

Article

Simple Aminated Modified Zeolite 4A Synthesized Using Fly Ash and Its Remediation of Mercury Contamination: Characteristics and Mechanism

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Abstract: In this study, through simple ammonia impregnation, more amine functional groups could be introduced into the zeolite 4A synthesized using fly ash, which efficiently improved the mercury ion removal capacity of modified zeolites. The impregnation-modification mechanism of $\text{NH}_3 \cdot \text{H}_2\text{O}$, ammonium chloride, and silane coupling agent (KH792) for zeolite 4A, and the Hg^{2+} ion removal-efficiency by aminated zeolites, were studied and compared. Through ion exchange and hydroxyl reactions, $\text{NH}_3 \cdot \text{H}_2\text{O}$ impregnation introduced the same kinds of nitrogen-containing groups into zeolite as KH792 grafting, which was more than the NH_4Cl modification. The Hg^{2+} ion adsorption capacity of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite was higher than those of KH792-zeolite and NH_4Cl -zeolite through ion exchange and the complexation of nitrogen-containing groups. When coexisting with Pb^{2+} , Cu^{2+} , and Zn^{2+} ions, the Hg^{2+} ion removal rate of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite was still higher than 99%. After five adsorption and desorption cycles, the Hg^{2+} ion removal rate of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite was 72.03%. When $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite was added to the leaching of mercury-contaminated soil, the content of soluble mercury significantly decreased. Therefore, we synthesized a potential cheap and safe adsorbent using fly ash as the main raw material through the simple $\text{NH}_3 \cdot \text{H}_2\text{O}$ impregnation modification for the treatment of mercury-contaminated water and soil.

Keywords: amination modification; fly ash; zeolite 4A; Hg^{2+} ion; mercury-contaminated soil



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1. Introduction

Mercury (Hg) has strong toxicity. After entering the human body, even a small amount of Hg will lead to multiple human diseases and neurological and renal dysfunction [1]. Therefore, mercury-contaminated water and soil may have adverse effects on human health. Among mercury-removal methods, the adsorption method is commonly used because of its low cost, fast treatment speed, simple operation, and renewable advantages [2,3]. Zeolite is a conventional adsorbent that can remove heavy metal ions from a solution through ion exchange. It is often used to remove Hg^{2+} ions in water [4].

Due to the fact that the main elements of zeolite are silicon and aluminum, industrial waste fly ash with silicon and aluminum as the main components is often used to synthesize zeolite to reduce the material cost and realize waste utilization [5,6]. However, the removal ability of zeolite for Hg^{2+} ions needs to be improved, so it is often modified to increase its adsorption capacity [7]. Due to the fact that amino groups can chelate with Hg^{2+} ions through the free-electron bimodal characteristics of nitrogen and have a strong adsorption ability for Hg^{2+} ions in solution [8], zeolites are often aminated to improve their mercury-removal capacities [9].

There are two main methods for the amination modification of a zeolite: one is high-temperature activation, the other is impregnation. High-temperature activation modification is to introduce an amino group from ammonia to the zeolite structure. NH_3 can only be decomposed with the removal of a H atom to form an amino group after being heated to above 600 °C, which is then connected with Si on the zeolite surface [10,11]. Therefore, NH_3 modification has a high energy consumption; in addition, the nitrogen content introduced into microporous zeolites is low, generally 1 wt%–2 wt% [12]. Impregnation modification involves impregnating the zeolite into inorganic ammonium salt or an organic nitrogen-containing substance solution, then introducing an ammonium ion or amine functional group in the zeolite channel and surface through ion exchange, loading, and grafting [13,14]. The impregnation is a commonly used method for the zeolite amination modification because of its simple operation and low energy consumption [15].

When inorganic ammonium salt is used to modify the zeolite by impregnation, ammonium ions can enter the zeolite channel by exchange with cations in zeolite [16], but due to the influence of the cation site of the zeolite, they can only exchange with cations in the quaternary ring and hexagonal ring on the zeolite surface [17], and the nitrogen content introduced is low. When organic nitrogen-containing substances are used to impregnate zeolites, the nitrogen-containing functional groups are easily grafted onto the zeolite surface [18]. Due to the fact that organic substances can contain more nitrogen-containing functional groups, more amino groups can be introduced in the zeolite; thus, zeolites modified by organic amines have a high adsorption efficiency for pollutants [19]. However, when a zeolite modified by organic amines is used to treat mercury-contaminated water and soil, due to the weak interaction between the introduced organic nitrogen-containing groups and the zeolite, the organic amines may leach into the environment and bring risks [20]. Thus, although organic impregnation modification can introduce many nitrogen-containing groups into a zeolite, the organic products may bring environmental risks, while the previous inorganic impregnation modification will not bring environment risks, but the ammonium content introduced into the zeolite is limited, and the adsorption capacity of modified zeolites for Hg^{2+} ions cannot be effectively improved. Therefore, it is necessary to study how to improve the content of nitrogen-containing groups introduced into zeolite by using the inorganic impregnation method.

In this study, a simple inorganic-ammonia-impregnation method was used to modify zeolite 4A synthesized using fly ash. The modification mechanism, the contents of the introduced amino groups, and the Hg^{2+} ions' removal efficiency were analyzed and compared with organic grafting modification and inorganic ammonium chloride modification. On this basis, the Hg^{2+} ion adsorption mechanism, the removal efficiency of multiple coexisting ions, and the reusability of the modified zeolite were further determined. Finally, the modified zeolite was added to the leaching solution of the mercury-contaminated soil and the Hg^{2+} ion content was analyzed.

This study attempts to supply an inorganic amination modification method of a zeolite with a low-energy operation and efficient removal of Hg^{2+} ions using fly ash as a raw material to synthesize a potential cheap and safe adsorbent for the treatment of mercury-contaminated water and soil.

2. Materials and Methods

2.1. Materials and Reagents

The raw materials used in the synthesis of zeolite 4A were fly ash (43.98% Al_2O_3 , 43.89% SiO_2) obtained from Ordos (Inner Mongolia, China) and diatomite (2.49% Al_2O_3 , 89.16% SiO_2) purchased from Fengsheng Mining of China as a supplementary Si source. The reagents used in this study included sodium hydroxide (NaOH, 96%, assay), ammonia monohydrate ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25%, assay), silane coupling agent (KH792, 99%, assay), hydrochloric acid (HCl, 38%, assay), sodium carbonate (Na_2CO_3 , 99.80%, assay), ammonium chloride (NH_4Cl , 99%, assay), and potassium iodide (KI, 99%, assay). The Hg-contaminated solution was prepared using mercury chloride (HgCl_2 , 99.50%, assay), and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

(99.00%, assay), $\text{Pb}(\text{NO}_3)_2$ (99.00%, assay), and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.50%, assay) were used to prepare multiple ion coexistence solutions.

2.2. Instruments

An X-ray diffractometer (XRD, Ultima IV, Rigaku Corporation, Tokyo, Japan) was used to analyze the diffraction patterns of the modified zeolite and the zeolite before and after the adsorption of the Hg^{2+} ions. A scanning electron microscope (SEM, SU8010, Hitachi Ltd., Tokyo, Japan) was used to observe the surface morphology of the zeolite. A surface area and porosity analyzer (ASAP 2460, Micromeritics Instrument Corporation, Norcross, GA, USA) was used to measure the BET surface area and N_2 adsorption–desorption isotherm of the adsorbents before and after modification. The contents of the organic materials before and after zeolite grafting were measured by an organic-element analyzer EA (UNICUBE, Elemental Analysis Systems Co., Ltd., Hanau, Germany). The functional groups before and after modification and the adsorption of the zeolite were measured by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Frontier, Perkin-Elmer Ltd., Waltham, MA, USA). An inductively coupled plasma optical emission spectrometer (ICP-OES, ICPE-9800, Shimadzu Company, Kyoto, Japan) was used to measure the Na^+ ion concentration before and after zeolite modification. The Hg^{2+} ion concentration in the solution was measured by flame atomic absorption spectrometry with a hydride generator (FAAS-HVG-100, Shimadzu Company, Kyoto, Japan).

2.3. Synthesis and Amination Modification of Zeolite 4A

2.3.1. Zeolite 4A Synthesis

The zeolite 4A used in the experiment was hydrothermally synthesized with fly ash as the raw material. The specific synthesis steps were described in our previous study [21]. Fly ash, diatomite supplemented with a silicon source, and the alkali activator NaOH were mixed in a proportion of 9.1:0.9:16, and zeolite 4A was obtained after alkali melting, stirring, aging, crystallization, washing, and drying.

2.3.2. Inorganic Amination Modification

First, zeolite 4A, synthesized using fly ash, was dried, ground and passed through 200 mesh sieves, and then 3 g was added into $\text{NH}_3 \cdot \text{H}_2\text{O}$ with different concentrations for 48 h. Through batch experiments, we determined that the best concentration of $\text{NH}_3 \cdot \text{H}_2\text{O}$ was 10 wt%. After impregnation, the zeolite was vacuum filtered, washed, dried at 50 °C for 12 h, and then sealed and stored. The zeolite modified by $\text{NH}_3 \cdot \text{H}_2\text{O}$ impregnation was named $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A.

The NH_4Cl modification mainly refers to Ikeda et al.'s method [22], but was further improved. The preparation steps were as follows: 3 g of zeolite 4A was slowly added into 0.5 M NH_4Cl , and then the mixture was stirred at 80 °C for 4 h, washed with deionized water, and filtered. Finally, the mixture was dried at 50 °C overnight and a modified zeolite was obtained, named NH_4Cl -zeolite 4A.

