

Article

Mechanism of Nitrogen Removal from Aqueous Solutions Using Natural Scoria

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Abstract: The efficiencies and mechanisms of nitrogen removal from groundwater by scoria were studied. When NH_4^+ -N concentration was 0.5–10 mg/L, the removal was 96–89%. When NO_2^- -N concentration was 0.1–5 mg/L, the removal was 93–85%. When NO_3^- -N concentration was 30–150 mg/L, the removal was 85–70%. Additionally, van der Waals forces had a positive impact on the adsorption, which promoted NH_4^+ -N adsorption. Ion exchange and dissolution did not exist. Functional groups of N-H, C-H, and C-N changed after adsorption. Overall, this study indicates that scoria is an ecologically friendly and safe material that can be utilized for groundwater purification to treat nitrogen-contaminated water.

Keywords: scoria; adsorption; nitrogen; mechanism; characterization

1. Introduction

The rapid development of industry and agriculture has led to increasing ecological and environmental problems. As a result, the need for water pollution treatment has become urgent [1]. Moreover, the extensive use of chemical fertilizers in agriculture has led to groundwater nitrogen pollution [2]. According to the Chinese hygienic standard for drinking water (GB5749-2006), the maximum allowable levels of ammonia nitrogen, nitrite nitrogen, and nitrate nitrogen in drinking water are 0.5, 1, and 20 mg/L, respectively. Many technologies, such as adsorption [3,4], biological denitrification [5,6], chemical precipitation [7,8] and ion exchange [9], have been applied to remove nitrogen from wastewater. For the removal of nitrogen in groundwater, adsorption [10] and biodegradation [11] are relatively commonly used. Adsorption methods have the advantages of being simple, rapid, and reasonably priced, with excellent treatment capacity [12,13]. Accordingly, the adsorption method is widely used in the treatment of ammonia nitrogen- and nitrate nitrogen-contaminated groundwater [14,15]. Using the correct materials is essential in the application of adsorption technology. The main materials used for ammonia nitrogen removal are zeolite [16], modified zeolite [17,18], coal gangue [19], and carbon [20]. These materials all have different abilities with respect to the removal of ammonia nitrogen and the interaction mechanisms were analyzed. The main minerals used for nitrate nitrogen removal are modified zeolite and charcoal. Guaya et al. modified natural zeolite with Fe(III) and Mizuta et al. made charcoal from bamboo manufacturing residue [15,21]. However, few methods of nitrite removal by adsorption have been reported, and information regarding the adsorption of ammonia nitrogen, nitrate nitrogen, and nitrite nitrogen using the same material is particularly lacking.

A large number of nitrogen compounds will lead to eutrophication of lakes and rivers which can cause death of microorganisms and fish. Furthermore, excessive nitrogen ingestion can do harm to the

human body. Nitrate and nitrite may form into N-nitroso compounds, which are carcinogenic and mutagenic. Consequently, blue-baby syndrome, stomach tumor growth, and cancer may develop [2]. For economically disadvantaged areas, especially which use groundwater as drinking water, nitrogen pollution treatment has become a very urgent issue.

Scoria is a basaltic vacuolar pyroclastic rock that is lightweight. As a natural adsorption material, it can be applied to treat and remediate water. Scoria is available in large reserves at a reasonable price and is easy to obtain. Especially, it is environmentally friendly and there is no secondary pollution in the process of purifying water. Scoria was studied for its potential to adsorb Zn^{2+} and Cu^{2+} from water [22,23]. Moreover, petroleum hydrocarbons and fluoride removal were investigated [24–26]. In this study, an adsorption efficiency experiment was conducted to evaluate the removal of nitrogen pollution from groundwater using scoria, and the adsorption mechanism was systematically investigated. To accomplish this, scoria was characterized. The interaction between scoria and nitrogen was then evaluated and found to occur via physical action and chemical action. The results of this study indicate that scoria is an environmentally friendly material that can be utilized in groundwater remediation technology. Moreover, the results presented herein provide a basis for the subsequent application of scoria in actual water pollution treatment engineering projects.

2. Materials and Methods

2.1. Materials

Scoria is a lightweight aggregate formed during volcanic eruptions that consists mainly of porous and vesicular volcanic glass and basaltic minerals. The scoria used in the experiments was purchased in Northeast China and had a gray and black appearance. The scoria adsorbent is shown in Figure 1.



Figure 1. Scoria adsorbent.

2.2. Characterization of Scoria

The specific surface area, pore size distribution, and porosity were determined using a surface area and porosity analyzer (3H-2000PS1, Bei Shi De Instrument Technology Co. Ltd., Beijing, China). The loose bulk density was detected (RZ-100, Meiyu Corporation, Shanghai, China). Radioactive elements in the samples were detected using a γ energy spectrometer (CIT3000, Hongda Corporation, Luancheng, Hebei, China). Scanning electron microscopy (SEM) (JSM-6700F, JEOL Ltd., Tokyo, Japan) was employed to obtain the surface features. In addition, energy-dispersive X-ray spectroscopy (EDX) (JSM-6700F, JEOL Ltd., Tokyo, Japan) was used to determine the chemical elements. The characteristics before and after adsorption were compared.

