

# Efficient Removal of Nitrate in Neutral Solution Using Zero-Valent Al Activated by Soaking

Yi-Gong Dai, Xiao-Han Guo, Gen-Wang Ma, Wei-Zhuo Gai, and Zhen-Yan Deng\*

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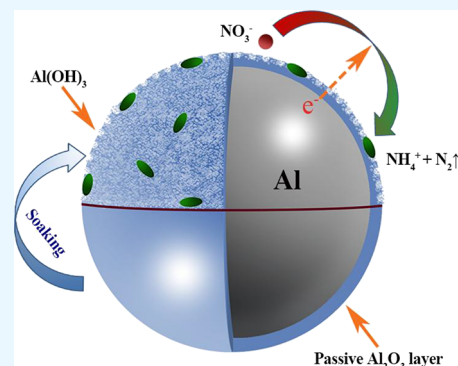


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**ABSTRACT:** Nitrate is a contaminant widely found in surface water, and a high concentration of nitrate can pose a serious threat to human health. Zero-valent iron is widely used to reduce nitrate in aqueous solution, but an acidic condition is required. Zero-valent aluminum has a much lower redox potential ( $E_0(\text{Al}^{3+}/\text{Al}^0) = -1.662 \text{ V}$ ) than zero-valent iron ( $E_0(\text{Fe}^{2+}/\text{Fe}^0) = -0.44 \text{ V}$ ), making it a better choice for reduction of nitrate. However, a passive oxide film covering on Al surfaces inhibits its electron transfer. In this work, metal Al powder was activated by a soaking procedure in deionized water. It was found that nitrate in neutral solution can be efficiently and completely reduced by soaked Al, even if the concentration of nitrate-N was up to  $100 \text{ mg L}^{-1}$ . Using an optimal soaking time, the soaked Al can remove  $>90\%$  of nitrate in aqueous solution within  $\sim 2 \text{ h}$  at  $50 \text{ }^\circ\text{C}$ . Furthermore, the nitrate reduction efficiency increased with increasing reaction temperature and dosage of Al powder. After reaction, only  $\sim 50\%$  of pristine N content was left in the form of ammonia ions ( $\text{NH}_4^+$ ) in aqueous solution. Mechanism analyses showed that after soaking, Al particle surfaces were covered by a layer of loose and fine  $\text{Al}(\text{OH})_3$  grains, which can shorten the induction time for the beginning of the reaction between inner Al and outside ions or molecules. This is the reason why soaked Al has a high efficiency for nitrate removal. The present results indicate that soaking is an effective way to activate Al to remove nitrate in water.



## 1. INTRODUCTION

Nitrate in surface water comes from a variety of sources, including waste manure, fertilizer, and industrial wastewater.<sup>1</sup> As nitrate is extremely soluble in water, it has become a prevalent contaminant in the water system and caused widespread concern about environmental pollution in recent years.<sup>2</sup> Nitrate itself is not yet known to be harmful to humans, but it will be converted into nitrite through the human digestive system, thus causing a series of diseases such as methemoglobin, blue baby syndrome, etc. Drinking water containing nitrate in a high concentration can seriously endanger human health.<sup>3–5</sup> The World Health Organization (WHO) has set a maximum concentration of  $11.3 \text{ mg L}^{-1}$  nitrate-N in drinking water,<sup>6</sup> while the Environmental Protection Agency of United States has established an upper limit of  $10 \text{ mg L}^{-1}$  nitrate-N in drinking water.<sup>5</sup>

There are a variety of ways developed for removing nitrate in surface water including biological, physical, and chemical methods.<sup>7,8</sup> For example, anaerobic bacteria in a bioreactor were used to convert nitrate into nitrogen,<sup>9–11</sup> but residual organic matter and bacterial pollution need bulk of complex technologies to handle. Some adsorbents such as nano-alumina and organo-zeolite can effectively remove nitrate from water,<sup>12,13</sup> and the regeneration of adsorbents and disposal of adsorbents containing nitrate are the problem. Nanofiltration and reverse osmosis membranes were used to remove nitrate from water,<sup>14–16</sup> and they have the possibilities of second

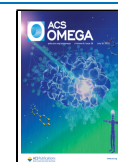
chemical pollution. Ion-exchange technology was used to exchange nitrate ions for chloride ions by means of strong base anion exchange resins,<sup>17</sup> but the operation process of this method is extremely complex and its cost is very high. Electrodialysis was used to remove nitrates from water by means of cation and anion exchange membranes under the action of an electric field,<sup>18,19</sup> but it produces concentrated waste streams including high concentrations of nitrate and other ions. The photocatalysis method, inspiring electron–hole pairs in semiconductor materials by ultraviolet light, was used to reduce nitrate in water,<sup>20</sup> and it is difficult to use in the practical application.

