.

diffusion. I is the rate constant with the boundary Layer thickness-related parameters; the greater the thickness of the boundary layer, the greater the value of I will be. The relevant parameters of kinetic fitting are shown in Table 1. By comparing the experimental data of pseudo-first-order fitting and pseudo-second-order fitting, it is found that the pseudo-second-order model best describes the adsorption of neodymium ions by BN. Among them, chemisorption is dominant (Shan et al. 2020). To further explore the adsorption mechanism of BN on neodymium ions, an intra-particle diffusion model was used for fitting. The result is shown in Fig. 2D. It can be seen that the adsorption process

Table 1: Adsorption kinetic model parameters.

Nd(III)/BN	Model							
	Pseudo first order		Pseudo second order		Intra-particle diffusion			
Parameters	q_e [mg.g^{-1}]	224.856	q_e [mg.g^{-1}]	209.643	I_1	4.320	I_2	182.544
	K_1	0.031	K_2 [g.mg^{-1} .min^{-1}]	7.58×10^{-4}	K_{d1}	31.239	K_{d2}	1.316
	R^2	0.560	R^2	0.999	R^2	0.967	R^2	0.967

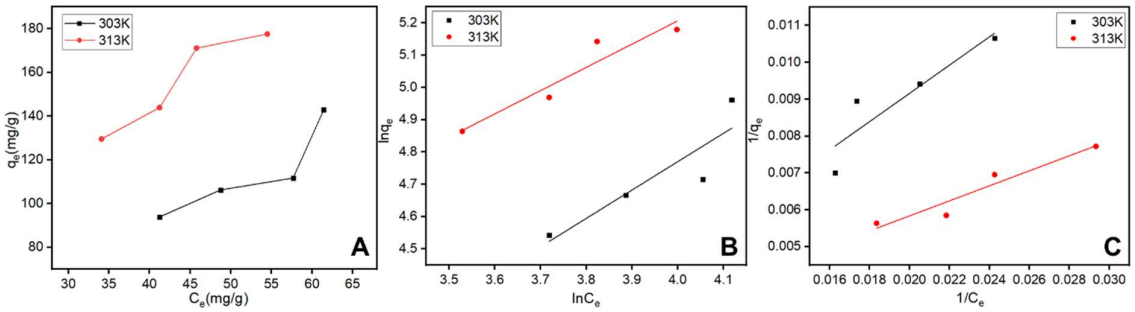

Fig. 3: Adsorption isotherms of BN on Nd(III) at T=303K and 313 (A), Freundlich model (B), Langmuir model(C), experimental conditions: initial pH is 6, m=20 mg, V=100 mL.

of BN is mainly divided into two stages. The first stage has a large slope and a short duration, indicating that the main adsorption process in this stage is the diffusion of neodymium ions to the material's surface to complete the adsorption. In the second stage, the slope is small, and the adsorption equilibrium is reached.

The adsorption isotherm describes the relationship between the adsorption capacity (q_e) and the adsorbent's equilibrium concentration (Ce) at equilibrium, which is very important for analyzing the adsorption process. Further, speculating on the adsorption mechanism (Li et al. 2014), Fig. 3 A shows the adsorption isotherms of BN for Nd(III) at 303K and 313K. It can be seen from the figure that with the increase of the remaining concentration, the adsorption capacity of the adsorbent is improved, which means that the higher concentration is favorable for the adsorption of BN. In addition, the increase in temperature also significantly improved the adsorption performance of the material, indicating that high temperature is beneficial to adsorption.

Table 2: Adsorption isotherm model parameters.

Nd(III)/BN	Model			
	Freundlich		Langmuir	
303K	1/n	1.138	q_m	666.667
	K_F	3.507	K_L	0.00392
	R^2	0.800	R^2	0.823
313K	1/n	1.388	q_m	568.182
	K_F	10.222	K_L	0.00864
	R^2	0.911	R^2	0.925

To gain a deeper understanding of the adsorption mechanism of BN, we adopted the Freundlich model and the Langmuir model, and the results are shown in Fig. 3B and Fig.3C. The linearization formulas of these two models are as follows 6-7) :

$$lnq_e = lnK_F + nlnC_e \quad \ldots(6)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L \times q_m} \cdot \frac{1}{C_e} \quad \ldots(7)$$

K_F((mg^{1-n}·L^n)/g) and n are constants of the Freundlich model, K_F reacts to the adsorption capacity, and n is a nonlinear factor corresponding to the heterogeneous energy of the adsorption surface. q_m(mg g^{-1}) is the maximum adsorption capacity of the adsorbent, and K_L(L.mg^{-1}) is a constant of the Langmuir model, which is related to the stability of the binding site. Fig. 3B and Fig. 3C are the fitting results of the isotherm model, and the relevant parameters are shown in Table 2. The fitting of the two models is not in good agreement with the experimental results. The main reason is that the adsorption mechanism of BN on Nd(III) is complex, including both monolayer adsorption and multi-layer adsorption.