2.3. Static Adsorption Experiments

Nitrogen solution in experiments was prepared by dissolving analytical-grade NH_4Cl , NaNO_2 , and NaNO_3 , respectively. Solution concentrations were set as follows: $\text{NH}_4^+\text{-N}$: 0.5, 1, 2, 5, 10, 100, 200, 300, 400 mg/L; $\text{NO}_3^-\text{-N}$: 30, 50, 80, 100, 150, 300, 400 mg/L; and $\text{NO}_2^-\text{-N}$: 0.1, 0.5, 1, 2, 5, 100, 200, 300 mg/L. Then $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, and $\text{NO}_3^-\text{-N}$ mixed solution was used and concentration was 5, 10 and 50 mg/L respectively. A total of 50 mL nitrogen solution was added into 100 mL glass bottles, after which scoria (1.00 g) was added. Bottles were shaken at 10 °C and 100 rpm. The nitrogen solution was then sampled every 10 min over 0–60 min.

2.4. Interaction between Scoria and Nitrogen

2.4.1. Physical Action

2.4.1.1. Van der Waals Force

A laser particle size analyzer (Mastersizer 2000, Melvin Corporation, Shanghai, China) was used to sieve and grade scoria of particles sized 0.25 mm–0.5 mm, 0.5 mm–0.75 mm, 0.75 mm–1.00 mm, and mixed size, and a particle size gradation curve and surface area parameter were attained. The $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, and $\text{NO}_3^-\text{-N}$ concentration was set at 5, 5, and 100 mg/L. In the beginning, nitrogen solution (50 mL) was added into 100 mL glass bottles and scoria (1.00 g) was added. Then the bottles were shaken in a shaking incubator at 10 °C and 100 rpm for 30 min to allow the solution to reach equilibrium. Finally, samples were collected and the nitrogen concentrations were measured, after which the removal percentages were compared.

2.4.1.2. Electrostatic Force

The salt titration method [27] was used and an analysis curve was attained. The zero point of charge was calculated by the curve and the pH range was analyzed with a positive charge and a negative charge. The interaction between scoria and nitrogen was analyzed and utilized to determine if it was related to the electrostatic force. Salt titration was conducted by adding 0.10 g of a scoria sample into 50 mL centrifuge tubes, after which 0.01 mol/L HCl or NaOH solution and a moderate amount of distilled water was added until the final volume was 10 mL, so that the pH distribution was in the proper range (1–6). The samples were allowed to equilibrate 3–4 days at 10 °C, and oscillated for 1 h per day. The pH of the suspension solution in the tube was then tested and designated as pH_0 . Next, 0.5 mL of 0.2 mol/L NaCl solution was added to each tube, oscillated for 4 h, and the pH tested, designated as pH_1 . The ΔpH was then calculated for each centrifuge tube ($\Delta\text{pH} = \text{pH}_1 - \text{pH}_0$). Using pH_0 as the abscissa and ΔpH as an ordinate to map the curve enabled the zero point of charge (ZPC) to be determined based on $\Delta\text{pH} = 0$.

2.4.2. Chemical Action

2.4.2.1. Ion Exchange Function

For the ion exchange experiment, 50 mL of nitrogen solution was added into 100 mL glass bottles with scoria (1.00 g), after which the bottles were shaken at 10 °C and 100 rpm for 30 min. The samples were then tested to determine if there were any exchange ions in the solution.

Dissolution experiment: 50 mL ultrapure water was added into 100 mL glass bottles, after which scoria (1.00 g) was added. From 0 to 12 h, samples were collected and tested at 2 h intervals to determine if there were any dissolution ions in the solution.

2.4.2.2. Functional Groups

The functional groups were analyzed using a Fourier transform infrared spectrophotometer (FT-IR) (Tensor 27-Advance, Bruker, Germany), after which the characteristics of the FT-IR spectrum and changes in functional groups before and after adsorption were compared.

2.5. Influencing Factors of Common Ions

NH_4^+ -N, NO_2^- -N, and NO_3^- -N concentrations were set as 2, 2, 50 mg/L. The effect of adsorption was studied for varying ions: Ca^{2+} , Mg^{2+} , CO_3^{2-} , HCO_3^- , and SO_4^{2-} . Generally, $\text{Ca}^{2+}/\text{Mg}^{2+}$ in groundwater in Northeast China is high and ranges from 200 to 550 mg/L [28]. In general, HCO_3^- was almost below 100 mg/L and CO_3^{2-} is less than 50 mg/L [29]. According to the Chinese "Hygienic Standard for Drinking Water (GB5749-2006)," the maximum level of SO_4^{2-} in drinking water is set to 250 mg/L. Considering the Chinese "Quality Standard for Ground Water (GB/T 14848-93)", and ion concentration in wastewater, the influencing factors of ion concentration were as follows: the Ca^{2+} , Mg^{2+} , and SO_4^{2-} concentrations were 0, 50, 100, 200, 300, and 500 mg/L; the CO_3^{2-} concentrations were 0, 1, 5, 10, 20, and 50 mg/L; and the HCO_3^- concentrations were 0, 10, 20, 50, 100, and 150 mg/L.

3. Results and Discussion

3.1. Removal Efficiency

The equilibrium removal percentages are shown in Figure 2. When NH_4^+ -N concentration was 0.5, 1.0, 2.0, 5.0, and 10 mg/L, the removal was 96%, 94%, 93%, 91%, and 89%, respectively. When NO_2^- -N concentration was 0.1, 0.5, 1, 2, and 5 mg/L, the removal was 93%, 92%, 90%, 88%, and 85%, respectively. When NO_3^- -N concentration was 30, 50, 80, 100, and 150 mg/L, the removal was 85%, 82%, 79%, 75%, and 70%. In order to analyze the concentration at which 1.00 g scoria into 50 mL solution are failed, NH_4^+ -N concentration was set as 100, 200, 300 and 400 mg/L; NO_2^- -N concentration was set as 100, 200 and 300 mg/L; NO_3^- -N concentration was set as 300 and 400 mg/L. When NH_4^+ -N, NO_2^- -N, and NO_3^- -N concentrations were 400, 300 and 400 mg/L, respectively, removal percentages were lower than 50% and scoria was overwhelmed. When NH_4^+ -N, NO_2^- -N, and NO_3^- -N mixed solution was used, the removal percentages were almost the same as the separate solution and it was obviously seen that scoria had better removal efficiency of NH_4^+ -N and NO_3^- -N than NO_2^- -N.