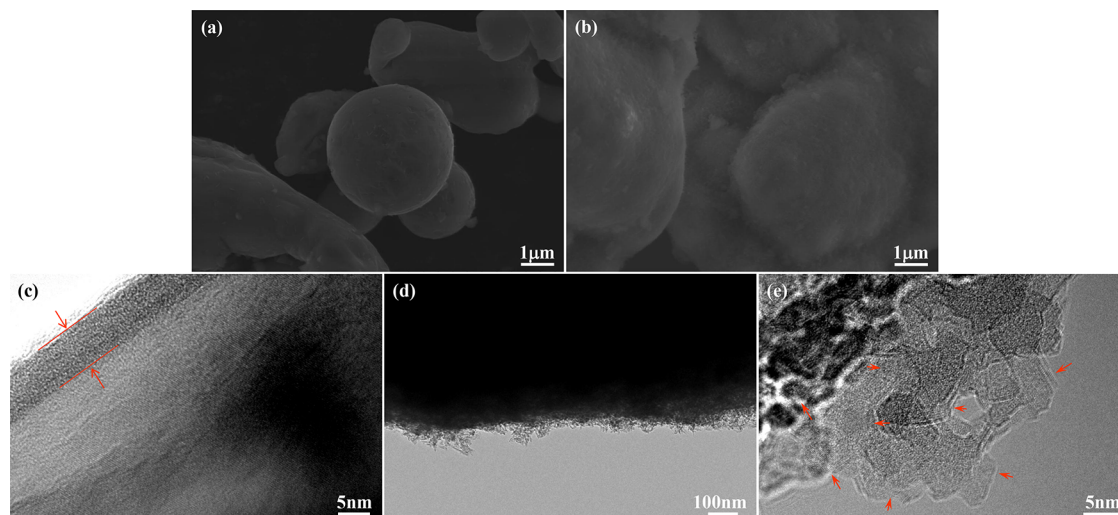
The chemical method has the advantages of simple operation, high efficiency, and low cost. In the past few years, zero-valent metals have been widely used to reduce and remove nitrate in aqueous solution, including zero-valent iron (ZVI),<sup>21–23</sup> zero-valent magnesium (ZVM),<sup>24–26</sup> zero-valent copper (ZVC),<sup>27–29</sup> zero-valent zinc (ZVZ),<sup>30,31</sup> zero-valent aluminum (ZVAL),<sup>32–35</sup> and their alloys.<sup>6</sup> Among them, ZVI

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**Figure 1.** SEM and TEM images of as-received 7.29  $\mu\text{m}$  Al powder (a, c) and that in panel (a) after soaking in deionized water at 25  $^{\circ}\text{C}$  for 35 h (b, d, and e).

has been the most commonly investigated due to its low cost and easy availability. However, almost all of the above zero-valent metals, especially for ZVI, just work in an acidic condition,<sup>22</sup> limiting their practical application in nitrate removal.

The byproducts of nitrate reduction by nano-ZVI in aqueous solutions were almost entirely ammonia, with a concentration of >99% pristine nitrate-N.<sup>36</sup> Fe alloys have a higher efficiency for nitrate removal, e.g., nanometer Fe-5.0% Cu alloy; however, their reduction byproducts included not only ammonia (60–80% of pristine nitrate-N) but also nitrite (20–40% of pristine nitrate-N) in the reacted solution.<sup>36</sup> By a reaction of ZVAl with nitrate in an alkaline solution (pH > 10), the reaction byproducts were ammonia, nitrite ions, and nitrogen, where ammonia ions have a concentration of 60–95% pristine nitrate-N.<sup>33</sup> Using Al-15% Fe, Cu, or Si alloys to reduce nitrate in aqueous solution, the byproducts were ammonia ions (80% pristine nitrate-N) and nitrogen (20% pristine nitrate-N).<sup>6</sup>

Aluminum is the most abundant metal in Earth's crust and has a much lower redox potential ( $E_0(\text{Al}^{3+}/\text{Al}^0) = -1.662\text{ V}$ ) than ZVI ( $E_0(\text{Fe}^{2+}/\text{Fe}^0) = -0.44\text{ V}$ ),<sup>37</sup> implying that metal Al is more favorable for transferring its electrons to nitrate in aqueous solution.<sup>38,39</sup> Usually, there is a passive oxide film covering Al surfaces, inhibiting the contact between inner Al and outside ions or molecules such that ZVAl can remove nitrate only in an acidic or alkaline condition.<sup>5,40</sup> However, in a practical water environment, a neutral pH condition is common. In this work, a simple procedure was used to activate Al, i.e., soaking Al powder in water and then freeze-drying. It was found that the soaked Al powder can shorten the induction time for the beginning of the reaction between inner Al and outside ions or molecules and efficiently reduce nitrate in neutral aqueous solution.

## 2. MATERIALS AND METHODS

**2.1. Chemicals and Materials.** Sodium nitrate ( $\text{NaNO}_3$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) were purchased from Shanghai Sinopharm Chemical Reagent Co. (99.9% purity; Shanghai, China). Al powder (7.29  $\mu\text{m}$ , 99.9% purity; High Purity Chemical Co., Tokyo, Japan) and  $\text{Al}(\text{OH})_3$  powder (2.5  $\mu\text{m}$ , 99.9% purity; High Purity Chemical Co., Tokyo, Japan)

were used in this work. Deionized water (resistivity, >18  $\text{M}\Omega\text{ cm}$ ; pH  $\approx 5.8$ ) was used in all the experiments.

