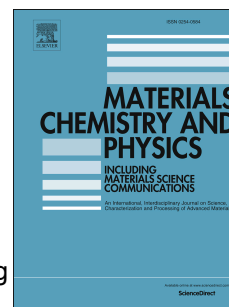


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Production of hydrogen, active zerovalent iron and ferroferric oxide octahedron by alkaline etching Al-Fe alloys

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Abstract

Hydrogen is becoming important clean energy while zerovalent iron (ZVI) and ferroferric oxide are of great interest to many applications including environmental remediation and chemical catalysis. Here, we report production of hydrogen, zerovalent iron and ferroferric oxide octahedron by etching Al-Fe alloys using NaOH solutions. The rate of hydrogen generation increased with increasing NaOH concentration and the alloy's particle size and decreasing the alloy's Fe concentration. Alkaline etching Al-Fe alloy particles of 425-850 μm produced 19-53 μm ZVI particles, which had paralleled ravines of 0.2-0.3 μm wide on the surface and possessed specific surface areas of 30-70 m^2/g . The microscale ZVI was highly active for the removal of a model pollutant acid orange 7 from water. After 3-6 h ageing in the alkaline etching solution, the microscale ZVI particles were transformed to octahedral ferroferric oxide with saturation magnetization of 68.2 emu/g and residual magnetization of 13.2 emu/g and a coercive force of 330 Oe. This study provides a new approach for a facile synthesis of highly active ZVI and octahedral ferroferric oxide along with on-board generation of hydrogen from Al-Fe alloys.

Keywords

Hydrogen, Al-Fe alloys, Zerovalent iron, Ferroferric oxide octahedron, Water treatment

1. Introduction

Clean energy and clean water are essential for a green and sustainable world. Unfortunately, the sustainability of our world has become a critical issue due to environmental pollution and climate change with the development of fossil economy [1]. Hydrogen economy was proposed to address the pitfalls of fossil economy in 1970s [2] and it was anticipated that hydrogen would provide 20% of total energy by 2050, which could contribute about 20% of the abatement to limiting the global warming to 2 °C [3]. Clearly, the development of hydrogen economy requires a large scale of hydrogen production in a sustainable manner. Currently, 95% of global hydrogen

supplies are produced from fossil fuels in that every ton of hydrogen brings a greenhouse gas emission of 10 tons [4, 5]. In this context, the development of non-carbon hydrogen production technologies is critical to maintain a green and sustainable world. This challenge can be addressed by the development of renewable energy (e.g., solar and wind) and advancement of hydrogen production by water electrolysis and biomass conversion [6-9]. Nevertheless, advanced and costly infrastructures for large-scale production, transportation and/or storage of hydrogen are the major constraints of hydrogen use, particularly in remote areas and closed vessels (e.g., aircraft, submarine) [10].

Therefore, on-board production of hydrogen is of great importance [11, 12] and the hydrolysis of Al metal for on-board hydrogen generation has attracted great attention [13, 14]. The cost of Al metal hydrolysis for hydrogen production is much lower (US\$3/kg) [15] than that of NaBH_4 method while the byproduct can be recycled through Hall-Heroult process [16]. Most importantly, Al has relatively high hydrogen production capacity (0.11 kg H_2 per kg Al) [17]. An electric car powered by hydrogen fuel cells with a driving distance of 400 km just requires 4 kg of hydrogen, corresponding to 36 kg Al metal [18]. However, the dense film of alumina on the surface protects Al metal underneath and the byproduct $\text{Al}(\text{OH})_3$ on the surface further inhibits hydrolysis reaction [19]. Use of high NaOH concentrations [20, 21] and alloying Al with other electrochemically noble metals (e.g., Ga, Bi and Ni) and common transition metals (Fe and Cu) [15, 19, 22-26] are efficient to promote hydrolysis reaction. In this regard, re-use of the alloyed metals after the hydrolysis is a concern.

Water contamination has become a global problem. Synthetic dyes are among the main organic pollutants and they are present in wastewaters from textile, printing, leather processing, and pharmaceutical industries, etc. The azo dyes occupy the largest and most important position of dyes for industrial applications, and these dyes are mostly non-biodegradable, toxic, and potentially carcinogenic [27]. Therefore, the treatment of azo dye contaminated water has attracted worldwide interest. Acid Orange 7 (AO7) as a typical azo dye has been commonly used as a model organic pollutant in studies related with advanced oxidation processes (AOPs) because it is resistant to photodegradation and biodegradation [28]. The development of new materials for water treatment is a core attention of water research and industry [29] and nano-zerovalent iron (nZVI) has been extensively investigated to remove and/or degrade inorganic and organic contaminants from water over the past decades [30, 31]. Typically, nZVI is prepared by reduction of ferrous sulfate in aqueous solutions using NaBH_4 [32]. However, the cost of NaBH_4 reduction method is relatively high (over US\$200/kg) [33] and transportation and storage of nZVI pose high risks of safety and health [34]. In addition, nZVI suffers rapid agglomeration and passivation under normal ambient conditions, thus losing its performance substantially [35, 36]. Therefore, on-demand production of nZVI (or equivalent) is of great interest in water treatment.