Jiang et al. used inorganic salt to modify zeolite and it had good efficiency in the treatment of ammonia nitrogen with a removal of more than 90%. Feng et al. modified zeolite with acid, alkali, and salt solution. It was found that 6–10% concentration NaCl solution had the best effect on the removal of ammonia nitrogen, and the removal was 95.3% [30]. Li et al. used activated carbon (GAC) to purify a low-concentration ammonia nitrogen solution and the removal was greater than 93% [31]. Li et al. modified natural zeolite under certain conditions, such as salt activation, thermal activation, salt and acid activation, and salt and alkali activation, respectively. Then, activated zeolite efficiencies were analyzed for ammonia nitrogen adsorption. It was found that zeolite activated under 100 °C and 0.3 mol/L NaCl solution had the best removal with 88.08% [32]. Xu used hydrotalcite to remove nitrate in water, and the removal was 96% [33]. Li et al. used graphene-loaded nano-iron to remove nitrate, and the removal was more than 80%. Consequently, scoria can be effectively applied to the removal of nitrogen in water [34].

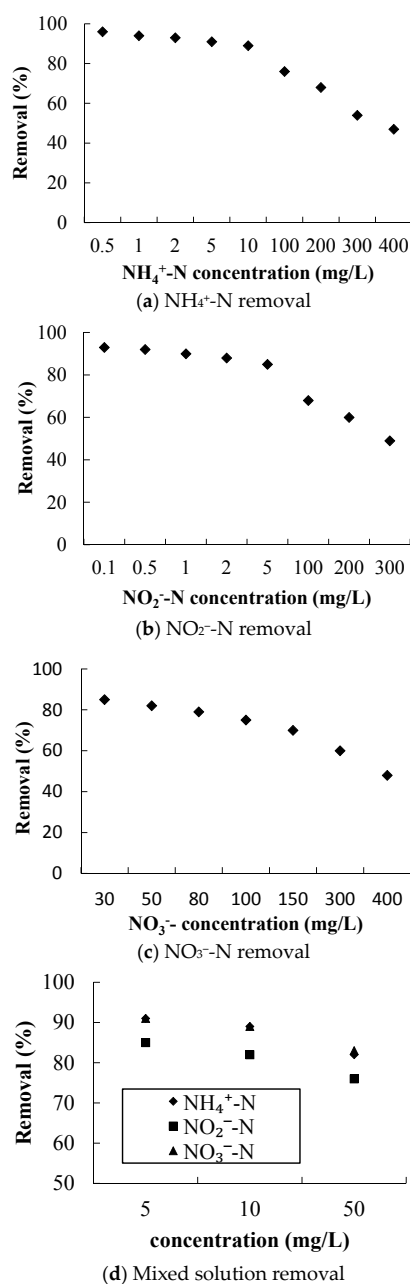


Figure 2. Nitrogen removal in different concentrations.

3.2. Characterization of Scoria

Characterization of materials is significant to describe and study its subsequent function and application. Scoria used in the experiments is included in basalt, which has many pores on the surface. The parameters tested are presented in Table 1. Scoria is formed by the eruption of volcanos; the natural particle sizes, surface pore sizes, and shapes are different. This experiment was conducted in order to purify a water solution in the laboratory. In addition, scoria was selected with appropriate particles sizes so that it can be used in subsequent experiments and engineering technology in the future. If the particles are too large or too small, it will affect the purification of water and cause problems with carrying, handling, and recycling in the actual application. Scoria used in the experiment is described as follows: The particle size was mainly distributed between 0.25 mm and 2.0 mm, with the largest size fraction being between 1 mm and 1.25 mm (26.11%). The pore diameters ranged from 2.0 nm to 50.0 nm (more than 70%). Thus, scoria absorbent could serve as a mesoporous material. Artificial γ

radiation was not seen in the sample. Due to its high specific surface area (30–150 m²/g) and excellent porosity (74–78%), scoria showed good adsorption. Additionally, scoria was lightweight due to its low bulk density. Thus, scoria has the potential for application in actual engineering technology. According to the relationship between SiO₂ content and rock properties, scoria adsorbent is a basic igneous rock (SiO₂ content: 45–52%) mineral material [35]. Lee et al. investigated the parameters related to adsorption. Scoria had high CEC (3.08–6.12 meq/100 g) and surface area, thus, showed high copper uptake [23].

Table 1. Scoria physical index.

Parameter	Value	Parameter	Value
Loose bulk density	500–600 kg/m ³	BET specific surface area	30–150 m ² /g
Specific gravity	2.4–2.6	Apparent specific gravity	1.4–1.6
Closed porosity	10–15%	Non-uniform coefficient	1.4–1.6
Total porosity	74–78%	Open porosity	60–70%

Scanning electron microscopy can express the surface shapes and structures before and after adsorption of NH₄⁺-N, NO₂⁻-N, and NO₃⁻-N of scoria. Scoria was very porous, and it showed a raw surface with rich, and differently-sized pores, which allowed pollutant attachment [36]. The pore distribution also appeared to be random in the structure. Similarly, Zhang et al. studied the scanning electron microscope images. It was observed that the scoria possesses grooves with a large amount of dense canal-like structure [25].