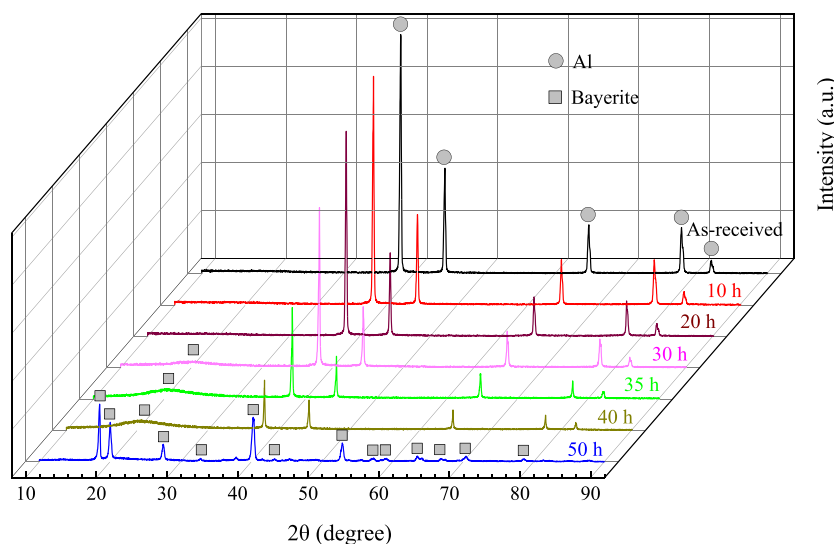
**2.2. Al Activation.** Al powder (6.0 g, 7.29  $\mu\text{m}$ ) was added into 300 mL of deionized water at 25  $^{\circ}\text{C}$  filled in a 500 mL Teflon beaker, which was placed in a thermostatic water bath to control temperature with an accuracy of  $\pm 1\text{ }^{\circ}\text{C}$  and then agitated with a speed of 500 rpm using a magnetic bar for a period. The soaked Al suspension was centrifuged for 10 min using a centrifuger (TDL-5-A, Anting Scientific Instrument Factory, China), then the up-layer water was removed, and a concentrated Al slurry was obtained. The concentrated Al slurry was sent for freeze-drying for 24 h using a freeze-dryer (Scientz-10nd, Ningbo Xinzhi Co., China) to obtain the soaked Al powder.<sup>41</sup> Before the nitrate reduction, the soaked Al powder was sieved with a 100-mesh sieve.

**2.3. Nitrate Reduction.** A suitable amount of sodium nitrate was added into deionized water to form a stock solution (1000  $\text{mg L}^{-1}\text{ NO}_3^{-}\text{-N}$ ), which was then diluted to a lower concentration for nitrate removal tests. A suitable amount of soaked Al powder was added into 400 mL nitrate solution filled in a 500 mL glass beaker and then agitated with a speed of 500 rpm using a magnetic bar. At pre-set time intervals, 15 mL of the suspension was taken from the glass beaker and then filtrated through a 0.22  $\mu\text{m}$  polyethersulfone (PES) filter for analyses.<sup>8,42,43</sup> The degradation rate of nitrate in aqueous solution is written as

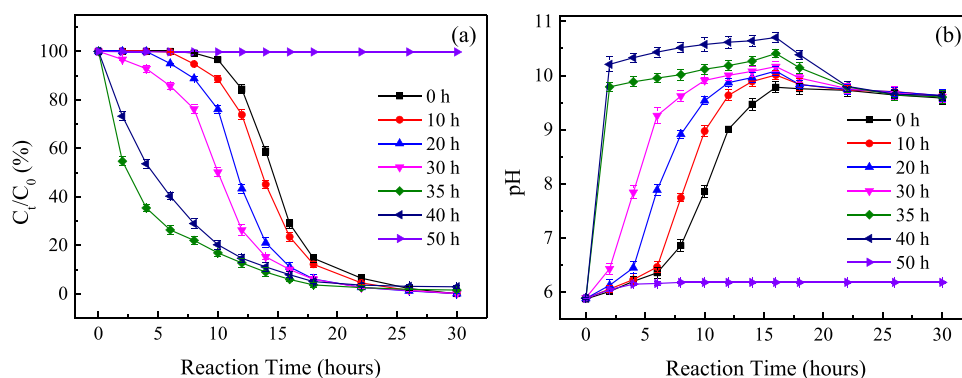
$$\alpha = \frac{C_t}{C_0} \times 100\% \quad (1)$$

where  $C_0$  and  $C_t$  are the concentrations of nitrate in aqueous solution at the initial time and time  $t$ , respectively. All the tests were repeated for three times to guarantee the reliability of the experimental data.

**2.4. Characterization.** The nitrate and ammonia ion concentrations in aqueous solution were detected by ion-selective electrodes (ISE,  $\text{PNO}_3\text{-1-01}$ ,  $\text{PNH}_3\text{-1-01}$ , INESA Scientific Instrument Co., Ltd., China).<sup>43,44</sup> Ion chromatography (IC, model no. MIC, Metrohm Co., Switzerland) was also carried out to analyze the concentrations of nitrate and nitrite in aqueous solution. The  $\text{Al}^{3+}$  ion concentration in aqueous solution was measured by inductively coupled plasma



**Figure 2.** X-ray diffraction patterns of as-received 7.29  $\mu\text{m}$  Al powder and those soaked for different times.



**Figure 3.** Time dependence of nitrate removal in aqueous solution using 7.29  $\mu\text{m}$  Al powder soaked for different times (a) and variation of pH value in the solution during the reaction (b), where  $C_0(\text{NO}_3^--\text{N}) = 20 \text{ mg L}^{-1}$ ,  $C_0(\text{Al}) = 4.0 \text{ g L}^{-1}$ , and the reaction temperature is 30  $^\circ\text{C}$ .

atomic emission spectroscopy (ICP-AES, ICAP 6300, Thermo Fisher Co., USA). The pH value in aqueous solution was measured by a pH meter (MP512, Shanghai Sanxin Instrument Co., China).