Liquid metals dealloying processes have been employed for the preparation of nano-porous metals and recovery of valuable metals from alloy scraps [37]. The hydrolysis of Al alloys in alkaline solutions is a chemical dealloying process and such a dealloying approach has also been investigated for preparation of nano-porous metals, intermetallic compounds (IMCs) and metal

oxide nanostructures [3, 38-41]. The hydrolysis of Al-Fe alloys in NaOH solutions involves the oxidation of Al and Fe atoms and their intermetallic phases by water to produce hydrogen and iron oxides and nano Fe₃O₄ octahedrons [42]. Nano Fe₃O₄ octahedrons with excellent magnetic properties have widespread applications in a variety of fields, including ferrofluids and information storage [43, 44]. Zhao et al. obtained α -Fe and Fe₃O₄ octahedrons from the hydrolysis of Al-Fe ribbons (10-25% Fe) in 5 M NaOH at 95 °C [44]. However, no studies have been reported regarding the property, stability and application of ZVI obtained from the hydrolysis of Al-Fe alloys.

Al-Fe alloys are typical deoxygenating agent in steel industry and it is of interest to explore Al-Fe alloys scraps for potential applications. This study was aimed at investigating the effect of alloy's Fe concentration, particle size, NaOH concentration and reaction time on the production of hydrogen, ZVI and magnetic nano Fe₃O₄ octahedrons with a focus on the characteristic, reactivity and the stability of the resultant ZVI for wastewater treatment where AO7 was employed as the model pollutant.

2. Materials and methods

2.1 Materials

Al-Fe10 and Al-Fe20 alloys (corresponding to 10 and 20 wt.% Fe) were prepared by melting high purity Al and Fe metals (>99.9%) in mass ratios of 90/10, 80/20 in a vacuum induction melting furnace (SGM, RL91/X, China). The detailed condition of the preparation has been described elsewhere [3]. Al-Fe50 alloy powders (50 wt.% Fe, particle size 250-380 μ m) were purchased from Hanchuan Tianhui Special Metal Materials Factory (Hubei Province, China). The content of Al and Fe in the alloy was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, ThermoFischer, iCAP 6000) after digestion using HCl-HNO₃. Commercial ZVI powder (75 μ m), NaOH, HCl, FeCl₃·6H₂O, NaBH₄, KNO₃ were purchased from Beijing Chemical Works (Beijing, China). Acid Orange 7 (AO7) was purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were analytical purity (AR) and aqueous solutions were prepared with deionized water.

2.2 Hydrolysis of Al-Fe alloys in NaOH solution

A glass bottle (250 mL) in a water bath was used for the etching experiment and a measuring cylinder was used for hydrogen collection by water drainage. A sample of Al-Fe alloy powders (1.0 g) was loaded to the bottle and 100 mL NaOH solution were quickly injected by a syringe. The solution was stirred by a magnetic stirring bar (300 rpm). The hydrogen generation yield was calculated by

$$\text{Hydrogen yield (\%)} = V/(a \times b \times 1361) \times 100 \quad (1)$$

where V is the volume of hydrogen, a is the amount of alloy and b is the percent concentration of aluminum in Al-Fe alloy. The solution was filtered through Buchner funnel under a circulating water vacuum pump and the solid residues were quickly rinsed using fresh NaOH solutions followed by deionized water for 3-5 times and then dried at 45 °C for 12 h in a vacuum oven.

2.3 Characterization of Al-Fe alloys and hydrolysis products

The chemical composition, surface morphology, structure and magnetic properties of Al-Fe alloys and the solid hydrolysis products were determined by X-ray diffraction (XRD, Bruker, D8 Advance), scanning electron microscopy (SEM, ZEISS, Supra55), energy-dispersive X-ray (EDS, OXFORD, INCAx-act), X-ray photoelectron spectroscopy (XPS, ThermoFischer, ESCALAB 250Xi), Transmission electron microscope (TEM, FEI, Tecnai G2 F20) and vibrating sample magnetometer (VSM, Quantum Design, MPMS-3). The specific surface areas (BET) of materials were measured by Micromeritics ASAP2460.