The EDX spectrum revealed the presence of oxygen, silicon, aluminum, and iron. Since the target pollutants needing purifying were NH₄⁺-N, NO₂⁻-N, and NO₃⁻-N, the average N content in three samples were summarized before and after adsorption by EDX. Changes before and after adsorption were shown in Table 2. Before adsorption, as a natural material formed by the eruption of the volcano, scoria has a certain amount of N and the weight percentage was about 3.25%. The weight percentage of N after adsorption of NH₄⁺-N increased to 3.95%. These findings may indicate that N was successfully adsorbed onto the material surface. Similarly, the weight percentage of N after adsorption onto NO₂⁻-N and NO₃⁻-N increased to 3.99% and 4.24%.

Table 2. Changes in N before and after adsorption.

Element	Weight Percentage	Atomic Percentage	Compound Percentage
N (raw scoria)	3.25	3.51	12.52
N (after adsorbed NH ₄ ⁺ -N)	3.95	4.35	15.24
N (after adsorbed NO ₂ ⁻ -N)	3.99	4.51	15.37
N (after adsorbed NO ₃ ⁻ -N)	4.24	4.70	16.35

3.3. Interaction between Scoria and Nitrogen

The external embodiment of the adsorption process can be seen from the interaction between the adsorbate molecule and the adsorbent. Based on the different interactions between the adsorbate and adsorbent, the adsorption can be divided into physical adsorption and chemical adsorption. Physical adsorption mainly consists of surface adsorption (van der Waals forces) and electrostatic adsorption (electrostatic forces), while chemical adsorption primarily includes an ion exchange function and chemical bonds.

3.3.1. Physical Action

3.3.1.1. Van der Waals Force

For the same category of adsorbent, a larger specific surface area is associated with more adsorption sites. The specific surface area of scoria was determined to be 30–150 m²/g, indicating that

it could be an excellent natural adsorption material. The change in the scoria structure before and after adsorption was evident upon SEM analysis, indicating that surface adsorption (van der Waals force) could play a certain role in the process of adsorption.

A laser particle size analyzer was utilized to sieve and grade scoria with particle sizes of 0.25 mm–0.5 mm, 0.5 mm–0.75 mm, and 0.75 mm–1.00 mm, as well as that of mixed particle size. The results of the weight percentage and accumulated weight percentage of different particle sizes are shown in Figure 3. The specific surface area was 99 m²/g, 85 m²/g, 62m²/g, and 78 m²/g, respectively. A finer particle size was associated with a higher specific surface area. In addition, while the specific surface area was 62 m²/g–99 m²/g, the removal of NH₄⁺-N, NO₂⁻-N, and NO₃⁻-N was 90–95%, 86–91%, and 75–81%, respectively. Scoria of different sizes can be mixed in proportion to meet the requirements in actual application projects.

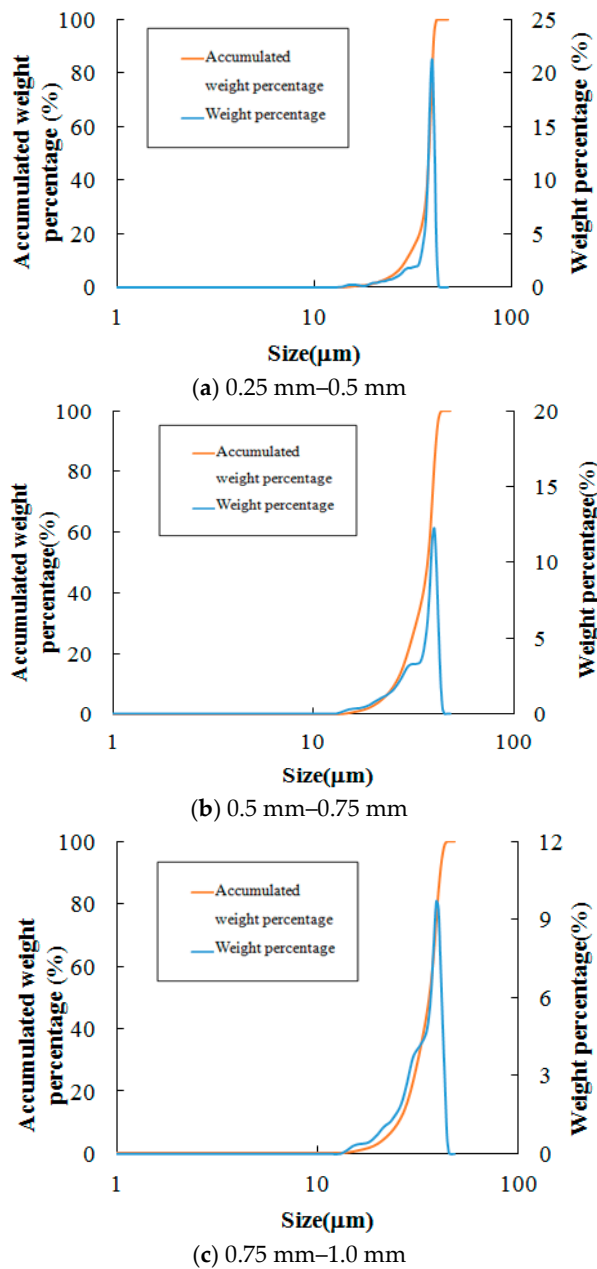
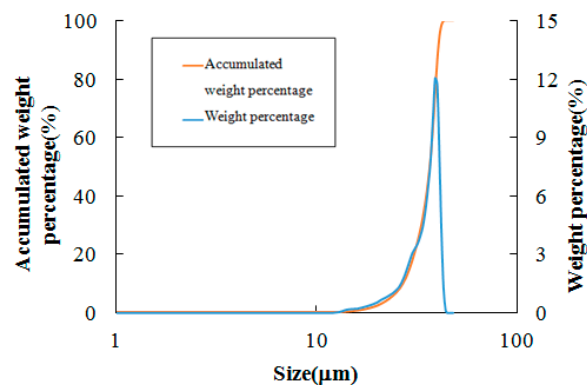


Figure 3. Cont.