Hydrogen-generation experiment by Al-water reaction was carried out in a closed glass vessel containing 250 mL of deionized water. The amount of generated hydrogen was calculated by the ideal gas equation using the gas pressure in the vessel measured by a pressure gauge (type: LEO 2, Keller Co., Switzerland).<sup>45,46</sup>

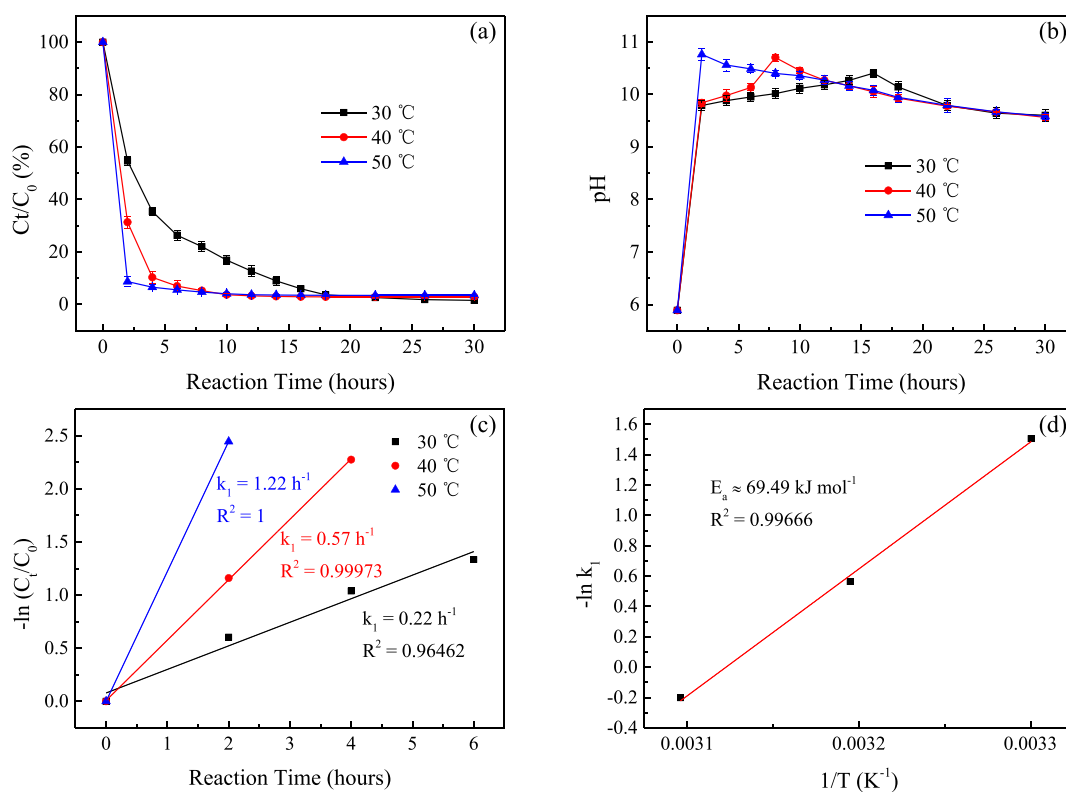
The morphology of Al powder was observed by scanning electron microscopy (SEM, model no. SU-5000, JEOL, Japan), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM). X-ray diffraction (XRD, model no. D/max-2500, Rigaku Co., Japan) was conducted to analyze the phase compositions of Al powder. Fourier transform infrared spectroscopy (FTIR, AVATAR 370, Thermo Nicolet) was performed to analyze the functional groups or chemical structures on Al particle surfaces.

### 3. RESULTS AND DISCUSSION

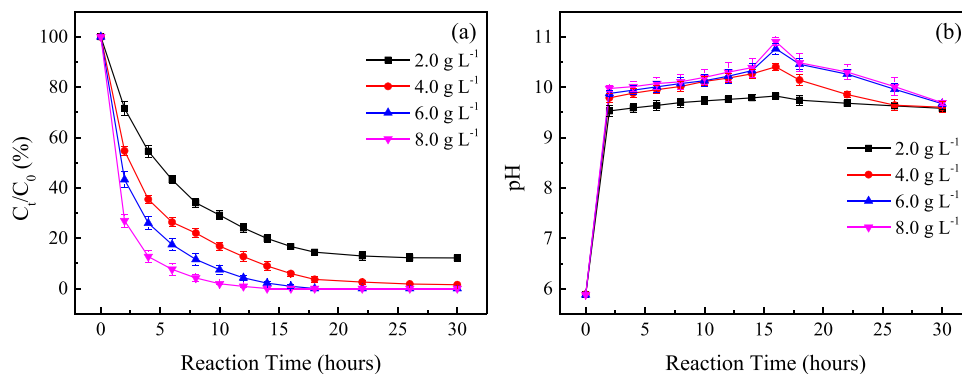
**3.1. Morphology of Al Powder.** Figure 1a,c shows SEM and TEM images of as-received 7.29  $\mu\text{m}$  Al powder. It can be seen that the surfaces of pristine Al particles are dense and smooth (Figure 1a). There is a dense passive oxide film

covering pristine Al surfaces, which is amorphous and has a thickness of  $\sim 7 \text{ nm}$  (Figure 1c). After soaking, the dense passive oxide film on pristine Al particles became loose, and there was a layer of fine flocculent particles on soaked Al particle surfaces (Figure 1b,d), because the passive oxide film on pristine Al particle surfaces underwent a hydration reaction during the soaking process.<sup>47,48</sup> The fine flocculent particles on soaked Al surfaces are crystallized aluminum hydroxides with the sizes of a few nanometers (arrows in Figure 1e), which are a bayerite ( $\text{Al}(\text{OH})_3$ ) phase confirmed by their X-ray diffraction patterns shown in Figure 2. The thickness of the crystallized aluminum hydroxides on soaked Al particles can be up to  $\sim 1 \mu\text{m}$  for a soaking time of  $\sim 35 \text{ h}$ .<sup>41</sup>