2.4 Removal of acid orange 7 (AO7) from wastewater

aZVI was obtained by a complete etching of Al-Fe20 alloy (380-830 μm) by 2 M NaOH. After etching, the solution was filtered and the retained materials were washed with de-oxygenated deionized water and then the retained material was added in 200 mL 200 mg/L AO7 solution. The solution was stirred by a magnetic bar at 300 rpm at ambient temperature (22-25 $^{\circ}\text{C}$). An aliquot of 2 mL was sampled at a given interval and filtrated with 0.22 μm membrane syringe for measuring AO7 concentration by a UV-vis spectrophotometer at a wavelength of 485 nm. For comparison, Al-Fe20 alloy and the etched alloy at 25%, 50% and 75% hydrogen yield were also used for the degradation of AO7. nZVI was prepared by conventional NaBH_4 reduction method [45]. Briefly, FeCl_3 solution (0.0036 M, 50 mL) was mixed with 50 mL 0.0108 M NaBH_4 solution and the mixed solution was stirred for 1 h in argon atmosphere. The solid product was filtered, washed with deoxygenated deionized water and then added in 200 mL AO7 solution (200 mg/L) for testing the degradation of AO7 as above. The removal rate of AO7 is calculated by

$$\text{Removal efficiency (\%)} = (C_0 - C_t)/C_0 \times 100 \quad (2)$$

where C_0 is initial concentration of AO7 and C_t is AO7 concentration at time t of the reaction.

2.5 Stability and preservation of aZVI

After a complete etching, the effect of ageing time (0-30 h) of aZVI in the etching solution and storage time (0-10 days) in deoxygenated deionized water and anhydrous ethanol was investigated by measuring the degradation rates of AO7 in water.

3. Results and Discussion

3.1 Hydrogen production

Hydrogen generation by the hydrolysis of Al-Fe alloys in NaOH solutions under different conditions (alloy's Fe concentration, NaOH concentration and alloy particle size) is shown in Fig. 1. Of the three Fe concentrations (Al-Fe10, Al-Fe20 and Al-Fe50, representing 10%, 20% and 50% wt., respectively), Al-Fe10 presents the highest rate of hydrogen generation from 0.5 M NaOH solution (Fig. 1a). Hydrogen generation increases with time and it is significantly higher for Al-Fe10 and Al-Fe20 than for Al-Fe50. There are no differences in hydrogen evolution between Al-Fe10 and Al-Fe20 at the initial 30 min but the rate by Al-Fe20 is getting slower afterwards. The hydrogen yield of Al-Fe10 reaches almost 100% by 50 min while that of Al-Fe20 and Al-Fe50 is 92% and 28% and then remains unchanged.

Increasing NaOH concentration enhances hydrogen generation rate as hydroxide ions act as a catalyst, which promotes electron transfer from Al to hydrogen ions [20]. Hydrogen generation rate increases with the increase of NaOH concentration (Fig. 1b, c). Hydrogen generation rate from the hydrolysis of Al-Fe20 alloy is 4.98, 5.14, 20.27, 41.30 and 82.14 mL/(g·min) in 0.1, 0.2, 0.5, 2 and 5 M NaOH, respectively while it is 6.40 mL/(g·min) for Al-Fe50 alloy. It is interesting that hydrogen yield of 250-380 μm Al-Fe20 by 0.5 M NaOH is 92% (Fig. 1a) while it is 100% by 380-830 μm Al-Fe20 in the same concentration of NaOH (Fig. 1b). A further investigation on the effect of particle size of Al-Fe20 shows that the hydrogen generation rate increases with increasing the particle size (Fig. 1d). This is an opposite trend to a general rule that the smaller particle size, larger surface area and higher hydrogen generation rate is by Al metal powders [46, 47] and Al-based alloys powders [48].

The rate of hydrogen generation by the hydrolysis of Al-based alloys is determined by the type and concentration of alloyed metals, NaOH concentration and the alloy's particle size [17, 47, 49, 50]. In general, galvanic corrosion may develop when two types of metals with different corrosion potential are contacted. The electrochemically active metal (i.e., lower corrosion potential) is corroded preferentially while the electrochemically noble metal is protected. Increasing the difference in the corrosion potential between the two metals, the corrosion rate of more active metal increases. Al-Fe alloys consist of three phases: Al, Fe and Al-Fe intermetallic compounds (Al_2Fe , Al_3Fe , Al_5Fe_2 , $\text{Al}_{13}\text{Fe}_4$) and the concentrations of Fe and the intermetallic compounds (IMCs) are the major factors influencing hydrogen generation rate via galvanic and intergranular corrosions [17]. Eom et al. demonstrated that Al-Fe IMCs are more resistant to the hydrolysis than Al metal and the higher concentration of IMCs in Al-Fe alloys are dependent on Fe concentration (Fig. 2). Al-Fe10 is dominated by Al phase while $\text{Al}_{13}\text{Fe}_4$ is the IMC only. Al-Fe20 alloy has the same composition with Al-Fe10, but has higher concentration of $\text{Al}_{13}\text{Fe}_4$. By contrast, Al-Fe50 alloy consists of $\text{Al}_2\text{Fe}/\text{FeAl}_2$ and Al_5Fe_2 phases. Therefore, the concentrations of Al and IMCs in the Al-Fe alloys account for hydrogen generation rate in an order of Al-Fe10 > Al-Fe20 > Al-Fe50. This trend is in agreement with the Al-Fe alloys with Fe concentrations of 1%, 3% and 6% where the lowest Fe-containing alloy achieved the highest rate of hydrogen generation in 2.5 M NaOH [17].