Characterization

To determine the morphology and structure of BN material, it was characterized by SEM and TEM. Fig. 4A and B are SEM characterization images of BN. It can be seen from the figure that BN material is overall flaky, with some defects and protrusions on the surface. These characteristics are conducive to improving the adsorption capacity of materials.

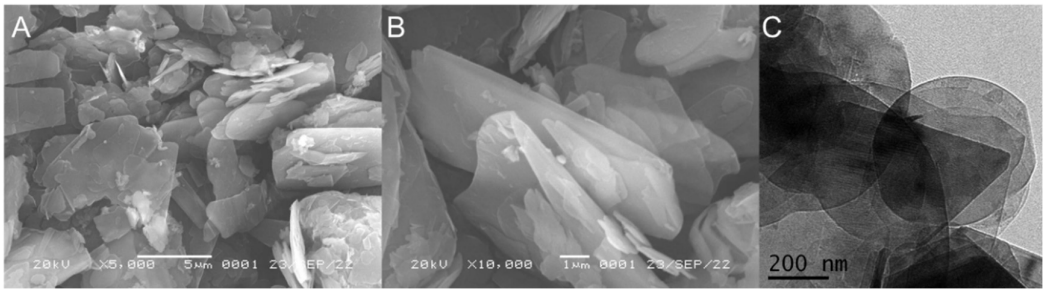

Fig. 4: SEM imagine (A, B) and TEM imagine (C) of BN.

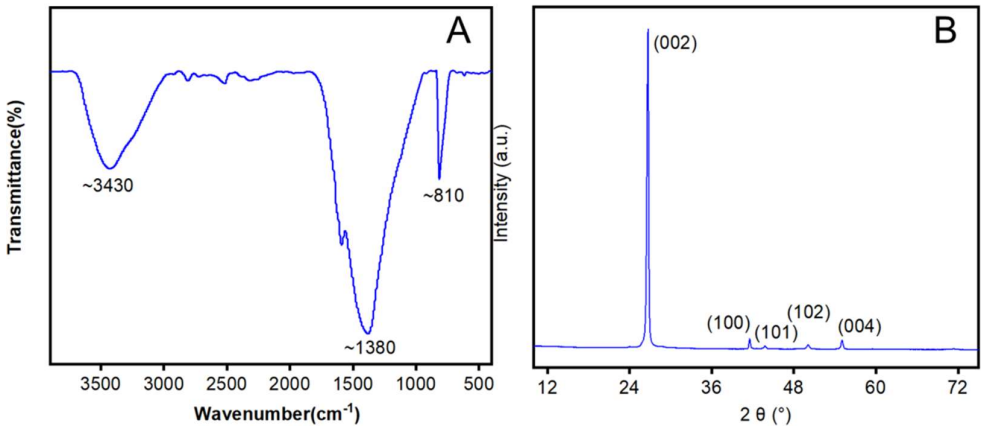

Fig. 5: FTIR spectra (A) and XRD pattern (B) of BN.

It can be seen from Fig. 4C that BN is an elliptical or circular sheet material, and the darker part in the figure is due to the overlapping of multi-layer sheet materials.

To determine the molecular structure and chemical composition of BN materials, such as functional groups, FT-IR was used to characterize them. The result is shown in Fig. 5A. Two characteristic absorption peaks were found at ~1380 and ~810cm^{-1}. According to the literature, the peaks were generated by B-N-B and B-N bending vibrations (Zhang et al. 2021). At ~3430cm^{-1}, a prominent broad peak may be because BN contains more - OH groups (Hou et al. 2019). Figure 5B is the XRD of BN material. The crystal plane diffraction peaks of BN appear at 26.7°, 41.5°, 43.8°, 50.1°, and 55.0° and correspond to the 002, 100, 101, 102, and 004 crystal planes of BN, respectively, which is consistent with the standard card 00-045-0893 (Matović et al. 2016).

CONCLUSION

Based on the above experiments and analysis, the BN material was prepared by a two-step synthesis method. The adsorption performance and mechanism of BN material for Nd (III) ions were investigated. The experimental results showed that the adsorption capacity of BN was closely related to pH, and when pH was 6, the adsorption capacity of BN was the best; The kinetic data showed that the adsorption rate of BN was very fast in the first 50 min, and gradually decreased in the following 50 min. The adsorption balance could be reached in about 150 min. The adsorption amount in equilibrium was 207.3 mg.g^{-1}.

Moreover, the kinetic data of BN well fitted the pseudo-second-order model, indicating that the adsorption process was dominated by chemical adsorption. In addition, the Freundlich and Langmuir models were used to fit and analyze the thermodynamic results. It was found that the adsorption process of BN on Nd (III) involves both monolayer adsorption and multilayer adsorption. SEM, TEM, FT-IR, and XRD also show that the surface morphology and functional groups of BN materials are conducive to improving their adsorption performance. In conclusion, BN is a low-cost material and a simple preparation method. It has a good adsorption effect for Nd (III) ions and has certain application prospects.

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