**3.2. Nitrate Removal.** Figure 3a shows nitrate removal in aqueous solution using 7.29  $\mu\text{m}$  Al powder soaked for different times, while Figure 3b shows the variation of pH value in the solution with the reaction time. The error bars in figures are the variance of the experimental data. It can be seen that the efficiency for nitrate removal using soaked Al powder in neutral solution is obviously higher than that of pristine Al powder, and it increases with increasing soaking time at first, then reaches a maximum at a soaking time of 35 h, and finally almost is null after the soaking time of 50 h. Meanwhile, it is noted that, first, the pH value in the reaction solution increases with the reaction time, then reaches a maximum, and finally decreases to a constant of  $\sim 9.6$  (except for Al powder soaked



**Figure 4.** Time dependence of nitrate removal in aqueous solution with different temperatures using 7.29 μm Al powder soaked for 35 h (a) and variation of pH value in the solution during the reaction (b), where  $C_0(\text{NO}_3^- \cdot \text{N}) = 20 \text{ mg L}^{-1}$ , and  $C_0(\text{Al}) = 4.0 \text{ g L}^{-1}$ . (c) Pseudo-first-order kinetic fittings for the experimental data of main reaction stage in panel (a) and (d) Arrhenius plot for the reaction rate constants of different temperatures in panel (c).



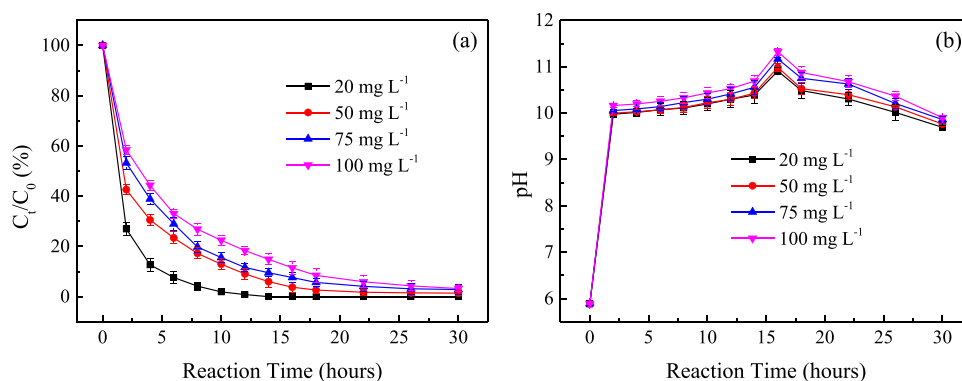
**Figure 5.** Time dependence of nitrate removal in aqueous solution at 30 °C using different dosage of 7.29 μm Al powder soaked for 35 h (a) and variation of pH value in the solution during the reaction (b), where  $C_0(\text{NO}_3^- \cdot \text{N}) = 20 \text{ mg L}^{-1}$ .

for 50 h). It seems that the reaction time to reach the peak pH value is almost the same for different Al powder. Furthermore, nitrate in aqueous solution can be completely removed at a reaction time of ~30 h by all of the Al powders used in this work (except for that soaked for 50 h).

Figure 4a shows nitrate removal in aqueous solution at different temperatures using 7.29 μm Al powder soaked for 35 h, while Figure 4b shows the variation of the pH value in the solution with the reaction time. It can be seen that the efficiency for nitrate removal increases with increasing reaction temperature. At 50 °C, >90% of nitrate in aqueous solution was removed within ~2 h. Also, the pH value in the reaction solution increases with the reaction time at first, then reaches a maximum, and finally decreases to a constant of ~9.6. However, the reaction time to reach the peak pH value

decreases rapidly when the reaction temperature increases from 30 to 50 °C.

Figure 5a shows nitrate removal in aqueous solution using different dosage of 7.29 μm Al powder soaked for 35 h, and Figure 5b shows the variation of pH value in the solution with the reaction time. It can be seen that the efficiency for nitrate removal increases with increasing dosage of soaked Al powder. When the dosage of soaked Al powder is below 4.0 g L<sup>-1</sup>, it seems that nitrate in aqueous solution cannot be completely removed even if the reaction time is long enough. Also, the pH value in the reaction solution increases with the reaction time at first, then reaches a maximum, and finally decreases to a constant of ~9.6. Furthermore, the reaction time to reach the peak pH value is independent of the dosage of soaked Al powder.



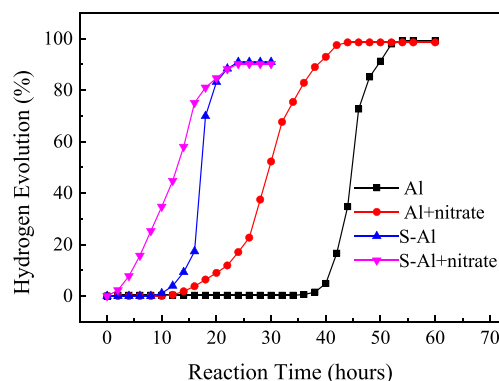
**Figure 6.** Time dependence of nitrate removal in aqueous solution at 30 °C with different nitrate concentrations using 7.29  $\mu\text{m}$  Al powder soaked for 35 h (a) and variation of pH value in the solution during the reaction (b), where  $C_0(\text{Al}) = 8.0 \text{ g L}^{-1}$ .

Figure 6a shows nitrate removal in aqueous solution with different nitrate concentrations using 7.29  $\mu\text{m}$  Al powder soaked for 35 h, and Figure 6b shows the variation of pH value in the solution with the reaction time. It can be seen that the efficiency for nitrate removal decreases with increasing nitrate concentration in aqueous solution. Also, it is noted that, first, the pH value in the reaction solution increases with the reaction time, then reaches a maximum, and finally decreases to a constant of  $\sim 9.6$ . The reaction time to reach the peak pH value is independent of the nitrate concentration.