It was found that the Fe concentration is higher in smaller particle size alloys (Table 1). There are no significant differences among three size ranges of 180-250, 250-380 and 380-830 μm but the Fe concentration in Al-Fe20 alloy of 75-80 μm sizes is 75% higher than larger particle sizes of 180-830 μm . Therefore, the Fe concentration in different particle sizes of Al-Fe20 alloy is likely to explain the lower rates of hydrogen generation from smaller particle size alloys. It is unclear why smaller particle size alloys have higher Fe concentration and a plausible explanation is that Fe aggregation might occur during the process of cutting Al-Fe20 alloy ingot (65 $\times$ 9 $\times$ 4 cm), ball milling and sieving of Al-Fe alloy particles.

3.2 Synthesis of octahedral Fe_3O_4 and active zerovalent iron (aZVI)

The hydrolysis of Al-Fe alloys in alkaline solutions is a dealloying process where Al is oxidized at first, the IMCs are followed and Fe is eventually oxidized to Fe_3O_4 [39, 42]. Jia et al.

reported the preparation of Fe_3O_4 octahedron by dealloying Al-Fe15 alloy using 5 M NaOH and ageing the products for 48 h in the alkaline solution at ambient temperature [43]. In this study, the effect of reaction time was investigated for Al-Fe20 by 2 M NaOH. The reaction time (3, 6 and 30 h) affected the composition, crystallinity, morphology, particle size and magnetic properties (Fig. 3). The composition was transformed from Fe and FeOOH to Fe_3O_4 , the crystallinity was improved, the magnetization was enhanced and the crystal size became uniform with increasing reaction time. Octahedral Fe_3O_4 were produced after 6 h. Of the three reaction times, the 6-h Fe_3O_4 product had the highest magnetization (saturation magnetization M_s 68.2 emu/g, residual magnetization M_r 13.2 emu/g) while the 3-h product had the highest coercive force (330 Oe) (Table 2). Gao and Gong et al. reported the preparation of Fe_3O_4 by hydrothermal or solvothermal processes using ferrous and ferric salts [51, 52] where the 3D flower-like Fe_3O_4 's M_s was 65.8 emu/g and the chain-like Fe_3O_4 's M_s and coercive force were 40 emu/g and 63 Oe, respectively.

Originally, we anticipated to obtain nano-porous Al-Fe IMCs by carefully controlling the etching process at various stages of etching (i.e., hydrogen production). Indeed, various compositions and surface structures were observed in Fig. 4, which shows the SEM images and XRD patterns before etching, at 25%, 75% and 100% etching by 0.5 M NaOH. Al-Fe20 alloy has a relatively smooth, silver-grey shiny surface (Fig. 4 a1), consisting of Al (PDF#85-1327), Fe (PDF#06-0696) and $\text{Al}_{13}\text{Fe}_4$ (PDF#50-0797) (Fig. 4 a2). At different stages of etching before a 100% etching, two types of solid materials were obtained. One was the etched alloy (Fig. 4 b, d) and the other was the etching product (Fig. 4 c, e). The surface of the alloy becomes rough with numerous pits and its silver-grey shiny surface was gradually lost with the etching process while the $\text{Al}_{13}\text{Fe}_4$ phase exfoliated completely from the etched alloy when the hydrogen yield reached 25% (Fig. 4 b2). The final etching product was in a format of black powders with a mossy surface on that there are relatively straight and parallel ravines of 0.2-0.3 μm wide and the material consists of $\text{Al}_{13}\text{Fe}_4$ and Fe (Fig. 4 c1, e1). The EDS analysis of the 75% etching product indicates that the material consists of 10.59 wt.% Al and 89.41 wt.% Fe (see insert graph of Fig. 4 e2). Upon a 100% etching, the sole solid product consisted of Fe_3O_4 and Fe (Fig. 4 f2). It was likely that the Al phase was oxidized preferentially and then $\text{Al}_{13}\text{Fe}_4$ was exposed and exfoliated from the alloy, thus creating ravines on the surface. Eventually, $\text{Al}_{13}\text{Fe}_4$ was decomposed to Al^{3+} ions and Fe^0 atoms. Therefore, it would be interest to investigate the capture of $\text{Al}_{13}\text{Fe}_4$ by using suitable concentrations of NaOH and carefully controlling the degree of etching. Fig. 5 shows the SEM images and XRD of the 75% etched alloy using 0.1 M NaOH. The protruded items of 1-2 μm wide and 10-100 μm long were most likely $\text{Al}_{13}\text{Fe}_4$, despite that no appreciate amounts of $\text{Al}_{13}\text{Fe}_4$ were captured. It was reported that Al_3Fe and Al_2Cu precipitated along grain boundaries from their respective Al-Fe and Al-Cu alloys, creating defects and cracks during the alkaline etching process [17, 25]. Al_3Fe from Al-Fe alloy was identified in an elliptical shape of 1-2 μm long and 0.1-0.4 μm wide [17].