2.3.3. Organic Graft Modification

The organic graft modification mainly refers to the method put forth by Han et al. [23]. First, 50 mL of 95 wt% ethanol solution was added to a flask and stirred at 25 °C for 5 min. Then, 5 g of zeolite was put into the ethanol solution and continuously stirred. Then, 50 mL of 90 wt% ethanol was added to another flask and stirred at 25 °C for 5 min, and 5 wt% silane coupling agent (KH792) was slowly dropped with a disposable syringe and then stirred with ultrasonication for 0.5 h to ensure reagent hydrolysis. The obtained hydrolysis solution was quickly added to the mixture of the zeolite and ethanol and stirred and reacted at 60 °C for 4 h. Then, the obtained product was washed repeatedly with absolute ethanol and filtered in vacuum to remove the unreacted KH792. The filtered product was dried in a vacuum oven at 80 °C for 2 h and then ground and passed through a 200 mesh sieve to obtain the modified zeolite named KH792-zeolite 4A.

2.4. Adsorption Experiment

HgCl₂ (0.1354 g) was dissolved in 100 mL of deionized water to obtain a 1 g/L standard solution. Then, the standard solution was diluted, and Hg²⁺ ion solutions with different concentrations were prepared. The pH of the solution was adjusted with 0.1 M HCl and 0.1 M NaOH. Without special instruction, the initial concentration of Hg²⁺ ions was 10 mg/L, the amount of adsorbent was 0.1 g, the adsorption temperature was 25 °C, and the adsorption time was 240 min.

To determine the adsorption efficiency and the mechanism of the adsorbent for Hg²⁺ ions, batch experiments were carried out on the dosage of adsorbent, pH of the initial solution, concentration of the initial solution, adsorption time, and adsorption temperature. According to our previous research [24], when the solution's pH was lower than 2, the zeolite structure could be destroyed under strong acid conditions. Moreover, due to the existence of Cl[−] ions in the solution, when the solution pH was low, the Cl[−] and Hg²⁺ ions could form anionic complexes, such as HgCl^{3−} [25–27], while when the pH was high, the Hg²⁺ ions would form negatively charged metal complexes with OH[−] ions in alkaline conditions [28]. Thus, the pH range of the Hg²⁺ initial solution in this study was set from 3 to 7. The Hg²⁺ ion concentration gradients of isothermal adsorption were set to 5, 10, 20, 30, 50, 80, 100, 200, 300, 400, 450, and 500 mg·L^{−1}. The time gradients of adsorption kinetics were 2, 7, 12, 30, 60, 120, 180, and 240 min, respectively. The thermodynamic temperature gradients were set at 25 °C, 35 °C, and 45 °C. All experiments were carried out in an oscillator at 180 rpm. After adsorption, the solution was filtered using a disposable syringe with a 0.45 µm filter membrane. Each adsorption experiment was repeated twice. The adsorption rate Q_c (%) and adsorption capacity Q_e (mg/g) of the adsorbent for the Hg²⁺ ions were calculated by the following equations:

$$Q_c = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

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

where C_0 and C_e are the Hg²⁺ ion concentrations in the initial and adsorption equilibrium solutions, respectively, mg/L; V is the volume of solution, L; and m is the adsorbent amount, g.

2.5. Cation Effect on Hg²⁺ Ion Adsorption

The Hg²⁺ ion adsorption rate of NH₃·H₂O-zeolite 4A with the coexistence of Pb²⁺, Cu²⁺, and Zn²⁺ ions at the same concentration in the solution was studied. The initial ion concentration was 10 mg/L, the pH was 6, and 0.1 g of NH₃·H₂O-zeolite 4A was added. After shaking for 4 h at 25 °C to reach adsorption equilibrium, the concentration of each cation was measured. The experiments were repeated twice, and the average value was taken as the final measured value.

2.6. Zeolite Reuse Experiment

A KI solution was used as the adsorbent eluent. After adsorption saturation with 1 g/L Hg²⁺ ions, 0.5 g of NH₃·H₂O-zeolite 4A was put into 50 mL of the 0.1 M KI solution, and the solution was shaken at 25 °C for 60 min with a frequency of 180 rpm for desorption. Then, the sample was filtered and washed with deionized water, and this process was repeated three times to fully desorb the adsorbed Hg²⁺ ions. Finally, the washed sample was dried for the next adsorption experiment. Five adsorption–desorption experiments were conducted. Each group of experiments was repeated twice.

2.7. Removal of Hg²⁺ Ions in Soil Leaching by the Modified Zeolite

According to our previous study, the soil around the Tangshan steel plant was seriously contaminated by mercury [29]. A 1 g soil sample with the highest mercury content around

the steel plant was added to 20 mL of deionized water, and then 0.01 g of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A was added. At the same time, a blank control experiment was set. The samples were shaken for 6, 18, 24, 36, and 48 h to measure the Hg^{2+} ion concentration in the soil-leaching solutions. Each experiment was repeated twice.

3. Results

3.1. Amination Modification of Zeolite

3.1.1. Characterization

Zeolite 4A was successfully synthesized using fly ash. The XRD pattern showed that the characteristic peaks of the synthesized zeolite 4A were 7.2° , 10.3° , 12.6° , 16.2° , 21.8° , 24.0° , 27.2° , 29.9° , and 34.2° (Figure 1a), which were consistent with the standard peaks of zeolite 4A [30]. The characteristic peaks of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A, KH792-zeolite 4A, and NH_4Cl -zeolite were the same as zeolite 4A, indicating that the three modifications did not affect the skeleton structure of zeolite (Figure 1b–d).

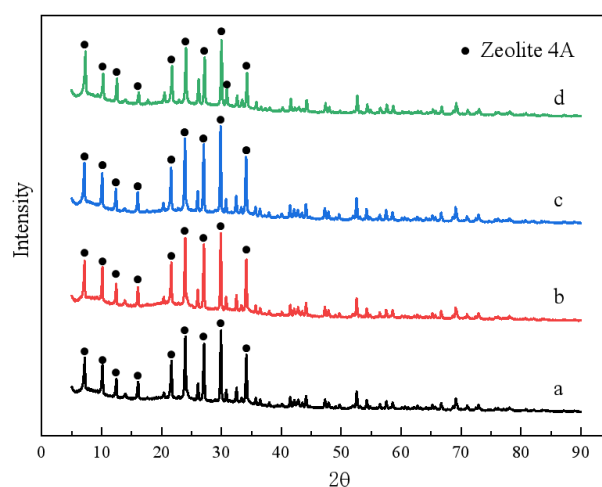


Figure 1. XRD patterns of zeolite 4A (a), $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A (b), KH792-zeolite 4A (c), and NH_4Cl -zeolite 4A (d).

Zeolite 4A synthesized using fly ash was a typical small cube (Figure 2a). The surface morphologies of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A and NH_4Cl -zeolite 4A showed no significant changes compared with the original zeolite (Figure 2b,c). However, compared with the original zeolite, the surface of KH792-zeolite 4A became rough (Figure 2d), which may have been because the silane group of KH792 reacted with the free hydroxyl group on the zeolite surface to form a covalent bond and reduce the surface tension of the modified zeolite, and the adhesion between the grafted amine functional groups of KH792 increased the trend of large agglomerate formation [31].

3.1.2. Synthesis Mechanism

In the FTIR spectrum, the peak at 465 cm^{-1} of zeolite 4A corresponded to the bending–stretching vibration of T–O (where T is Al or Si), the peak at 558 cm^{-1} was the characteristic peak of the double-ring vibration in the tetrahedron, the peak at 993 cm^{-1} corresponded to the characteristic peak of the tetragonal stretching vibration of TOT (where T is Al or Si), and 3430 cm^{-1} was related to the stretching vibration of Si–OH. These characteristic peaks were the characteristic peaks of typical zeolite 4A [32] (Figure 3a). The peak at 1401 cm^{-1} of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A was assigned to the deformation vibration of the NH_4^+ ions [33], indicating that the partial Na^+ ions of zeolite 4A might have exchanged with NH_4^+ in the solution. The peak intensity at 993 cm^{-1} decreased, indicating that ion exchange might have had an impact on the ring structure. The peak at 3421 cm^{-1} was attributed to the Si– NH_2 vibration [34], indicating that amino functional groups were formed on $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A (Figure 3b). In the FTIR spectrum of KH792-zeolite 4A, the characteristic peak

at 1635 cm^{-1} was attributed to -N-H bonds [35], and the peaks at 2850 and 2920 cm^{-1} were attributed to -CH- asymmetric and symmetric stretching vibrations [36], indicating that KH792 was successfully grafted onto the zeolite. The peak at 3430 cm^{-1} of KH792-zeolite 4A was significantly lower than that of zeolite 4A, indicating that KH792 consumed some silanol groups on the surface of the zeolite after grafting (Figure 3c). The peak of NH_4Cl -zeolite 4A at 1401 cm^{-1} was assigned to the deformation vibration of NH_4^+ [33], and the obvious peak height indicated that more NH_4^+ ions had exchanged with Na^+ ions (Figure 3d). However, no vibration peak of Si-NH_2 was found in the FTIR spectrum of NH_4Cl -zeolite 4A.

Through experimental detection, it was found that the concentration of Na^+ ions in the solution after impregnating zeolite 4A with $\text{NH}_3\cdot\text{H}_2\text{O}$ was higher than that with deionized-water impregnation (Figure 4a), which shows that Na^+ ions in the zeolite exchanged with NH_4^+ ions in $\text{NH}_3\cdot\text{H}_2\text{O}$, and the cation exchange capacity reached 41.28%. Both this and the FTIR results prove that NH_4^+ ions successfully entered the structure of zeolite 4A after ammonia impregnation. The determination results of the element analyzer show that the amount of N and C in KH792-zeolite 4A increased compared with that of zeolite 4A (Figure 4b). Thus, the experimental detection and FTIR results prove that amine groups were successfully grafted onto zeolite 4A.