From Figure 3b to Figure 6b, it is observed that the reaction time to reach the peak pH value in aqueous solution just depends on the reaction temperature and is independent of Al soaking time, Al dosage, and nitrate concentration. Moreover, the peak pH value in aqueous solution increases with Al soaking time, reaction temperature, Al dosage, and nitrate concentration. The final pH value in aqueous solution after nitrate removal is  $\sim 9.6$ , independent of the reaction conditions.

**3.3. Physicochemical Mechanism.** **3.3.1. Al Activated Mechanism.** It is well known that there is a dense passive oxide film on Al surfaces (see Figure 1c), which prevents the transfer of electrons from inner Al to the outside.<sup>49,50</sup> This implies that in a real water environment with a pH value close to neutral, pristine Al powder has low efficiency to remove nitrate. Therefore, an acidic or alkaline condition was used to eliminate the Al surface passive oxide film so that inner Al can directly contact outside ions or molecules in aqueous solutions, leading to the nitrate reduction efficiently.

In fact, there is an induction time for the beginning of Al-water reaction in neutral aqueous solution, which results from the hydration process of the Al surface passive oxide film.<sup>45,46,48,51</sup> In this work, a soaking procedure was used to activate Al powder so that Al particle surfaces were covered by a layer of fine nanometer  $\text{Al}(\text{OH})_3$  particles. This layer of fine  $\text{Al}(\text{OH})_3$  particles is porous (Figure 1b,d) and has low tensile strength so that outside ions and molecules can contact and react with inner Al more easily, leading to shorter induction time for the beginning of Al-water reaction, which was confirmed by many of previous works<sup>41,43,52,53</sup> and also by this work shown in Figure 7. The Al surface modification method was successfully used to speed up Al-water reaction to generate hydrogen, and its detailed mechanisms are discussed in previous works.<sup>47,48</sup> Figure 7 indicates that the induction time for the beginning of Al-water reaction using soaked Al powder is much shorter than that using pristine Al powder, and



**Figure 7.**  $\text{H}_2$  generation in aqueous solution at 30 °C with and without nitrate using as-received 7.29  $\mu\text{m}$  Al powder and that soaked for 35 h (S-Al), where  $C_0(\text{NO}_3^- \text{-N}) = 100 \text{ mg L}^{-1}$ , and  $C_0(\text{Al}) = 4.0 \text{ g L}^{-1}$ .

nitrate in aqueous solution promotes Al-water reaction as well due to its weak alkalinity.<sup>54</sup>

**3.3.2. Nitrate Reduction.** There are two possible ways to remove nitrate in neutral aqueous solution: one is reduction of nitrate by metal Al, and the other is adsorption of nitrate by the loose fine  $\text{Al}(\text{OH})_3$  grains covering Al particle surfaces. Figure S1a shows nitrate adsorption in neutral solution using different dosage of  $\text{Al}(\text{OH})_3$  powder. It can be seen that there is almost no adsorption of nitrate on  $\text{Al}(\text{OH})_3$  surfaces, even if the dosage of  $\text{Al}(\text{OH})_3$  powder is 4  $\text{g L}^{-1}$  and the nitrate-N concentration is up to 100  $\text{mg L}^{-1}$ , while the pH value in the solution almost has no change during adsorption test (Figure S1b). This indicates that the decrease in the induction time for the beginning of Al-water reaction (acceleration of electron transfer from inner Al to the outside) is the reason for increasing nitrate reduction by soaked Al powder.

When the soaking time increases, the hydration reaction on Al particles increases and the thickness of the fine  $\text{Al}(\text{OH})_3$  layer on Al particle surfaces increases, as shown in Figure 2, leading to an increase in the efficiency for nitrate reduction (Figure 3a). However, when the soaking time is too long, e.g., 50 h, most of inner Al in Al particles is consumed (Figure 2) so that there is no enough Al to reduce nitrate in aqueous solution, resulting in a decrease in nitrate reduction (Figure 3a). This means that there is optimal soaking time, which can maximize nitrate reduction efficiency using soaked Al (Figure 3a).

**Table 1. Nitrate, Nitrite, Ammonia, and Al<sup>3+</sup> Ion Concentrations in Aqueous Solution at 30 °C after the Reaction for 30 h Using 7.29 μm Al Powder Soaked for 35 h, where C<sub>0</sub>(Al) = 8.0 g L<sup>-1</sup>**

initial NO <sub>3</sub> <sup>-</sup> -N concentration (mg L <sup>-1</sup> )	final NO <sub>3</sub> <sup>-</sup> -N concentration (mg L <sup>-1</sup> )	final NO <sub>2</sub> <sup>-</sup> -N concentration (mg L <sup>-1</sup> )	final NH <sub>4</sub> <sup>+</sup> -N concentration (mg L <sup>-1</sup> )	Al <sup>3+</sup> concentration (mg L <sup>-1</sup> )
20	0.002	0.000	11.84	0.274
50	0.005	0.000	24.13	1.302
100	0.007	0.000	49.85	4.428

When the reaction temperature increases, the molecule and ion motion in aqueous solution is accelerated; therefore, the nitrate reduction efficiency by soaked Al increases (Figure 4a). When the dosage of soaked Al powder increases or the initial nitrate concentration decreases, the active sites on Al particle surfaces for per unit of nitrate ions in aqueous solution increase, leading to an increase in the efficiency for nitrate reduction (Figures 5a and 6a).

**3.3.3. Reaction Kinetics.** A pseudo-first-order reaction kinetic equation was used to calculate the reaction rate constant *k* for nitrate reduction using soaked Al powder<sup>55</sup>

$$-\ln\left(\frac{C_t}{C_0}\right) = kt \quad (2)$$

where C<sub>0</sub> and C<sub>t</sub> (mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>-N) are the nitrate concentrations at the initial time and time *t*, respectively. The linear fittings of the data in the main reaction stage in Figure 4a by eq 2 are given in Figure 4c, indicating that the reaction rate constant increases rapidly with the reaction temperature.