Interestingly, we observed that the 100% etching product ignited spontaneously when exposed to air and identified that the ignited material was irregular, large particles (19-53 μm) of ZVI

covered by a thin layer of Fe_3O_4 by XRD, SEM, XPS and TEM (Fig. 4 f and Fig. 6). These results indicate that the material of the 100% etching product was active zerovalent iron (aZVI). In addition, the product has a specific surface area of 30-70 m^2/g , whereas the ZVI particles of 10 μm have a specific surface area of 0.9 m^2/g [53] and nZVI particles of 10-100 nm were typically characterized with specific surface areas of 10-50 m^2/g [35].

3.3 Removal of acid orange 7 from water

nZVI has been widely investigated for removing a wide variety of pollutants from contaminated water [30, 32]. Usually, nZVI is synthesized by the reduction of ferrous sulfate or ferric chloride using NaBH_4 [54-56]. In this work, aZVI was compared with nZVI, commercial ZVI (cZVI) and Al-Fe20 alloy for the removal of acid range (AO7) from water and the stability of aZVI in alkaline solutions and ethanol was tested (Fig. 7). aZVI and nZVI have the same removal efficiency of 98% for AO7 in 30 min although aZVI has a slower rate in initial period of 20 min (Fig. 7a). Overall, the removal rate of AO7 by aZVI is 2.4 and 4.6 times higher than that of cZVI and Al-Fe20 alloy, respectively. The removal efficiency of 10-500 mg/L AO7 from water by 1 g/L aZVI at neutral pH is greater than 97% (Table 3). A removal efficiency of 98.3% was achieved in 10 min by biochar-supported nZVI (2 g/L) at pH 2 (Table 3) and it was resulted from a combination of chemical degradation by nZVI and physical adsorption by biochar [56]. The chemical reactivity of ZVI increased with the decrease of water pH and was 2 orders of magnitude higher at acidic pH 2 than alkaline pH 9 [56]. A complete removal was observed in 10 min at neutral pH for 70 mg/L AO7 by 2 g/L nZVI-rectorite composite and it was attributed to the adsorption of Na-rectorite and chemical degradation by nZVI [57]. In summary, microparticles of ZVI obtained from the hydrolysis of Al-Fe alloys are of highly chemical reactivity for pollutants removal from water and the removal of a wide variety of inorganic and organic pollutants are under investigation.

As observed previously, after hydrogen evolution in the NaOH etching solution, Al-Fe alloy was decomposed, leaving zerovalent iron (ZVI), which was gradually transformed to Fe_3O_4 . Therefore, the stability of Al-Fe alloy derived active ZVI (aZVI) after the etching process was investigated by ageing in the NaOH etching solution (Fig. 7b) and storing in deoxygenated deionized water and anhydrous ethanol (Fig. 7c). The removal efficiency of AO7 by aZVI decreased with increasing ageing time in the NaOH etching solution and after 2 h of etching, the activity was lost by 50%. By contrast, storing aZVI in anhydrous ethanol for 10 days still maintained its original activity. This indicates that aZVI is slowly oxidized by water and a coating layer of Fe_3O_4 may develop on the surface.

4. Conclusions

Alkaline etching of Al-Fe alloys is efficient to produce high-purity hydrogen, highly active zerovalent iron and ferroferric oxide octahedron. Hydrogen yield increases with increasing NaOH concentration and particle size of Al-Fe alloy and decreasing Fe's concentration. NaOH concentrations of 0.2-0.5 M achieve greater than 90% hydrogen yield for Al-Fe alloys with 10-20% Fe while 10 M NaOH is required to achieve 90% hydrogen yield for 50% Fe's Al-Fe alloy.

The alkaline etching process involves a rapid corrosion of Al phase, a progressive transformation of intermetallic compounds into zerovalent iron and a final oxidation to ferroferric oxide octahedron, which shows saturation magnetization of 68.2 emu/g, residual magnetization of 13.2 emu/g and a coercive force of 330 Oe. The Al-Fe alloy-derived active ZVI is in particle sizes of 19-53 μm and is highly active for the removal of model pollutant acid orange 7 from wastewater. The high activity of microscale ZVI is likely derived from its unique surface morphologies and structures (parallel ravines of 0.2-0.3 μm wide and 1.0-2.0 μm distance) and structural transformation such as agglomerating into islands and clusters for partial Fe atoms, leading to high specific surface areas of 30-70 m^2/g . The findings of this study demonstrate that Al-Fe alloy scraps can be useful in closed vessels, aircraft carriers and naval crafts where on-board hydrogen generation is required and the byproduct ZVI can be used for highly efficient treatment of on-board wastewater.

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Notes

The authors declare no conflict of interest.