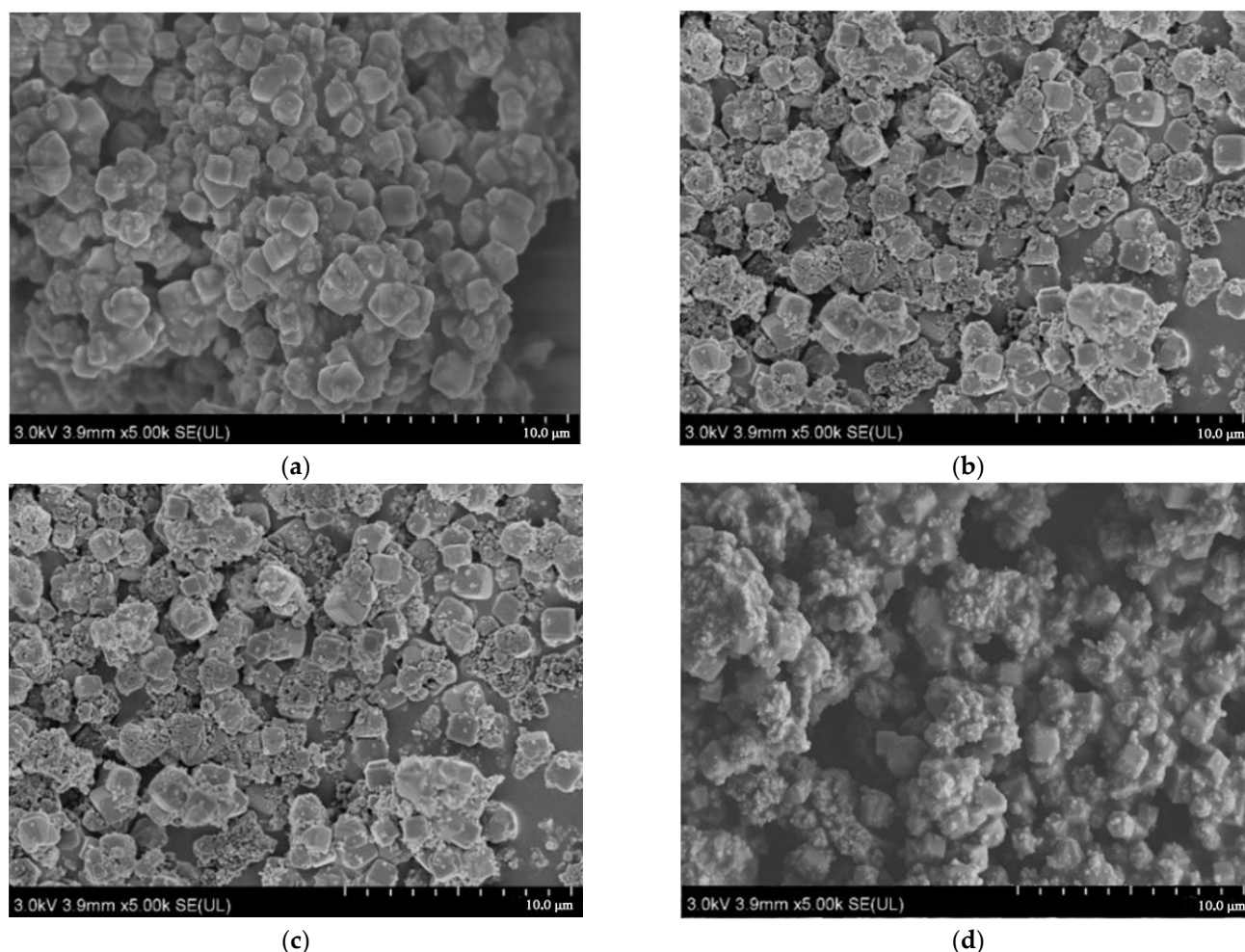


Figure 2. Morphological characteristics of zeolite 4A (a), $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A (b), NH_4Cl -zeolite 4A (c), and KH792-zeolite 4A (d).

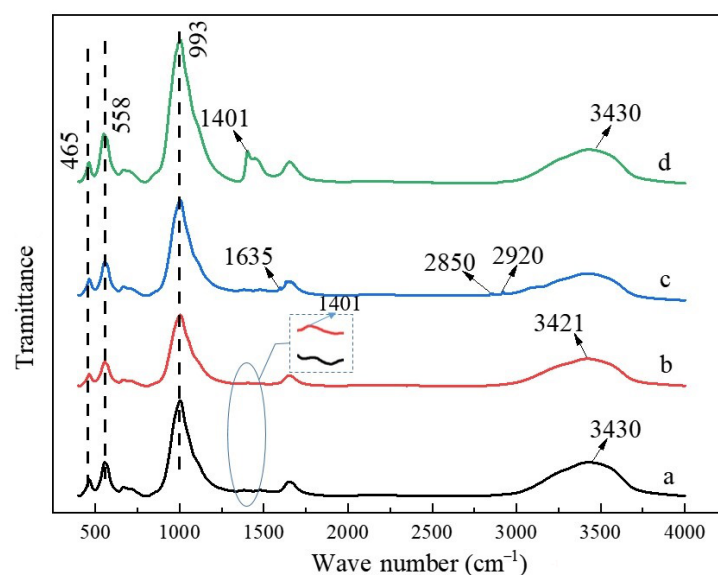


Figure 3. FTIR spectra of zeolite 4A (a), $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A (b), KH792-zeolite 4A (c), and NH_4Cl -zeolite 4A (d).

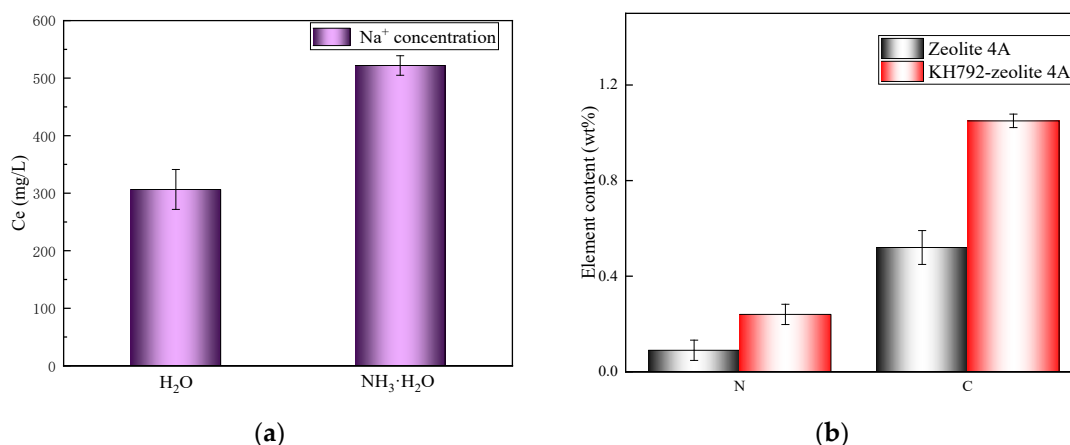
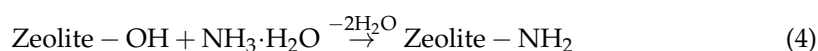
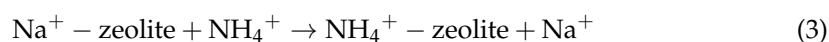


Figure 4. Na^+ ion concentration in H_2O and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (a) and the contents of N and C elements in zeolite 4A and KH792-zeolite 4A (b).

According to the above analysis, the inorganic and organic modification mechanisms of zeolite could be determined. In the $\text{NH}_3 \cdot \text{H}_2\text{O}$ and NH_4Cl modifications, the Na^+ ions in zeolite 4A could exchange with the NH_4^+ ions in the solution to form nitrogen-containing groups and enter the zeolite structure (Equation (3)). In addition, a large number of hydroxyl groups on the surface of zeolite 4A could react with $\text{NH}_3 \cdot \text{H}_2\text{O}$ and introduce $-\text{NH}_2$ groups into the zeolite [37] (Figure 3b, Equation (4)). Therefore, $\text{NH}_3 \cdot \text{H}_2\text{O}$ modification could introduce more nitrogen-containing groups than NH_4Cl modification, which might improve the Hg^{2+} ion-removal efficiency of the modified zeolite in the solution.



During organic modification, the silicon atom in KH792 could react with the hydroxyl group on the zeolite surface [38] and introduce amino functional groups onto zeolite 4A (Figure 5). Due to the fact that KH792 contains two amino functional groups, the amount of amino functional groups introduced by the organic grafting modification was the same as those introduced by inorganic $\text{NH}_3 \cdot \text{H}_2\text{O}$ impregnation.

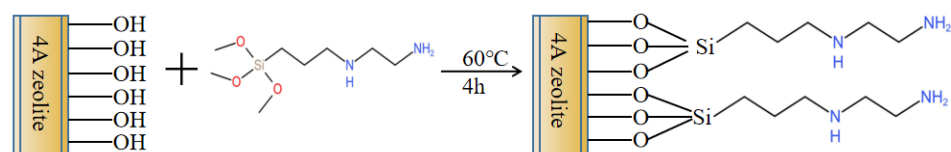


Figure 5. Chemical-grafting process between KH792 and zeolite 4A.

3.1.3. Pore Size Distribution

Through the N_2 adsorption–desorption isotherms (Figure 6), the specific surface areas of zeolite 4A, $NH_3 \cdot H_2O$ -zeolite 4A, and KH792-zeolite 4A were $20.9 \text{ m}^2/\text{g}$, $28.4 \text{ m}^2/\text{g}$, and $31.33 \text{ m}^2/\text{g}$, respectively, indicating that the specific surface areas of the modified zeolites were improved. The isotherms of all of the adsorbents were type I [39], which belonged to a typical microporous structure, indicating that aminated modification could not change the microporous structure of zeolite 4A.