To quantify the temperature effect, the Arrhenius equation was used<sup>56,57</sup>

$$k = A \exp(-E_a/RT) \quad (3)$$

where *A* is a pre-exponential factor, *E<sub>a</sub>* is the activation energy, *T* is the reaction temperature, and *R* is the ideal gas constant. The activation energy for nitrate reduction using optimal soaked Al powder was calculated from the plot of the reaction rate constant *k* against the reciprocal temperature, with a linear fitting using eq 3, as shown in Figure 4d. The calculated activation energy is 69.49 kJ mol<sup>-1</sup>. Meanwhile, a pseudo-second-order reaction kinetic equation was also used to calculate the reaction rate constant and activation energy (see the Supporting Information), and it seems that the pseudo-first-order reaction kinetic equation is better fitted to the experimental data for nitrate reduction using soaked Al powder (Figure S2).

**3.3.4. Reaction Byproducts.** It is understood that there are following reactions occurring when Al powder is put into nitrate aqueous solution<sup>33,34,58</sup>

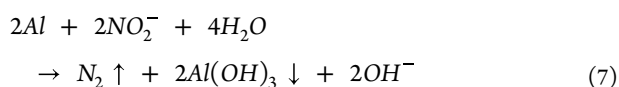
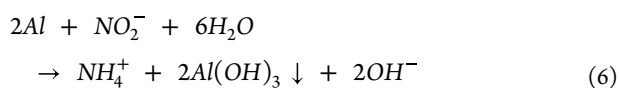
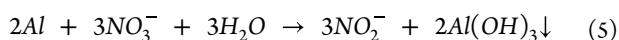
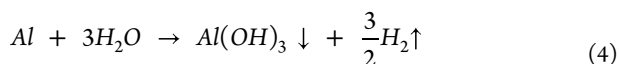
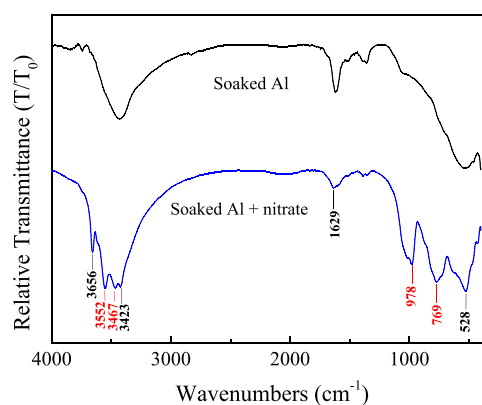


Table 1 lists nitrate, nitrite, ammonia, and Al<sup>3+</sup> ion concentrations in aqueous solution after the reaction using

optimal soaked powder (Figure 6a), indicating that almost all of nitrate in aqueous solution was reduced by soaked Al powder. There is no nitrite (NO<sub>2</sub><sup>-</sup>) detected in the reaction solution, and ~50% of initial nitrate-N was detected in the form of ammonia ions (NH<sub>4</sub><sup>+</sup>) after reaction. These indicate that the main byproduct of the reaction of soaked Al with nitrate in neutral solution is ammonia ions. The FTIR spectra of soaked Al powder before and after reaction are given in Figure 8,<sup>59</sup> showing that there are new characteristic peaks

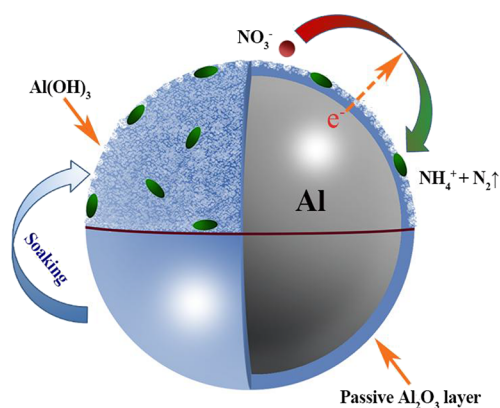


**Figure 8.** FTIR spectra of 7.29 μm Al powder soaked for 35 h before and after reaction with nitrate in aqueous solution at 30 °C, where C<sub>0</sub>(NO<sub>3</sub><sup>-</sup>-N) = 100 mg L<sup>-1</sup>, and C<sub>0</sub>(Al) = 8.0 g L<sup>-1</sup>.

related to the N element on soaked Al surfaces after reaction, where the peaks at 3552, 3467, 978, and 796 cm<sup>-1</sup> correspond to the vibration of -NH.<sup>60-62</sup> This indicates that part of ammonia ions (NH<sub>4</sub><sup>+</sup>) in reaction solution were adsorbed on the fine Al(OH)<sub>3</sub> layer of soaked Al particles. Figure S3 shows the dependence of ammonia adsorption in aqueous solution on time using Al(OH)<sub>3</sub> powder, indicating that the amount of ammonia-N adsorbed on soaked Al surfaces after reaction is ~10% of initial nitrate-N concentration. The above results imply that ~40% of initial nitrate-N was released into air in the form of gas after the reaction, indicating that the left nitrate-N in the reacted solution by soaked Al is obviously lower than those by ZVI, ZVAL, or their alloys reported in previous works.<sup>6,33,36</sup> Although ammonia ions (NH<sub>4</sub><sup>+</sup>) are the main byproduct of nitrate reduction by soaked Al powder, it is easy to remove ammonia ions using activated carbon or zeolite adsorption or convert ammonia ions to nitrogen by chlorine disinfection through a fold-point chlorination reaction.<sup>5</sup> A schematic representation of nitrate reduction by soaked Al powder is given in Scheme 1.