Abbreviations

ZVI, zero valent iron; aZVI, active zero valent iron; nZVI, nano zero valent iron; cZVI, commercially available zerovalent iron; AO7, acid orange 7; XRD, X-ray diffraction; SEM, scanning electron microscope; EDS, energy dispersive spectrometer; XPS, X-ray photoelectron spectroscopy; TEM, transmission electron microscope; ICP-OES, inductively coupled plasma optical emission spectrometry; VSM, vibrating sample magnetometer; BET, specific surface areas.

References

- [1] BP, BP statistical review of world energy 2018, 2018.
- [2] D.E. Balk, Book Reviews, *Death Studies*, 29 (2005) 179-184.
- [3] J. Xu, Y. Pu, W.K. Qi, X.J. Yang, Y. Tang, P. Wan, A. Fisher, Chemical removal of nitrate from water by aluminum-iron alloys, *Chemosphere*, 166 (2017) 197-202.
- [4] A. Abánades, The challenge of hydrogen production for the transition to a CO_2 -free economy, *Agron Res Biosyst Eng Spec Issue*, 1 (2012) 11-16.
- [5] M.K. Heiman, B.D. Solomon, Fueling U.S. Transportation: The Hydrogen Economy and Its Alternatives, *Environment: Science and Policy for Sustainable Development*, 49 (2007) 10-25.
- [6] Q. Lei, B.G. Wang, P.C. Wang, S. Liu, Hydrogen generation with acid/alkaline amphoteric water electrolysis, *J. Energy Chem.*, 38 (2019) 162-169.

- [7] J. Chi, H.M. Yu, Water electrolysis based on renewable energy for hydrogen production, *Chinese Journal Of Catalysis*, 39 (2018) 390-394.
- [8] G. Badea, G.S. Naghiu, I. Giurca, I. Aşchilean, E. Megyesi, Hydrogen Production Using Solar Energy - Technical Analysis, *Energy Procedia*, 112 (2017) 418-425.
- [9] W.X. Peng, L.S. Wang, M. Mirzaee, H. Ahmadi, M.J. Esfahani, S. Fremaux, Hydrogen and syngas production by catalytic biomass gasification, *Energy Convers. Manage.*, 135 (2017) 270-273.
- [10] A.M. Abdalla, S. Hossain, O.B. Nisfindy, A.T. Azad, M. Dawood, A.K. Azad, Hydrogen production, storage, transportation and key challenges with applications: A review, *Energy Convers. Manage.*, 165 (2018) 602-627.
- [11] H.Y. Lian, J.L. Liu, X.S. Li, X.B. Zhu, A.Z. Weber, A.M. Zhu, Plasma chain catalytic reforming of methanol for on-board hydrogen production, *Chem. Eng. J.*, 369 (2019) 245-252.
- [12] S. Santra, D. Das, N.S. Das, K.K. Nanda, An efficient on-board metal-free nanocatalyst for controlled room temperature hydrogen production, *Chemical Science*, 8 (2017) 2994-3001.
- [13] L. Schlapbach, A. Züttel, Hydrogen-storage materials for mobile applications, *Nature*, 414 (2001) 353-358.
- [14] S. Elitzur, V. Rosenband, A. Gany, On-board hydrogen production for auxiliary power in passenger aircraft, *Int. J. Hydrogen Energy*, 42 (2017) 14003-14009.
- [15] M.Q. Fan, L.X. Sun, F. Xu, Experiment assessment of hydrogen production from activated aluminum alloys in portable generator for fuel cell applications, *Energy*, 35 (2010) 2922-2926.
- [16] J.P. Murray, 99/03911 Aluminum production using high-temperature solar process heat, *Fuel and Energy Abstracts*, 40 (1999).
- [17] K.S. Eom, J.Y. Kwon, M.J. Kim, H.S. Kwon, Design of Al-Fe alloys for fast on-board hydrogen production from hydrolysis, *J. Mater. Chem.*, 21 (2011).
- [18] H.Z. Wang, D.Y.C. Leung, M.K.H. Leung, M. Ni, A review on hydrogen production using aluminum and aluminum alloys, *Renewable & Sustainable Energy Reviews*, 13 (2009) 845-853.
- [19] Y.Y. Jia, J. Shen, H.X. Meng, Y.M. Dong, Y.J. Chai, N. Wang, Hydrogen generation using a ball-milled Al/Ni/NaCl mixture, *J. Alloys Compd.*, 588 (2014) 259-264.
- [20] R. Padash, A.H. Jafari, E. Jamalizadeh, Experimental and theoretical study of aluminium corrosion in NaOH, NaCl and HCl solutions, *Anti-Corrosion Methods And Materials*, 65 (2018) 350-360.
- [21] H.B. Dai, G.L. Ma, H.J. Xia, P. Wang, Reaction of aluminium with alkaline sodium stannate solution as a controlled source of hydrogen, *Energy & Environmental Science*, 4 (2011) 2206-2212.
- [22] D.X. Qiao, Y.P. Lu, Z.Y. Tang, X.S. Fan, T.M. Wang, T.J. Li, P.K. Liaw, The superior hydrogen-generation performance of multi-component Al alloys by the hydrolysis reaction, *Int. J. Hydrogen Energy*, 44 (2019) 3527-3537.
- [23] T. Zhang, W. Yang, S. Zhang, J. Zhou, J. Liu, Hydrogen production by the reaction of Al-based metals with water vapor, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 40 (2017) 9-14.
- [24] Z. Zhao, X. Chen, M. Hao, Hydrogen generation by splitting water with Al-Ca alloy, *Energy*, 36 (2011) 2782-2787.
- [25] M.J. Kim, K.S. Eom, J.Y. Kwon, E.A. Cho, H.S. Kwon, On-board hydrogen production by