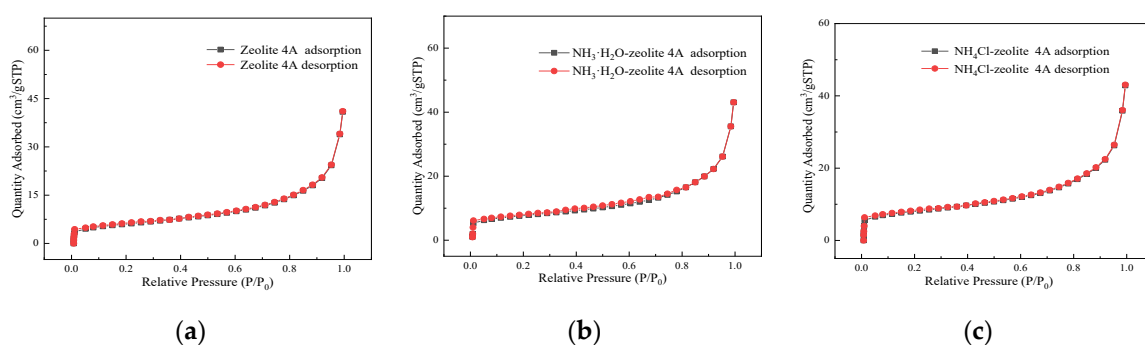


Figure 6. N_2 adsorption–desorption isotherms of zeolite 4A (a), $NH_3 \cdot H_2O$ -zeolite 4A (b), and KH792-zeolite 4A (c).

3.2. Hg^{2+} Ion Adsorption by Modified Zeolite

3.2.1. Adsorption Efficiency

The Hg^{2+} ion-adsorption rate of zeolite 4A was only 75.5%, while the Hg^{2+} ion-adsorption rates of $NH_3 \cdot H_2O$ -zeolite 4A and KH792-zeolite 4A were 99.25% and 98.31%, respectively, indicating that the Hg^{2+} ion-removal abilities of these two kinds of modified zeolites were significantly improved ($p < 0.05$) (Figure 7). The Hg^{2+} ion-adsorption rate of NH_4Cl -zeolite 4A was 85.05%, which was significantly improved compared with that of the original zeolite 4A, but was significantly lower than those of the other two modified zeolites ($p < 0.05$), which might be due to the small amount of nitrogen-containing groups introduced into NH_4Cl -zeolite 4A. Thus, the adsorptions of Hg^{2+} ions by $NH_3 \cdot H_2O$ -zeolite 4A and KH792-zeolite 4A were mainly studied and compared.

3.2.2. Effect of Initial Solution pH

The Hg^{2+} ion removal rates of $NH_3 \cdot H_2O$ -zeolite 4A and KH792-zeolite 4A gradually increased with an increasing initial solution pH (Figure 8). When the initial solution pH was three, the Hg^{2+} ion removal rates of $NH_3 \cdot H_2O$ -zeolite 4A and KH792-zeolite 4A were 85.83% and 81.51%, respectively. When the initial solution pH was six, the Hg^{2+} ion removal rates of $NH_3 \cdot H_2O$ -zeolite 4A and KH792-zeolite 4A were the highest, reaching 99.25% and 98.31%, respectively. Due to the fact that the amino functional groups might have been protonated to form $-NH_3^+$ when the pH value was low [40], which would have reduced the adsorption ability of the modified zeolite for Hg^{2+} ions, the initial solution pH was set to six.

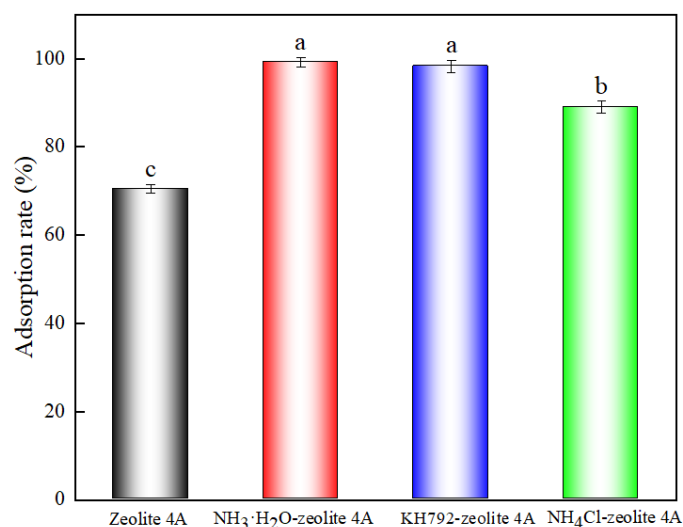


Figure 7. Hg²⁺ ion-adsorption rates of zeolite 4A and amination-modified zeolites (adsorbent dosage of 0.1 g, pH 6, temperature 25 °C, and Hg²⁺ ion concentration of 10 mg/L). (The same letter on the column shows no significant difference, while different letters indicate a significant difference $p < 0.05$).

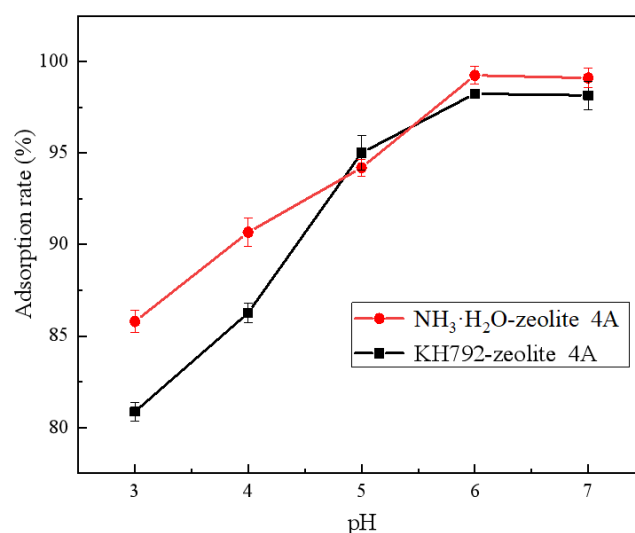


Figure 8. Effect of initial solution pH on the Hg²⁺ ion-adsorption efficiency of modified zeolites (adsorbent dosage of 0.1 g, temperature 25 °C, and Hg²⁺ ions concentration of 10 mg/L).

3.2.3. Adsorption Model

With an increase in Hg²⁺ concentration, the adsorption capacity of the modified zeolite gradually reached saturation, and the maximum Hg²⁺ ion-adsorption capacities of NH₃·H₂O-zeolite 4A and KH792-zeolite 4A were 49.45 mg/g and 40.64 mg/g, respectively (Figure 9a). Through isotherm adsorption model fitting (Figure 9b,c and Table 1), the Langmuir model had the highest correlation coefficient for the modified zeolite, indicating that the removal of Hg²⁺ ions by NH₃·H₂O-zeolite 4A and KH792-zeolite 4A was the single-layer surface adsorption and irreversible [41]. According to the isothermal adsorption model fitting, the maximum Hg²⁺ ion-adsorption capacities of NH₃·H₂O-zeolite 4A and KH792-zeolite 4A were 53.55 mg/g and 42.93 mg/g, respectively, which were basically consistent with the experimental data. Therefore, the maximum Hg²⁺ ion-adsorption capacity of NH₃·H₂O-zeolite 4A was slightly higher than that of KH792-zeolite 4A.

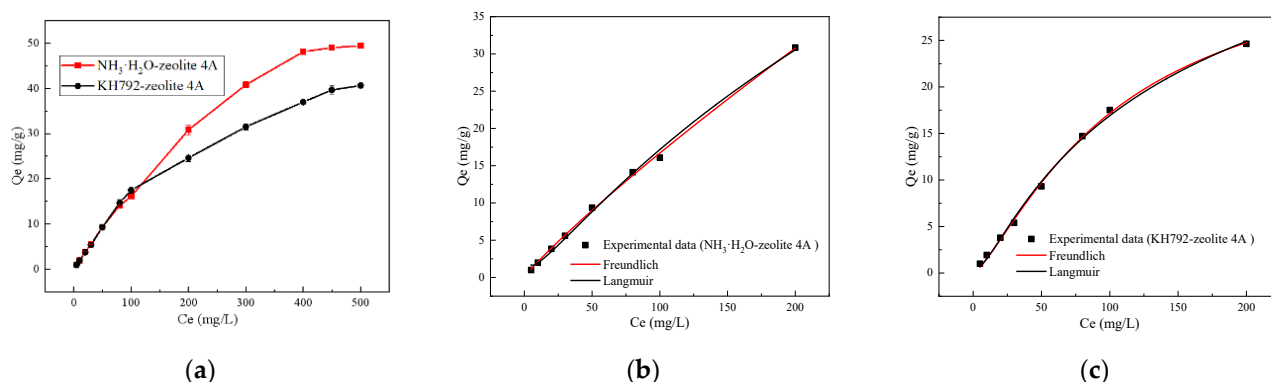


Figure 9. Effect of Hg^{2+} ion concentration on the adsorption capacities of modified zeolites (a) and the isothermal Hg^{2+} ion-adsorption model fitting of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A (b) and KH792-zeolite 4A (c).

Table 1. Isothermal adsorption parameters for the adsorption of Hg^{2+} ions by modified zeolites.

Isothermal Adsorption Model	Parameter	$\text{NH}_3\cdot\text{H}_2\text{O}$ -Zeolite 4A	KH792-Zeolite 4A
Langmuir model	$Q_{\max}$ (mg/g)	53.55	42.93
	K_L (L/mg)	0.003	0.0014
	R_L	0.625	0.78
	R^2	0.9997	0.9993
Freundlich model	K_f (mg/g)	25.36	0.29
	R^2	0.9958	0.9977

Explanation of model parameters in Supplementary Materials.