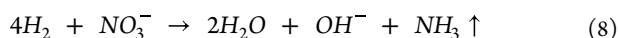
Table 1 indicates that the residual Al<sup>3+</sup> ion concentration in aqueous solution after nitrate reduction using soaked Al powder increases with the nitrate concentration. It is noted that the residual Al<sup>3+</sup> ion concentration is close to the WHO guideline of 0.2 mg L<sup>-1</sup> aluminum in drinking water when a

### Scheme 1. Schematic Representation of Al Surface Modification by Soaking and Nitrate Removal in Aqueous Solution

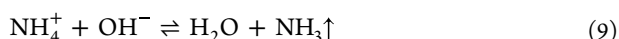


lower nitrate concentration was in neutral aqueous solution.<sup>63,64</sup>

From Figures 6a and 7, it can be seen that the nitrate reduction reaction and the reaction of Al with water to generate hydrogen occur simultaneously, which are competitive for consuming Al. The present results indicate that soaked Al powder can provide enough electrons to efficiently reduce nitrate in neutral aqueous solution. Furthermore, hydrogen generated from Al-water reaction also is a reductant, which can reduce nitrate in aqueous solution as well.<sup>37,54</sup>



**3.3.5. pH Value in Reaction Solution.** Equations 6–8 indicate that the reactions of nitrate reduction are with the generation of hydroxide ions ( $\text{OH}^-$ ); therefore, the pH value in aqueous solution increases with the progress of nitrate reduction, as shown in Figures 3b–6b. However, when the nitrate reduction by soaked Al reaches a definite time, the pH value in reaction solution decreases (Figures 3b–6b). This is because the dissolution reaction of ammonia in water is reversible; when the pH value in aqueous solution is too high, ammonia ions will react with hydroxide ions to generate ammonia gas.



Figures 3b–6b indicate that the equilibrium pH value for the reversible reaction of eq 9 is  $\sim 9.6$ .

When the temperature increases, the reaction becomes fast so that the pH value in reaction solution increases more rapidly and the reaction time to reach the peak pH value decreases (Figure 4b). In fact, Al-water reaction will increase the pH value in aqueous solution as well due to part of its byproduct  $\text{Al}(\text{OH})_3$  dissolving into water.<sup>65</sup> When the Al soaking time, reaction temperature, Al dosage, and nitrate concentration increase, the Al-water reaction will speed up and more hydroxide ions ( $\text{OH}^-$ ) are generated, leading to an increase in peak pH value in aqueous solution (Figures 3b–6b). It seems that the reaction kinetics of eq 9 just depends on temperature, because the reaction time to reach the peak pH value in aqueous solution is independent of Al soaking time, Al dosage, and nitrate concentration (Figures 3b, 5b, and 6b).

## 4. CONCLUSIONS

In this work, a simple procedure was used to activate Al, i.e., soaking Al powder in deionized water and then freeze-drying. It was found that the soaked Al powder can efficiently reduce nitrate in neutral aqueous solution and its efficiency for nitrate reduction is high among different methods so far. The efficiency for nitrate removal increased with increasing Al soaking time at first, then reached a maximum, and finally decreased with further increasing soaking time. At the optimal soaking time, the soaked Al powder can remove  $>90\%$  of nitrate in aqueous solution within  $\sim 2$  h at  $50^\circ\text{C}$ . Mechanism analyses indicated that a fine  $\text{Al}(\text{OH})_3$  layer on soaked Al particle surfaces can accelerate the electron transfer from inner Al to the outside, leading to an increase in nitrate reduction in neutral solution. The results also indicated that the reaction byproduct of nitrate reduction by soaked Al powder in neutral solution is ammonia ions, and just  $\sim 50\%$  of initial nitrate-N was left in the form of ammonia ions ( $\text{NH}_4^+$ ) in the reacted solution. The left nitrate-N in the reacted solution by soaked Al is obviously lower than those by ZVI, ZVAL, or their alloys reported in previous works. This work provides a new efficient approach to removing nitrate in neutral solution.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c01347>.

Data of nitrate and ammonia adsorption by  $\text{Al}(\text{OH})_3$ ; pseudo-second-order kinetic fittings for the experimental data of nitrate reduction reaction by soaked Al and Arrhenius plot for the reaction rate constants (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Zhen-Yan Deng – Energy Materials & Physics Group, Department of Physics and Institute of Low-Dimensional Carbon and Device Physics, Shanghai University, Shanghai 200444, China; [orcid.org/0000-0002-4368-7039](https://orcid.org/0000-0002-4368-7039); Phone: +86-21-66134334; Email: [zydeng@shu.edu.cn](mailto:zydeng@shu.edu.cn)

### Authors

Yi-Gong Dai – Energy Materials & Physics Group, Department of Physics and Institute of Low-Dimensional Carbon and Device Physics, Shanghai University, Shanghai 200444, China

Xiao-Han Guo – Energy Materials & Physics Group, Department of Physics and Institute of Low-Dimensional Carbon and Device Physics, Shanghai University, Shanghai 200444, China

Gen-Wang Ma – Energy Materials & Physics Group, Department of Physics and Institute of Low-Dimensional Carbon and Device Physics, Shanghai University, Shanghai 200444, China

Wei-Zhuo Gai – College of Physics and Electronic Information & Henan Key Laboratory of Electromagnetic Transformation and Detection, Luoyang Normal University, Luoyang 471934, China; [orcid.org/0000-0001-8815-1919](https://orcid.org/0000-0001-8815-1919)

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsomega.3c01347>

### Notes

The authors declare no competing financial interest.

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