(d) Mixed particle size

Figure 3. Weight percentage and accumulated weight percentage of different particle sizes.

Physical adsorption is mainly caused by Van der Waals forces, and the value of the specific surface area is an important parameter that influences the adsorbance performance. As shown in Figure 4, while the particle size of scoria was finer, the specific surface area was higher and the removal of $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, and $\text{NO}_3^-\text{-N}$ was increased. This is because increases in the specific surface area led to increased adsorption binding sites of unit mass. Then, van der Waals forces played a greater role and had stronger effect. Therefore, physical adsorption on the surface is one of the mechanisms of adsorption for scoria which has a large amount of surface energy. Liao studied the adsorption mechanism of bamboo charcoal onto NHCs, and analyzed the influence of BET specific surface area and van der Waals force on the adsorption [37]. Kwon et al. conducted experiments on Zn(II) sorption by scoria which were separated into four size fractions (<0.1, 0.1–0.2, 0.2–0.5, and 0.5–2.0 mm in diameter) using nylon sieves. It is suggested that the removal increased systematically with decreasing particle size because the total surface area per unit mass of a sorbent is generally inversely proportional to the particle size [22]. Lee et al. investigated the relationship between surface area (32–99 m^2/g) and the removal on copper ion adsorption. It was found that when the surface area was higher, the removal increased [23].

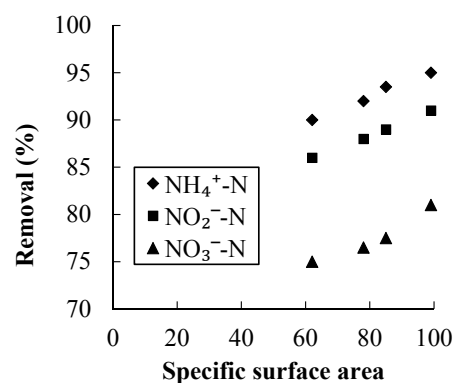


Figure 4. Effect of specific surface area on nitrogen removal.

3.3.1.2. Electrostatic Force

The charged colloidal surface can be divided into two types: permanent and variable surface charges. Once the permanent charge forms, the number and symbol will not change, but the number and symbol of the variable charge will change depending on the pH value of the medium, electrolyte concentration, and properties of the variable charge surface. The zero point of charge (PZC) of colloid refers to the pH value of the system when the variable charge is zero. This is an important influence on adsorption. As shown in Figure 5, the zero point of charge of scoria was at approximately pH = 5.2.

When the solution pH was greater than 5.2, the surface was negatively-charged, while a solution with a pH value of less than 5.2 resulted in a positively-charged surface. The nitrogen solution was close to neutral, so scoria was negatively charged. NH_4^+ , NO_2^- , and NO_3^- was positively-charged, negatively-charged, and negatively-charged, respectively. Based on the interactions between charged particles, the adsorption capacity for NH_4^+ was greater than for NO_2^- and NO_3^- , which was consistent with the actual experimental data. Therefore, electrostatic adsorption during physical adsorption was another mechanism of adsorbance by scoria. Especially for NH_4^+ -N, it played a positive role in adsorption. Cui judged if electrostatic force could affect adsorption when pretreated tea residue removed heavy metal ions by the salt titration method [38].

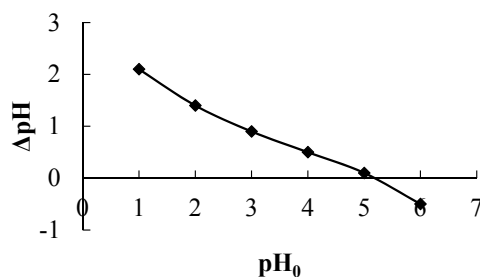


Figure 5. Zero point of charge (PZC) of scoria.

3.3.2. Chemical Action

3.3.2.1. Ion Exchange Function

Ion exchange is often used in water purification technology, but materials can cause secondary pollution if ion exchange appears in the adsorption process. Cations such as Ca^{2+} , Mg^{2+} , Na^+ and K^+ were the common ions in the process of ion exchange. When NH_4^+ -N was removed, samples were measured after reaction whether there were Ca^{2+} , Mg^{2+} , Na^+ and K^+ . And these metal ions were not released. Anions such as Cl^- , CO_3^{2-} , HCO_3^- , and SO_4^{2-} were the common ions in the process of ion exchange. When NO_2^- -N, and NO_3^- -N were removed, samples were measured after reaction whether there were Cl^- , CO_3^{2-} , HCO_3^- , and SO_4^{2-} . And these ions were not released. Thus, no substitute ions appeared during nitrogen adsorption and ion exchange did not occur. Dissolution experimental data revealed that no ions were found after scoria was soaked in ultrapure water for 2, 4, 6, 8, 10, and 12 h; thus, dissolution did not occur. These findings indicated that scoria is an ecologically safe material that will not cause any secondary pollution problems, making it suitable for application in drinking water projects. Kwon et al. conducted experiments on Zn(II) sorption by scoria. That suggested ion exchange existed and the sequence of releasing concentrations was $\text{Ca(II)} > \text{Mg(II)} > \text{Na(I)} > \text{K(I)}$ [22].