Through adsorption kinetic model fitting, it was found that $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A and KH792-zeolite 4A showed similar adsorption kinetic characteristics, and the Hg^{2+} ion desorption kinetics models of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A and KH792-zeolite 4A were better fits with the pseudo second-order adsorption model (Figure 10 and Table 2), indicating that chemisorption was the reaction-rate control step and chemisorption was the main reaction mechanism of Hg^{2+} ion-removal by the two kinds of modified zeolite [42]. The kinetic parameter K_2 of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A was significantly greater than that of KH792-zeolite 4A, indicating that $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A adsorbed Hg^{2+} ions in solution faster than KH792-zeolite 4A, which might be due to the large molecular polymer of KH792 grafted on the zeolite surface filling or blocking the micropores of the zeolite [43] and affecting the diffusion of Hg^{2+} ions.

Table 2. The adsorption kinetic model fitting parameters.

	Pseudo First-Order Dynamics			Pseudo Second-Order Dynamics		
	Q_e (mg/g)	K_1	R^2	Q_e (mg/g)	K_2	R^2
$\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A	1.79	0.27	0.4194	1.97	0.21	0.9063
KH792-zeolite 4A	1.74	0.28	0.4293	1.87	0.16	0.9617

Explanation of model parameters in Supplementary Materials.

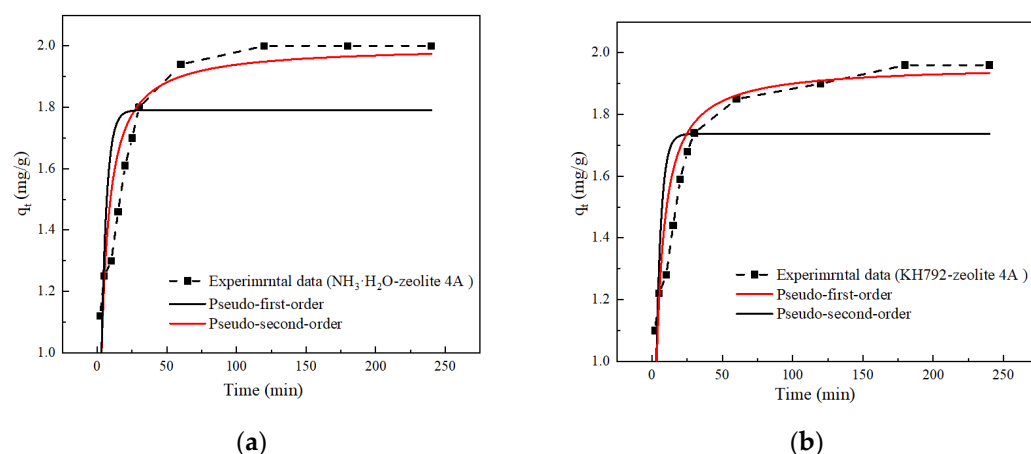


Figure 10. The Hg^{2+} ion-adsorption kinetic model fitting of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A (a) and KH792-zeolite 4A (b).

The adsorption abilities of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A and KH792-zeolite 4A for Hg^{2+} ions in the solution increased with increasing temperatures (Figure 11). From the thermodynamic parameter calculation (Table 3), the ΔH° of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A and KH792-zeolite 4A were less than 0, indicating that the adsorption processes of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A and KH792-zeolite 4A for Hg^{2+} ions was exothermic; the ΔS° was greater than 0, showing that the Hg^{2+} ion adsorptions by $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A and KH792-zeolite 4A were entropy-increasing processes, which might be because the generated chemical bonds increased the chaos of the system [44]; and the ΔG° of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A and KH792-zeolite 4A were less than 0, indicating that the adsorptions of Hg^{2+} ions by these kinds of modified zeolites were spontaneous without energy supply until the zeolites reached adsorption saturation. Usually, when the ΔH° value was in the range of 80–200 kJ/mol, the adsorption method was mainly chemical adsorption [45]. Therefore, the Hg^{2+} ion-removals by $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A and KH792-zeolite 4A were mainly conducted through chemical adsorption.

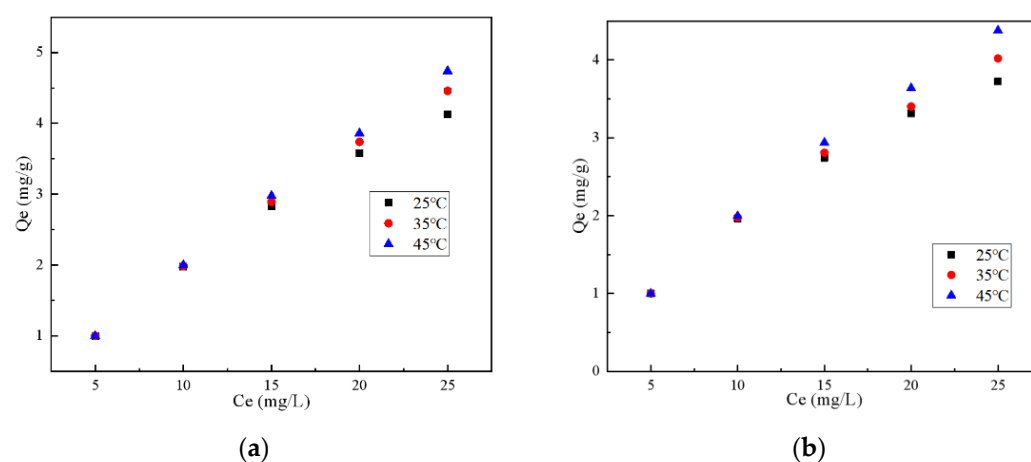


Figure 11. Langmuir isothermal adsorption models of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A (a) and KH792-zeolite 4A (b) at different temperatures.

Therefore, because the content of nitrogen-containing groups introduced by simple $\text{NH}_3 \cdot \text{H}_2\text{O}$ impregnation was the same as that introduced by the grafting method, $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A could effectively remove Hg^{2+} ions in the solution by chemical adsorption. Its Hg^{2+} ion adsorption rate was faster than that of KH792-zeolite 4A due to the fact that the micropores of the zeolite were not blocked, unlike in organic grafting.

Table 3. Thermodynamic parameters of Hg^{2+} ion-adsorption by $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A and KH792-zeolite 4A.

	ΔH° (kJ/mol)	ΔS° (kJ/mol·K)	ΔG° (kJ/mol)		
			25 °C	35 °C	45 °C
$\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A	−89.22	0.13	−127.96	−130.56	−133.16
KH792-zeolite 4A	−93.08	0.17	−143.74	−147.14	−150.54

Explanation of model parameters in Supplementary Materials.

3.2.4. Adsorption Mechanism

The XRD pattern shows that the peak value had no obvious change before and after Hg^{2+} ion adsorption by $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A (Figure 12a), indicating that no crystal phase formed. However, the diffraction intensity of the characteristic peak after adsorption was significantly lower than that before adsorption, indicating that the crystallinity of the zeolite after adsorption was reduced and that the amorphous phase might have been increased [46]. According to the FTIR spectrum (Figure 12(b)), the peak at 1401 cm^{-1} of $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A before adsorption was the NH_4^+ characteristic peak, and this peak was not found after adsorption (Figure 12(b2)), indicating that the ion-exchange reaction between NH_4^+ ions and Hg^{2+} ions had taken place. In addition, the peak at 1640 cm^{-1} was characteristic of the Si-OH group peak and at 3421 cm^{-1} was characteristic of the Si-NH₂ group peak in $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A. After the adsorption of the Hg^{2+} ions, the peak value was obviously lower than that before adsorption, indicating that these groups complexed with Hg^{2+} ions (Figure 12c).

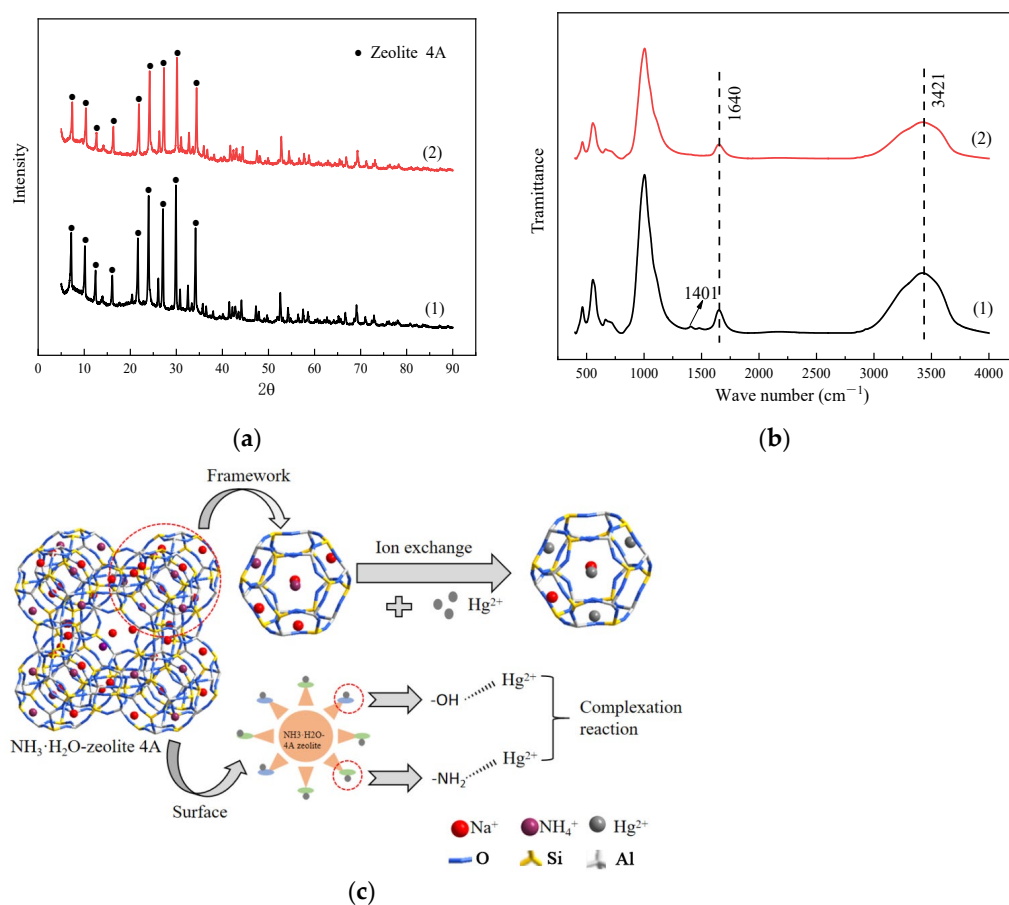


Figure 12. XRD patterns before (1) and after (2) the adsorption of Hg^{2+} ions by $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A (a); FTIR spectra before (1) and after (2) the adsorption of Hg^{2+} ions by $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A (b); and the reaction mechanism of Hg^{2+} ion adsorption by $\text{NH}_3 \cdot \text{H}_2\text{O}$ -zeolite 4A (c).