- hydrolysis from designed Al–Cu alloys and the application of this technology to polymer electrolyte membrane fuel cells, *J. Power Sources*, 217 (2012) 345-350.
- [26] K. Eom, E. Cho, H. Kwon, Feasibility of on-board hydrogen production from hydrolysis of Al–Fe alloy for PEMFCs, *Int. J. Hydrogen Energy*, 36 (2011) 12338-12342.
- [27] F. Guo, J. Lu, Q. Liu, P. Zhang, A. Zhang, Y. Cai, Q. Wang, Degradation of Acid Orange 7 by peroxymonosulfate activated with the recyclable nanocomposites of g-C₃N₄ modified magnetic carbon, *Chemosphere*, 205 (2018) 297-307.
- [28] X. Yu, W. Fu, M. Jiang, G. Liu, Y. Zou, S. Chen, Automatic microbial electro-Fenton system driven by transpiration for degradation of acid orange 7, *Sci. Total Environ.*, 725 (2020) 138508.
- [29] M. Mon, R. Bruno, J. Ferrando-Soria, D. Armentano, E. Pardo, Metal–organic framework technologies for water remediation: towards a sustainable ecosystem, *Journal of Materials Chemistry A*, 6 (2018) 4912-4947.
- [30] N. Shukla, A. Saxena, V. Gupta, A.S. Rawat, S. Shrivastava, P.K. Rai, Nano Zero Valent Iron Composites for Water Decontamination: A Review, *Current Environmental Engineering*, 5 (2018) 88-101.
- [31] M. Stefaniuk, P. Oleszczuk, Y.S. Ok, Review on nano zerovalent iron (nZVI): From synthesis to environmental applications, *Chem. Eng. J.*, 287 (2016) 618-632.
- [32] X. Zhao, W. Liu, Z.Q. Cai, B. Han, T.W. Qian, D.Y. Zhao, An overview of preparation and applications of stabilized zero-valent iron nanoparticles for soil and groundwater remediation, *Water Res.*, 100 (2016) 245-266.
- [33] W.L. Yan, H.L. Lien, B.E. Koel, W.X. Zhang, Iron nanoparticles for environmental clean-up: recent developments and future outlook, *Environmental Science-Processes & Impacts*, 15 (2013) 63-77.
- [34] W. Xue, D. Huang, G. Zeng, J. Wan, M. Cheng, C. Zhang, C. Hu, J. Li, Performance and toxicity assessment of nanoscale zero valent iron particles in the remediation of contaminated soil: A review, *Chemosphere*, 210 (2018) 1145-1156.
- [35] T. Tosco, M.P. Papini, C.C. Viggi, R. Sethi, Nanoscale zerovalent iron particles for groundwater remediation: a review, *Journal Of Cleaner Production*, 77 (2014) 10-21.
- [36] Y. Sun, J. Li, T. Huang, X. Guan, The influences of iron characteristics, operating conditions and solution chemistry on contaminants removal by zero-valent iron: A review, *Water Res.*, 100 (2016) 277-295.
- [37] X. Guo, C. Zhang, Q. Tian, D. Yu, Liquid metals dealloying as a general approach for the selective extraction of metals and the fabrication of nanoporous metals: A review, *Materials Today Communications*, 26 (2021).
- [38] T. Wada, P.A. Geslin, H. Kato, Preparation of hierarchical porous metals by two-step liquid metal dealloying, *Scripta Mater.*, 142 (2018) 101-105.
- [39] T.T. Song, Y.L. Gao, Z.H. Zhang, Q.J. Zhai, Microstructure and phase evolution during the dealloying of bi-phase Al–Ag alloy, *Corros. Sci.*, 68 (2013) 256-262.
- [40] W.B. Liu, S.C. Zhang, N. Li, J.W. Zheng, S.S. An, Y.L. Xing, A general dealloying strategy to nanoporous intermetallics, nanoporous metals with bimodal, and unimodal pore size distributions, *Corros. Sci.*, 58 (2012) 133-138.
- [41] J. Erlebacher, M.J. Aziz, A. Karma, N. Dimitrov, K. Sieradzki, Evolution of nanoporosity in dealloying, *Nature*, 410 (2001) 450-453.
- [42] C.X. Xu, R.Y. Wang, Y. Zhang, Y. Ding, A general corrosion route to nanostructured metal oxides, *Nanoscale*, 2 (2010) 906-909.