3.3.2.2. Functional Groups Analysis

The FT-IR analysis is one of the most important methods for the qualitative identification of compounds and their structures. The FT-IR patterns of scoria before and after adsorption of ammonia nitrogen, nitrite nitrogen, and nitrate nitrogen are shown in Figures 6–8. The peak at 3400 cm^{-1} , which corresponded to N-H stretching vibration, changed obviously in response to adsorption. After N was absorbed onto the surface of the material, the area of the stretching vibration peak was enhanced and the peak increased. These findings suggest that the adsorption properties of the material can be expressed based on the N-H change. The peak reflecting C-H stretching of aliphatic $-\text{CH}_3$ and $-\text{CH}_2$ at 1450 cm^{-1} was also enhanced after ammonia nitrogen was adsorbed. In addition, the peak at 1050 cm^{-1} changed before and after adsorption. These findings may indicate that this peak reflects C-N stretching vibration. After adsorbing N, C-N will change; therefore, these findings indicate that scoria has the ability to absorb N. Thus, for scoria, in the process of nitrogen adsorption, functional groups

have certain changes, and chemical adsorption also has certain effects and can be one of the actions. Sara et al. used Iranian scoria to remove copper and cadmium from aqueous solutions. The results of FT-IR were analyzed. The stretching bands at 3427 cm^{-1} and 3424 cm^{-1} indicate the presence of water molecules. The stretching bands at 1632 cm^{-1} present O-H stretches, and the Si-O-Si stretching sharp bands are observed at 1027 cm^{-1} [39].

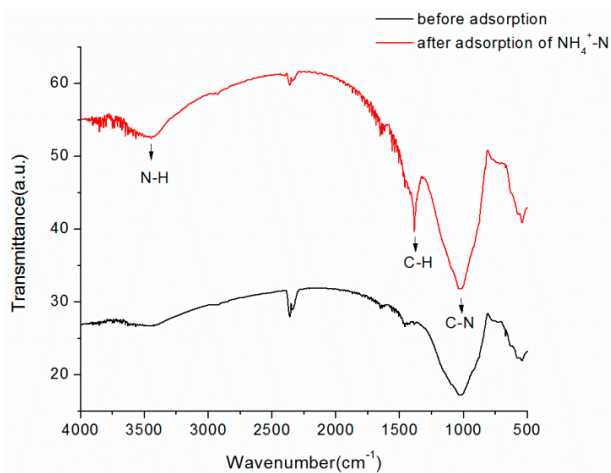


Figure 6. Fourier transform infrared (FT-IR) spectrum of scoria before and after NH_4^+ -N removal.

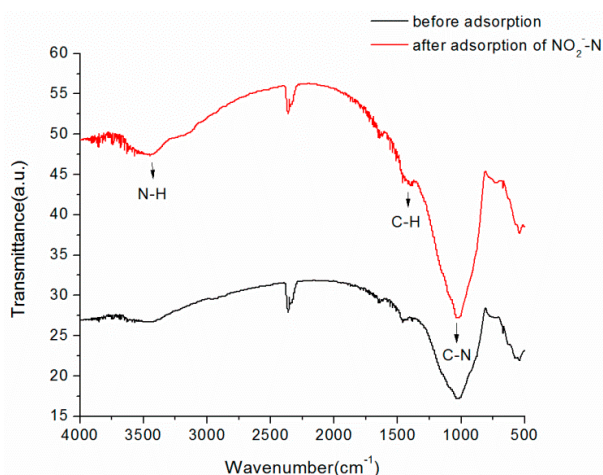


Figure 7. FT-IR spectrum of scoria before and after NO_2^- -N removal.

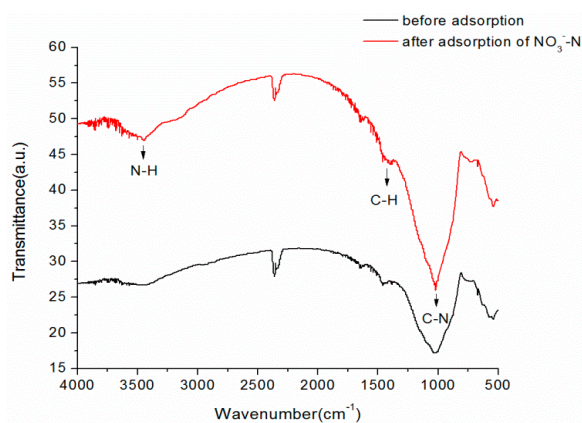


Figure 8. FT-IR spectra of scoria before and after NO_3^- -N removal.