Therefore, through the thermodynamic analysis, the Hg^{2+} ion removal by $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite was demonstrated to have mainly taken place through chemical adsorption, and the FTIR analysis shows that the main Hg^{2+} ions-removal mechanism was ion exchange with NH_4^+ introduced and a complexation reaction with the NH_2 group introduced. Thus, the zeolite 4A modified by simple $\text{NH}_3\cdot\text{H}_2\text{O}$ impregnation has a higher adsorption capacity for Hg^{2+} ions than that of other products (Table 4) due to the introduction of more inorganic nitrogen-containing functional groups.

Table 4. Comparison of Hg^{2+} ion-adsorption capacities of various adsorbents.

Sample	Adsorption Condition	Maximum Adsorption Capacity (mg/g)	References
Thiol- and hydroxyl-containing bifunctional vermiculite	pH 4 and dosage 2 g/L	8.57	[47]
Adsorption columns using activated carbon and zeolite	pH from 0 to 7 and dosage 1 g/L	5.5	[48]
Opal-palygorskite clay zeolite 4A	pH 3 and dosage 1 g/L	41.99	[49]
13X zeolite	pH from 5 to 6 and dosage 100 g/L	16.35	[50]
KH792-zeolite 4A	pH 6 and 5 g/L	42.93	This work
$\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A	pH 6 and 5 g/L	53.55	This work

3.3. Coexisting Multiple Ion Effect and Reusability

When Hg^{2+} was mixed with Cu^{2+} , Pb^{2+} , and Zn^{2+} ions, the Hg^{2+} removal rate of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A in the solution was basically unchanged, and remained at 99.325%. When Hg^{2+} coexisted with Cu^{2+} , Pb^{2+} , and Zn^{2+} ions, the removal rate of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A for Hg^{2+} ions remained 99.325%, for Cu^{2+} ions was 26.05%, for Zn^{2+} ions was 5.95%, and for Pb^{2+} ions reached 99.05% (Figure 13). Thus, $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A had a high adsorption capacity for Hg^{2+} and Pb^{2+} ions, while exhibiting weak removal rates for Cu^{2+} and Zn^{2+} ions, which could be explained by RG Pearson's soft-and-hard acid-base theory. Hg^{2+} and Pb^{2+} ions are soft acids, and the amino groups of soft bases in the modified zeolite have the ability of preferential adsorption [51]. Although the Cu^{2+} ion is also a soft acid, the Pb^{2+} ion has more orbital overlap with the lone pair electrons of nitrogen atoms, and the adsorption energy of the Pb^{2+} ion is less than that of the Cu^{2+} ion, so the Pb^{2+} ion would be adsorbed preferentially, and the Cu^{2+} ion has difficulty occupying the Pb^{2+} ion-adsorption site [52]. Therefore, when there were a variety of heavy metal ions in the solution, $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A maintained a high adsorption ability for Hg^{2+} ions.

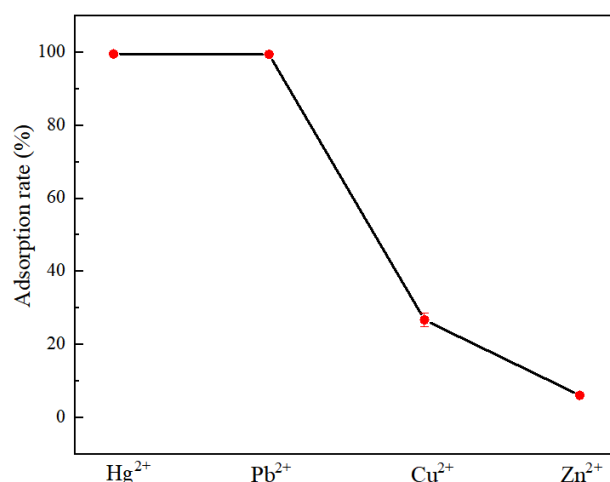


Figure 13. Adsorption rate of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A for Hg^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} ions when these ions coexist (adsorbent dosage of 0.1 g, pH 6, temperature of 25 °C, and coexisting ion concentration of 10 mg/L).

The reusability of the adsorbent is very important to save costs in practical applications. The results of the recycling experiment show that the Hg^{2+} ion-adsorption efficiency of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A was 87.22% after four cycles and 72.03% after five cycles (Figure 14a), which indicates that $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A had good reusability. FTIR spectra showed that the surface functional groups of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A had almost no change (Figure 14b), which indicates that the nitrogen-containing functional groups introduced into the zeolite after $\text{NH}_3\cdot\text{H}_2\text{O}$ impregnation would not be affected by multiple elution. The gradual decline of the removal rate might be due to the loss of adsorbents during elution.

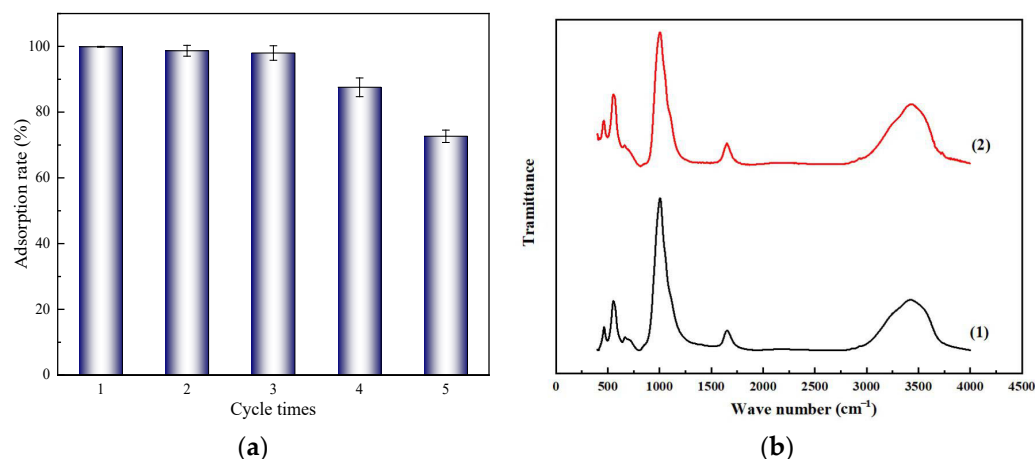


Figure 14. The reusability of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A for the adsorption of Hg^{2+} ions (a) and FTIR spectra before (1) and after 5 cycles (2) of adsorption of Hg^{2+} ions by $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A (b).

3.4. Hg^{2+} Ion Adsorption in Soil Leaching

After adding deionized water to mercury-contaminated soil, the concentration of Hg^{2+} ions in the leaching solution reached equilibrium after 24 h (Table 5). The maximum content of Hg^{2+} ions in the soil leaching was 5.82 mg/kg, while the content of Hg^{2+} ions in the soil leaching was only 0.17 mg/kg after adding 1% (0.01 g) $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A. Therefore, in mercury-contaminated soil leaching, $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A could efficiently remove Hg^{2+} ions and reduce additional soil-pollution risks.

Table 5. Concentration of Hg^{2+} ions (mg/kg) in the soil leaching at different times.

	Washing Time (h)				
	6	12	24	36	48
Adding $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A	0.013	0.112	0.157	0.142	0.170
No adding	1.065	3.355	5.76	5.74	5.82

4. Conclusions

In this study, zeolite 4A synthesized using fly ash was modified by simple inorganic ammonia impregnation, which could introduce more kinds of inorganic amine functional groups into the zeolite, thus improving the removal capacity of the modified zeolite for Hg^{2+} ions. The mechanism of impregnation modifications with $\text{NH}_3\cdot\text{H}_2\text{O}$, KH792, and NH_4Cl for zeolite 4A, and the removal capacity of Hg^{2+} ions by modified zeolites, were studied and compared. It was found that $\text{NH}_3\cdot\text{H}_2\text{O}$ modification could introduce nitrogen-containing groups through ion exchange and a reaction with hydroxyl groups on the zeolite surface, while NH_4Cl modification could introduce NH_4^+ into the zeolite through ion exchange, and organic modification could introduce KH792 containing two kinds of nitrogen-containing groups into the zeolite through grafting. Therefore, $\text{NH}_3\cdot\text{H}_2\text{O}$ modification and organic grafting introduced more nitrogen-containing groups than NH_4Cl modification.