3.4. Effect of Interfering Ions

Groundwater contains common ions, such as Ca^{2+} , Mg^{2+} , CO_3^{2-} , HCO_3^- , and SO_4^{2-} . If they are high in drinking water and taken in by the human body, a series of diseases, such as diarrhea and gastroenteritis, can be suffered. In addition, the removal efficiency of $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, and $\text{NO}_3^-\text{-N}$ is tested when these interfering ions exist. For $\text{NH}_4^+\text{-N}$, when Ca^{2+} and Mg^{2+} concentration did not exceed 300 mg/L, the amount adsorbed decreased very slightly, and when Ca^{2+} and Mg^{2+} concentration exceeded 300 mg/L, the amount adsorbed decreased more rapidly. For $\text{NO}_2^-\text{-N}$ and $\text{NO}_3^-\text{-N}$, scoria adsorption capacity reduced very slightly as the Ca^{2+} and Mg^{2+} concentration increased. When CO_3^{2-} concentration did not exceed 20 mg/L, as the CO_3^{2-} concentration increased, the amount adsorbed was unaffected. When CO_3^{2-} concentration exceeded 20 mg/L, CO_3^{2-} inhibited the adsorption of $\text{NH}_4^+\text{-N}$. When CO_3^{2-} concentration exceeded 30 mg/L, CO_3^{2-} inhibited the adsorption of $\text{NO}_2^-\text{-N}$. CO_3^{2-} had little effect on $\text{NO}_3^-\text{-N}$ adsorption. HCO_3^- had almost no effect on ammonia nitrogen, nitrite nitrogen, and nitrate nitrogen removal. SO_4^{2-} had little effect on removal. Consequently, scoria adsorbent could be widely applied to purify nitrogen in groundwater and other natural water sources; furthermore, wastewater could also be treated because it was slightly affected by basic water chemistry conditions.

4. Conclusions

Scoria is mesoporous and enriched with aluminum and iron. When $\text{NH}_4^+\text{-N}$ concentration was 0.5–10 mg/L, the removal was 96–89%. When $\text{NO}_2^-\text{-N}$ concentration was 0.1–5 mg/L, the removal was 93–85%. When $\text{NO}_3^-\text{-N}$ concentration was 30–150 mg/L, the removal was 85–70%. The surface structure of scoria, especially its micro-pores, and its high specific area further promote its adsorption potential, which occurs via Van der Waals and electrostatic forces. During adsorption, ion exchange actions and dissolution do not occur; however, functional groups are changed. The results presented herein will facilitate the use of scoria in groundwater remediation and for the treatment of nitrogen-contaminated water.

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References

1. Ghose, M.K. Complete physico-chemical treatment for coke plant effluents. *Water Res.* **2002**, *36*, 1127. [[CrossRef](#)]
2. Hallberg, G.R. Agricultural chemicals in groundwater: Extent and implications. *Am. J. Altern. Agric.* **1987**, *2*, 3–15. [[CrossRef](#)]
3. Jiang, Z.; Ning, P.; Pu, H.P.; Deng, C.L.; Huang, X.F. Research on removing ammonia-nitrogen from water by activated zeolite. *J. Saf. Environ.* **2004**, *4*, 40–43.
4. Ji, Z.Y.; Yuan, J.S.; Li, X.G. Removal of ammonium from wastewater using calcium form clinoptilolite. *J. Hazard. Mater.* **2007**, *141*, 483–488. [[CrossRef](#)] [[PubMed](#)]
5. Hu, Z.; Lotti, T.; Loosdrecht, M.V.; Kartal, B. Nitrogen removal with the anaerobic ammonium oxidation process. *Biot. Lett.* **2013**, *35*, 1145–1154. [[CrossRef](#)] [[PubMed](#)]
6. Gregory, S.P.; Dyson, P.J.; Fletcher, D.; Gatland, P.; Shields, R.J. Nitrogen removal and changes to microbial communities in model flood/drain and submerged biofilters treating aquaculture wastewater. *Aquacult. Eng.* **2012**, *50*, 37–45. [[CrossRef](#)]
7. Wen, T.; Zhang, X.; Zhang, H.Q.; Liu, J.D. Ammonium removal from aqueous solutions by zeolite adsorption together with chemical precipitation. *Water Sci. Technol.* **2010**, *61*, 1941–1947. [[CrossRef](#)] [[PubMed](#)]