The Hg^{2+} ion-removal rates of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A were significantly higher than those of KH792-zeolite 4A and NH_4Cl -zeolite 4A. According to the isothermal adsorption model fitting, the maximum Hg^{2+} ion-adsorption capacity of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A achieved was 53.55 mg/g. The thermodynamic analysis showed that the Hg^{2+} ion adsorption of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A in the solution was mainly achieved through chemical adsorption. The XRD and FTIR analyses showed that the adsorption of Hg^{2+} ions by $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A was mainly achieved through ion exchange between NH_4^+ and Hg^{2+} ions and the complexation of nitrogen-containing functional groups of the modified zeolite with Hg^{2+} ions.

When Cu^{2+} , Pb^{2+} , Zn^{2+} , and Hg^{2+} ions coexisted, the Hg^{2+} ion adsorption ability of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A was not affected. After five adsorption and desorption cycles, the Hg^{2+} ion-adsorption rate of $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A was 72.03%. Therefore, $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A had good reusability. When $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A was added to the leaching of mercury-contaminated soil, the content of soluble mercury in the leaching could be reduced from 5.82 mg/kg to 0.17 mg/kg. Thus, $\text{NH}_3\cdot\text{H}_2\text{O}$ -zeolite 4A exhibited an efficient Hg^{2+} ion-removal ability.

In this study, we used cheap industrial solid-waste fly ash as a raw material to synthesize zeolite 4A, then applied simple $\text{NH}_3\cdot\text{H}_2\text{O}$ impregnation with low energy consumption to obtain a modified zeolite with an effective adsorption capacity for Hg^{2+} ions. The modified zeolite was not only low in synthesis cost and simple in modification method, but also had environmental safety due to inorganic modification. Therefore, our synthesis product has broad potential application prospects in the treatment of mercury-contaminated water and soil. However, to avoid environmental risks, further research is needed on the recovery of mercury in eluate during the reuse of modified zeolites. In addition, our study was only based on a laboratory experiment, so small-scale research on the practical applications of modified products needs to be further carried out to provide a feasible technical basis for the practical applications of modified products.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su142315924/s1>. References [53–57] are cited in the Supplementary Materials.

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References

1. Mon, M.; Lloret, F.; Ferrando-Soria, J.; Martí-Gastaldo, C.; Armentano, D.; Pardo, E. Selective and Efficient Removal of Mercury from Aqueous Media with the Highly Flexible Arms of a BioMOF. *Angew. Chem. Int. Ed.* **2016**, *55*, 11167–11172. [[CrossRef](#)] [[PubMed](#)]
2. Ma, L.; Islam, S.; Xiao, C.; Zhao, J.; Liu, H.; Yuan, M.; Sun, G.; Li, H.; Ma, S.; Kanatzidis, M. Rapid simultaneous removal of toxic anions $[\text{HSeO}_3]$, $[\text{SeO}_3]^{2-}$, and $[\text{SeO}_4]^{2-}$, and metals Hg^{2+} , Cu^{2+} , and Cd^{2+} by MoS_4^{2-} intercalated layered double hydroxide. *J. Am. Chem. Soc.* **2017**, *139*, 12745–12757. [[CrossRef](#)]
3. Bolisetty, S.; Peydayesh, M.; Mezzenga, R. Sustainable technologies for water purification from heavy metals: Review and analysis. *Chem. Soc. Rev.* **2019**, *48*, 463–487. [[CrossRef](#)] [[PubMed](#)]
4. Chojnacki, A.; Chojnacka, K.; Hoffmann, J.; Górecki, H. The application of natural zeolites for mercury removal: From laboratory tests to industrial scale. *Miner. Eng.* **2004**, *17*, 933–937. [[CrossRef](#)]
5. Murukutti, M.K.; Jena, H. Synthesis of nano-crystalline zeolite-A and zeolite-X from Indian coal fly ash, its characterization and performance evaluation for the removal of Cs^+ and Sr^{2+} from simulated nuclear waste. *J. Hazard. Mater.* **2021**, *423*, 127085. [[CrossRef](#)]

6. Belviso, C. State-of-the-art applications of fly ash from coal and biomass: A focus on zeolite synthesis processes and issues. *Prog. Energy Combust. Sci.* **2018**, *65*, 109–135. [[CrossRef](#)]
7. Yang, H.-M.; Jeon, H.; Lee, Y.; Choi, M. Sulfur-modified zeolite A as a low-cost strontium remover with improved selectivity for radioactive strontium. *Chemosphere* **2022**, *299*, 134309. [[CrossRef](#)] [[PubMed](#)]
8. Zhou, G.; Wang, Y.; Zhou, R.; Wang, C.; Jin, Y.; Qiu, J.; Hua, C.; Cao, Y. Synthesis of amino-functionalized bentonite/CoFe₂O₄@MnO₂ magnetic recoverable nanoparticles for aqueous Cd²⁺ removal. *Sci. Total Environ.* **2019**, *682*, 505–513. [[CrossRef](#)] [[PubMed](#)]
9. Jawed, A.; Saxena, V.; Pandey, L.M. Engineered nanomaterials and their surface functionalization for the removal of heavy metals: A review. *J. Water Process. Eng.* **2020**, *33*, 101009. [[CrossRef](#)]
10. Srasra, M.; Delsarte, S.; Gaigneaux, E.M. Nitrided Zeolites: A Spectroscopic Approach for the Identification and Quantification of Incorporated Nitrogen Species. *J. Phys. Chem. C* **2010**, *114*, 4527–4535. [[CrossRef](#)]
11. Agarwal, V.; Huber, G.W.; Conner, W.C., Jr.; Auerbach, S.M. DFT study of nitrided zeolites: Mechanism of nitrogen substitution in HY and silicalite. *J. Catal.* **2010**, *269*, 53–63. [[CrossRef](#)]
12. Wu, G.; Wang, X.; Yang, Y.; Li, L.; Wang, G.; Guan, N. Confirmation of NH species in the framework of nitrogen-incorporated ZSM-5 zeolite by experimental and theoretical studies. *Microporous Mesoporous Mater.* **2010**, *127*, 25–31. [[CrossRef](#)]
13. Li, X.; Meng, C.; Meng, Y.; Gu, L.; Chen, Q.; Liu, H. Amino acid modified molecular sieves with different pore size for chiral separation. *Colloid Surface A* **2019**, *581*, 123789. [[CrossRef](#)]
14. Kim, K.; Lee, S.; Ryu, J.H.; Lee, K.S.; Lee, W.B. An improved CO₂ adsorption efficiency for the zeolites impregnated with the amino group: A molecular simulation approach. *Int. J. Greenh. Gas. Con.* **2013**, *19*, 350–357. [[CrossRef](#)]
15. Zhao, A.; Samanta, A.; Sarkar, P.; Gupta, R. Carbon Dioxide Adsorption on Amine-Impregnated Mesoporous SBA-15 Sorbents: Experimental and Kinetics Study. *Ind. Eng. Chem. Res.* **2013**, *52*, 6480–6491. [[CrossRef](#)]
16. Tsintskaladze, G.; Eprikashvili, L.; Mumladze, N.; Gabunia, V.; Sharashenidze, T.; Zautashvili, M.; Kordzakhia, T.; Shatakishvili, T. Nitrogenous zeolite nanomaterial and the possibility of its application in agriculture. *Ann. Agrar. Sci.* **2017**, *15*, 365–369. [[CrossRef](#)]
17. Ramos-Martinez, V.; Ramirez-Vargas, E.; Medellin-Rodriguez, F.; Ávila-Orta, C.; Gallardo-Vega, C.; Jasso-Salcedo, A.; Andrade-Guel, M. Zeolite 13X modification with gamma-aminobutyric acid (GABA). *Microporous Mesoporous Mater.* **2019**, *295*, 109941. [[CrossRef](#)]
18. Wang, Y.; Du, T.; Song, Y.; Che, S.; Fang, X.; Zhou, L. Amine-functionalized mesoporous ZSM-5 zeolite adsorbents for carbon dioxide capture. *Solid State Sci.* **2017**, *73*, 27–35. [[CrossRef](#)]
19. Zhang, W.; Liu, H.; Sun, C.; Drage, T.C.; Snape, C.E. Performance of polyethyleneimine–silica adsorbent for post-combustion CO₂ capture in a bubbling fluidized bed. *Chem. Eng. J.* **2014**, *251*, 293–303. [[CrossRef](#)]
20. Sandhu, N.K.; Pudasainee, D.; Sarkar, P.; Gupta, R. Steam Regeneration of Polyethylenimine-Impregnated Silica Sorbent for Postcombustion CO₂ Capture: A Multicyclic Study. *Ind. Eng. Chem. Res.* **2016**, *55*, 2210–2220. [[CrossRef](#)]
21. Yang, L.; Qian, X.; Yuan, P.; Bai, H.; Miki, T.; Men, F.; Li, H.; Nagasaka, T. Green synthesis of zeolite 4A using fly ash fused with synergism of NaOH and Na₂CO₃. *J. Clean. Prod.* **2018**, *212*, 250–260. [[CrossRef](#)]
22. Ikeda, T.; Yoshida, Y.; Nakazawa, N.; Inagaki, S.; Kubota, Y. Solid-state NMR and powder X-ray diffraction studies on ammonium ion-exchanged and dealuminated zeolite YNU-5. *Microporous Mesoporous Mater.* **2020**, *302*, 110197. [[CrossRef](#)]
23. Zhang, C.; Yu, J.; Cao, Z.; Wang, R.; Du, W.; He, P.; Ge, Y. Preparation and properties of silane coupling agent modified zeolite as warm mix additive. *Constr. Build. Mater.* **2020**, *244*, 118408. [[CrossRef](#)]
24. Li, Y.; Yang, L.; Li, X.; Miki, T.; Nagasaka, T. A composite adsorbent of ZnS nanoclusters grown in zeolite NaA synthesized from fly ash with a high mercury ion removal efficiency in solution. *J. Hazard. Mater.* **2021**, *411*, 125044. [[CrossRef](#)] [[PubMed](#)]
25. Zhou, L.; Liu, Z.; Liu, J.; Huang, Q. Adsorption of Hg(II) from aqueous solution by ethylenediamine-modified magnetic crosslinking chitosan microspheres. *Desalination* **2010**, *258*, 41–47. [[CrossRef](#)]
26. Falter, R.; Schöler, H.F. Determination of mercury species in natural waters at picogram level with online RP C18 preconcentration and HPLC-UV-PCO-CVAAS. *Fresenius J. Anal. Chem.* **1995**, *353*, 34–38. [[CrossRef](#)]
27. Laperdina, T.; Melnikova, M.; Koval, A.; Sidorov, Y.; Nagorny, V.; Ostapchuk, V. Gold mining in Siberia and the Far East as a source of mercury contamination of the environment. *J. Environ. Sci.* **2000**, *12*, 51–58.
28. Zhang, S.; Zhang, Y.; Liu, J.; Xu, Q.; Xiao, H.; Wang, X.; Xu, H.; Zhou, J. Thiol modified Fe₃O₄@SiO₂ as a robust, high effective, and recycling magnetic sorbent for mercury removal. *Chem. Eng. J.* **2013**, *226*, 30–38. [[CrossRef](#)]
29. Yang, L.; Li, S.; Wen, T.; Meng, F.; Chen, G.; Qian, X. Influence of ferrous-metal production on mercury contamination and fractionation in farmland soil around five typical iron and steel enterprises of Tangshan, China. *Ecotoxicol. Environ. Saf.* **2019**, *188*, 109774. [[CrossRef](#)]
30. Wang, P.; Sun, Q.; Zhang, Y.; Cao, J. Effective removal of methane using nano-sized zeolite 4A synthesized from kaolin. *Inorg. Chem. Commun.* **2019**, *111*, 107639. [[CrossRef](#)]
31. Amooghini, A.; Omidkhah, M.; Kargari, A. The effects of aminosilane grafting on NaY zeolite–Matrimid®5218 mixed matrix membranes for CO₂/CH₄ separation. *J. Membr. Sci.* **2015**, *490*, 364–379. [[CrossRef](#)]
32. Purnomo, C.; Salim, C.; Hinode, H. Synthesis of pure Na–X and Na–A zeolite from bagasse fly ash. *Micropor. Mesopor. Mater.* **2012**, *162*, 6–13. [[CrossRef](#)]
33. Mahata, B.K.; Chung, K.-L.; Chang, S.-M. Removal of ammonium nitrogen (NH₄⁺-N) by Cu-loaded amino-functionalized adsorbents. *Chem. Eng. J.* **2021**, *411*, 128589. [[CrossRef](#)]