8. Xu, J.; Pu, Y.; Qi, W.K.; Yang, X.; Tang, Y.; Wan, P.; Fisher, A. Chemical removal of nitrate from water by aluminum-iron alloys. *Chemosphere* **2017**, *166*, 197–202. [[CrossRef](#)] [[PubMed](#)]
9. Aiyuk, S.; Xu, H.; Van, H.A.; Verstraete, W. Removal of ammonium nitrogen from pretreated domestic sewage using a natural ion exchanger. *Environ. Technol.* **2004**, *25*, 1321–1330. [[CrossRef](#)] [[PubMed](#)]
10. Yang, Y.Z. Improvement and optimization of permeable reactive barrier technology to remove ammonium from groundwater. *China Univ. Geosci.* **2013**, *1*, 1–7.
11. Wang, X.L. Study on in-situ microbial remediation of nitrate contaminated groundwater simulator. *Anhui Hefei Univ. Technol.* **2010**, *1*, 7–13.
12. Sarioglu, M. Removal ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite. *Sep. Purif. Technol.* **2005**, *41*, 1–11. [[CrossRef](#)]
13. Yu, Y.; Zhuang, Y.Y.; Wang, Z.H. Adsorption of water-soluble dye onto functionalized resin. *J. Colloid Interface Sci.* **2001**, *242*, 288–293. [[CrossRef](#)]
14. Saltali, K.; Sari, A.; Aydın, M. Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality. *J. Hazard. Mater.* **2007**, *141*, 258–263. [[CrossRef](#)] [[PubMed](#)]
15. Mizuta, K.; Matsumoto, T.; Hatate, Y.; Nishihara, K.; Nakanishi, T. Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal. *J. Bioresour. Technol.* **2004**, *95*, 255–257. [[CrossRef](#)] [[PubMed](#)]
16. Huang, H.; Xiao, X.; Bo, Y.; Yang, L. Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent. *J. Hazard. Mater.* **2010**, *175*, 247–252. [[CrossRef](#)] [[PubMed](#)]
17. Zhao, Y.; Niu, Y.; Hu, X.; Xi, B.; Peng, X.; Liu, W.; Guan, W.; Wang, L. Removal of ammonium ions from aqueous solutions using zeolite synthesized from red mud. *Desalin. Water Treat.* **2015**, *57*, 4720–4731.
18. Haji, S.; Al-Buqaishi, B.A.; Bucheeri, A.A.; Bu-Ali, Q.; Al-Aseeri, M.; Ahmed, S. The dynamics and equilibrium of ammonium removal from aqueous by Na-Y zeolite. *Desalin. Water Treat.* **2015**, *57*, 18992–19001. [[CrossRef](#)]
19. Zhang, L.Y.; Zhang, H.Y.; Guo, W.; Tian, Y.L. Sorption characteristics and mechanisms of ammonium by coal by-products: Slag, honeycomb-cinder and coal gangue. *Int. J. Environ. Sci. Technol.* **2013**, *10*, 1309–1318. [[CrossRef](#)]
20. Zhu, Y.; Kolar, P.; Shah, S.B.; Cheng, J.J.; Lim, P.K. Avocado seed-derived activated carbon for mitigation of aqueous ammonium. *Ind. Crops Prod.* **2016**, *92*, 34–41. [[CrossRef](#)]
21. Guaya, D.; Valderrama, C.; Farran, A.; Cortina, J.L. Modification of a natural zeolite with Fe(III) for simultaneous phosphate and ammonium removal from aqueous solutions. *J. Chem. Technol. Biot.* **2016**, *91*, 1737–1746. [[CrossRef](#)]
22. Kwon, J.S.; Yun, S.T.; Kim, S.O.; Mayer, B.; Hutcheon, I. Sorption of Zn(II) in aqueous solutions by scoria. *Chemosphere* **2015**, *60*, 1416–1426. [[CrossRef](#)] [[PubMed](#)]
23. Lee, M.G.; Lim, J.H.; Hyun, S.S.; Kam, S.K. Adsorption characteristics of copper ion by Jeju scoria. *Hwahak Konghak* **2002**, *40*, 252–258.
24. Zhang, Y.L.; Zhang, S.Y.; Song, F.; Huang, J.Y.; Zhang, Y.; Bai, X.D. Utilization of scoria as PRB reactive media for the removal of petroleum hydrocarbon from groundwater. *J. Adv. Mater. Res.* **2012**, *535–537*, 2457–2461. [[CrossRef](#)]
25. Zhang, S.Y.; Lu, Y.; Lin, X.Y.; Su, X.S.; Zhang, Y.L. Removal of fluoride from groundwater by adsorption onto La(III)-Al(III) loaded scoria adsorbent. *J. Appl. Surf. Sci.* **2014**, *303*, 1–5. [[CrossRef](#)]
26. Zhang, Y.L.; Dong, T.Z.; Su, X.S.; Qian, H.; Wang, J.L. Effect of high fluoride groundwater purification by lightweight. *Environ. Earth Sci.* **2016**, *75*, 10. [[CrossRef](#)]
27. Uehara, G.; Gillman, G.P. Charge characteristics of soils with variable and permanent charge minerals: I. Theory. *Soil Sci. Soc. Am. J.* **1980**, *44*, 250–252. [[CrossRef](#)]
28. Tie, Z.Y. Research on the removal of hardness from groundwater. *Shandong Jianshu Univ.* **2013**, *1*, 1–4.
29. Xie, B.H. Research on groundwater quality of large-scale irrigation—A case of Jinghuiqu irrigation district. *Chang'an Univ.* **2013**, *1*, 13–18.
30. Feng, L.; Mai, W.; Wu, L. Test study on ammonia-nitrogen removal using activated zeolite. *Henan Sci.* **2006**, *24*, 294–295.
31. Li, D.; Xie, H.; Li, B.; Wang, Q. Effects of ammonia nitrogen concentration on the selection of advanced treatment process with activated carbon. *Chin. J. Environ. Eng.* **2007**, *1*, 65–68.
32. Li, R.; Li, J.; Wang, J. Zeolite activation and ammonia-nitrogen removal from wastewater by adsorption on activated zeolite. *Acta Sci. Circumstantiae* **2008**, *28*, 1618–1624.

33. Xv, P. Physicochemical characterization and behavior of hydrotalcite-like compound toward nitrate removal. *South China Univ. Technol.* **2013**, *1*, 24–27.
34. Li, B. Technology research of graphene supported nanometer iron removal of nitrate nitrogen in groundwater. *Chang'an Univ.* **2013**, *1*, 21–27.
35. Yang, K.G.; Yuan, Y.M. *Geology*, 1st ed.; China University of Geosciences Press: Beijing, China, 2009; pp. 160–161.
36. Amin, M.M.; Rahimi, A.; Bina, B. Performance evaluation of a scoria-compost biofilter treating xylene vapors. *J. Environ. Health Sci. Eng.* **2014**, *12*, 140. [[CrossRef](#)] [[PubMed](#)]
37. Liao, P. Adsorption mechanism of nitrogen-heterocyclic compounds in wastewater on porous bamboo charcoal. *Huazhong Univ. Sci. Technol.* **2013**, *1*, 28–30.
38. Cui, X.N. Studies on adsorption characteristics and mechanism of heavy metal ions from wastewater onto pretreated tea residue. *Huazhong Agric. Univ.* **2011**, *1*, 39–43.
39. Sara, S.; Amir, R.A.; Mahdi, G.; Abbas, M. Usage of Iranian scoria for copper and cadmium removal from aqueous solutions. *J. Cent. South Univ.* **2015**, *22*, 3760–3769.



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