34. Kawano, A.; Moteki, T.; Ogura, M. Effect of delamination on active base site formation over nitrated MWW-type zeolite for Knoevenagel condensation. *Microporous Mesoporous Mater.* **2020**, *299*, 110104. [\[CrossRef\]](#)
35. Liu, Y.; Liu, J.; Yao, W.; Cen, W.; Wang, H.; Weng, X.; Wu, Z. The effects of surface acidity on CO₂ adsorption over amine functionalized protonated titanate nanotubes. *RSC Adv.* **2013**, *3*, 18803–18810. [\[CrossRef\]](#)
36. Drage, T.; Arenillas, A.; Smith, K.; Snape, C. Thermal stability of polyethylenimine based carbon dioxide adsorbents and its influence on selection of regeneration strategies. *Microporous Mesoporous Mater.* **2008**, *116*, 504–512. [\[CrossRef\]](#)
37. Xu, X.; Zheng, Y.; Gao, B.; Cao, X. N-doped biochar synthesized by a facile ball-milling method for enhanced sorption of CO₂ and reactive red. *Chem. Eng. J.* **2019**, *368*, 564–572. [\[CrossRef\]](#)
38. Zendehelel, M.; Bodaghifard, M.A.; Behyar, H.; Mortezaei, Z. Alkylaminopyridine-grafted on HY Zeolite: Preparation, characterization and application in synthesis of 4H-Chromenes. *Microporous Mesoporous Mater.* **2018**, *266*, 83–89. [\[CrossRef\]](#)
39. Diôgo, P.; Francisco, W.; Pedro, A.; Allyson, G.; Rodrigo, S.; Enrique, R.; Diana, C. CO₂ adsorption in amine-grafted zeolite 13X. *Appl. Surf. Sci.* **2014**, *314*, 314–321.
40. Chen, Y.; Zhao, Y. Synthesis and characterization of polyacrylonitrile-2-amino-2-thiazoline resin and its sorption behaviors for noble metal ions. *React. Funct. Polym.* **2003**, *55*, 89–98. [\[CrossRef\]](#)
41. Xiong, C.; Li, Y.; Wang, G.; Fang, L.; Zhou, S.; Yao, C.; Chen, Q.; Zheng, X.; Qi, D.; Fu, Y.; et al. Selective removal of Hg(II) with polyacrylonitrile-2-amino-1,3,4-thiadiazole chelating resin: Batch and column study. *Chem. Eng. J.* **2015**, *259*, 257–265. [\[CrossRef\]](#)
42. Monier, M.; Abdel-Latif, D.A. Modification and characterization of PET fibers for fast removal of Hg(II), Cu(II) and Co(II) metal ions from aqueous solutions. *J. Hazard. Mater.* **2013**, *250*, 122–130. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Puspitasari, T.; Kadja, G.; Radiman, C.L.; Darwis, D.; Mukti, R. Two-step preparation of amidoxime-functionalized natural zeolites hybrids for the removal of Pb²⁺ ions in aqueous environment. *Mater. Chem. Phys.* **2018**, *216*, 197–205. [\[CrossRef\]](#)
44. Wu, J.; Xu, Z.; Zhang, W.; Lv, L.; Pan, B.; Nie, G.; Li, M.; Du, Q. Application of heterogeneous adsorbents in removal of dimethyl phthalate: Equilibrium and heat. *AIChE J.* **2010**, *56*, 2699–2705. [\[CrossRef\]](#)
45. Yang, L.; Gao, M.; Wei, T.; Nagasaka, T. Synergistic removal of As(V) from aqueous solution by nanozero valent iron loaded with zeolite 5A synthesized from fly ash. *J. Hazard. Mater.* **2021**, *424*, 127428. [\[CrossRef\]](#)
46. Li, S.; Bai, H.; Wang, J.; Jing, X.; Liu, Q.; Zhang, M.; Chen, R.; Liu, L.; Jiao, C. In situ grown of nano-hydroxyapatite on magnetic CaAl-layered double hydroxides and its application in uranium removal. *Chem. Eng. J.* **2012**, *193–194*, 372–380. [\[CrossRef\]](#)
47. Tran, L.; Wu, P.; Zhu, Y.; Liu, S.; Zhu, N. Comparative study of Hg(II) adsorption by thiol- and hydroxyl-containing bifunctional montmorillonite and vermiculite. *Appl. Sur. Sci.* **2015**, *356*, 91–101. [\[CrossRef\]](#)
48. Wan, C.; Xie, Q.; Liu, J.; Liang, D.; Huang, X.; Zhou, H.; Tang, Y.; Liu, D. Pilot-scale combined adsorption columns using activated carbon and zeolite for hazardous trace elements removal from wastewater of entrained-flow coal gasification. *Process. Saf. Environ. Prot.* **2021**, *147*, 439–449. [\[CrossRef\]](#)
49. Wu, Z.; Chen, T.; Liu, H.; Wang, C.; Chen, P.; Chen, D.; Xie, J. An insight into the comprehensive application of opal-palygorskite clay: Synthesis of 4A zeolite and uptake of Hg²⁺. *Appl. Clay Sci.* **2018**, *165*, 103–111. [\[CrossRef\]](#)
50. Czarna, D.; Baran, P.; Kunecki, P.; Panek, R.; Zmuda, R.; Wdowin, M. Synthetic zeolites as potential sorbents of mercury from wastewater occurring during wet FGD processes of flue gas. *J. Clean. Prod.* **2018**, *172*, 2636–2645. [\[CrossRef\]](#)
51. Sun, Y.; Lv, D.; Zhou, J.; Zhou, X.; Lou, Z.; Baig, S.A.; Xu, X. Adsorption of mercury (II) from aqueous solutions using FeS and pyrite: A comparative study. *Chemosphere* **2017**, *185*, 452–461. [\[CrossRef\]](#) [\[PubMed\]](#)
52. Xu, L.; Liu, Y.; Wang, J.; Tang, Y.; Zhang, Z. Selective adsorption of Pb²⁺ and Cu²⁺ on amino-modified attapulgite: Kinetic, thermal dynamic and DFT studies. *J. Hazard. Mater.* **2020**, *404*, 124140. [\[CrossRef\]](#) [\[PubMed\]](#)
53. Li, Y.; Zhang, P.; Du, Q.; Peng, X.; Liu, T.; Wang, Z.; Xia, Y.; Zhang, W.; Wang, K.; Zhu, H.; et al. Adsorption of fluoride from aqueous solution by graphene. *J. Colloid Interface Sci.* **2011**, *363*, 348–354. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Freundlich, H. Over the adsorption in solution. *J. Phys. Chem.* **1906**, *57*, 385–471.
55. Ho, Y.; McKay, G. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.* **2000**, *34*, 735–742. [\[CrossRef\]](#)
56. Ho, Y.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **1999**, *34*, 451–465. [\[CrossRef\]](#)
57. Fan, L.; Luo, C.; Sun, M.; Li, X.; Qiu, H. Highly selective adsorption of lead ions by water-dispersible magnetic chitosan/graphene oxide composites. *Colloids Surf. B* **2013**, *103*, 523–529. [\[CrossRef\]](#)