- [43] S. Jia, T.T. Song, B.G. Zhao, Q.J. Zhai, Y.L. Gao, Regular Fe₃O₄ octahedrons with excellent soft magnetic properties prepared by dealloying technique, *J. Alloys Compd.*, 585 (2014) 580-586.
- [44] B.G. Zhao, S. Jia, Y.L. Yuan, T.T. Song, H.L. Ma, Q.J. Zhai, Y.L. Gao, Paving the way to Fe₃O₄ nano- and microoctahedra by dealloying Al-Fe binary alloys, *Mater. Charact.*, 156 (2019).
- [45] Y.-P. Sun, X.-q. Li, J. Cao, W.-x. Zhang, H.P. Wang, Characterization of zero-valent iron nanoparticles, *Adv. Colloid Interface Sci.*, 120 (2006) 47-56.
- [46] S. Liu, M.-q. Fan, C. Wang, Y.-x. Huang, D. Chen, L.-q. Bai, K.-y. Shu, Hydrogen generation by hydrolysis of Al–Li–Bi–NaCl mixture with pure water, *Int. J. Hydrogen Energy*, 37 (2012) 1014-1020.
- [47] H.B. Zou, S.Z. Chen, Z.H. Zhao, W.M. Lin, Hydrogen production by hydrolysis of aluminum, *J. Alloys Compd.*, 578 (2013) 380-384.
- [48] S. Al Bacha, M. Zakhour, M. Nakhl, J.L. Bobet, Effect of ball milling in presence of additives (Graphite, AlCl₃, MgCl₂ and NaCl) on the hydrolysis performances of Mg₁₇Al₁₂, *Int. J. Hydrogen Energy*, 45 (2020) 6102-6109.
- [49] K. Eom, M. Kim, S. Oh, E. Cho, H. Kwon, Design of ternary Al–Sn–Fe alloy for fast on-board hydrogen production, and its application to PEM fuel cell, *Int. J. Hydrogen Energy*, 36 (2011) 11825-11831.
- [50] X.-n. Huang, C.-j. Lv, Y.-x. Huang, S. Liu, C. Wang, D. Chen, Effects of amalgam on hydrogen generation by hydrolysis of aluminum with water, *Int. J. Hydrogen Energy*, 36 (2011) 15119-15124.
- [51] Q. Gao, A.W. Zhao, Z.B. Gan, W.Y. Tao, D. Li, M.F. Zhang, H.Y. Guo, D.P. Wang, H.H. Sun, R.R. Mao, E.H. Liu, Facile fabrication and growth mechanism of 3D flower-like Fe₃O₄ nanostructures and their application as SERS substrates, *Crystengcomm*, 14 (2012) 4834-4842.
- [52] J.Y. Gong, S.Z. Li, D.G. Zhang, X.B. Zhang, C. Liu, Z.W. Tong, High quality self-assembly magnetite (Fe₃O₄) chain-like core-shell nanowires with luminescence synthesized by a facile one-pot hydrothermal process, *Chem. Commun.*, 46 (2010) 3514-3516.
- [53] C.-B. Wang, W.-x. Zhang, Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs, *Environmental Science & Technology*, 31 (1997) 2154-2156.
- [54] J.H. Li, L.X. Yang, J.Q. Li, W.H. Yin, Y. Tao, H.Q. Wu, F. Luo, Anchoring nZVI on metal-organic framework for removal of uranium(VI) from aqueous solution, *J. Solid State Chem.*, 269 (2019) 16-23.
- [55] Y.L. Han, M.D.Y. Yang, W.X. Zhang, W.L. Yan, Optimizing synthesis conditions of nanoscale zero-valent iron (nZVI) through aqueous reactivity assessment, *Frontiers Of Environmental Science & Engineering*, 9 (2015) 813-822.
- [56] G.X. Quan, W.J. Sun, J.L. Yan, Y.Q. Lan, Nanoscale Zero-Valent Iron Supported on Biochar: Characterization and Reactivity for Degradation of Acid Orange 7 from Aqueous Solution, *Water Air And Soil Pollution*, 225 (2014).
- [57] S. Luo, P.F. Qin, J.H. Shao, L. Peng, Q.R. Zeng, J.D. Gu, Synthesis of reactive nanoscale zero valent iron using rectorite supports and its application for Orange II removal, *Chem. Eng. J.*, 223 (2013) 1-7.
- [58] X.Y. Wang, P. Wang, J. Ma, H.L. Liu, P. Ning, Synthesis, characterization, and reactivity of cellulose modified nano zero-valent iron for dye discoloration, *Appl. Surf. Sci.*, 345 (2015)

57-66.

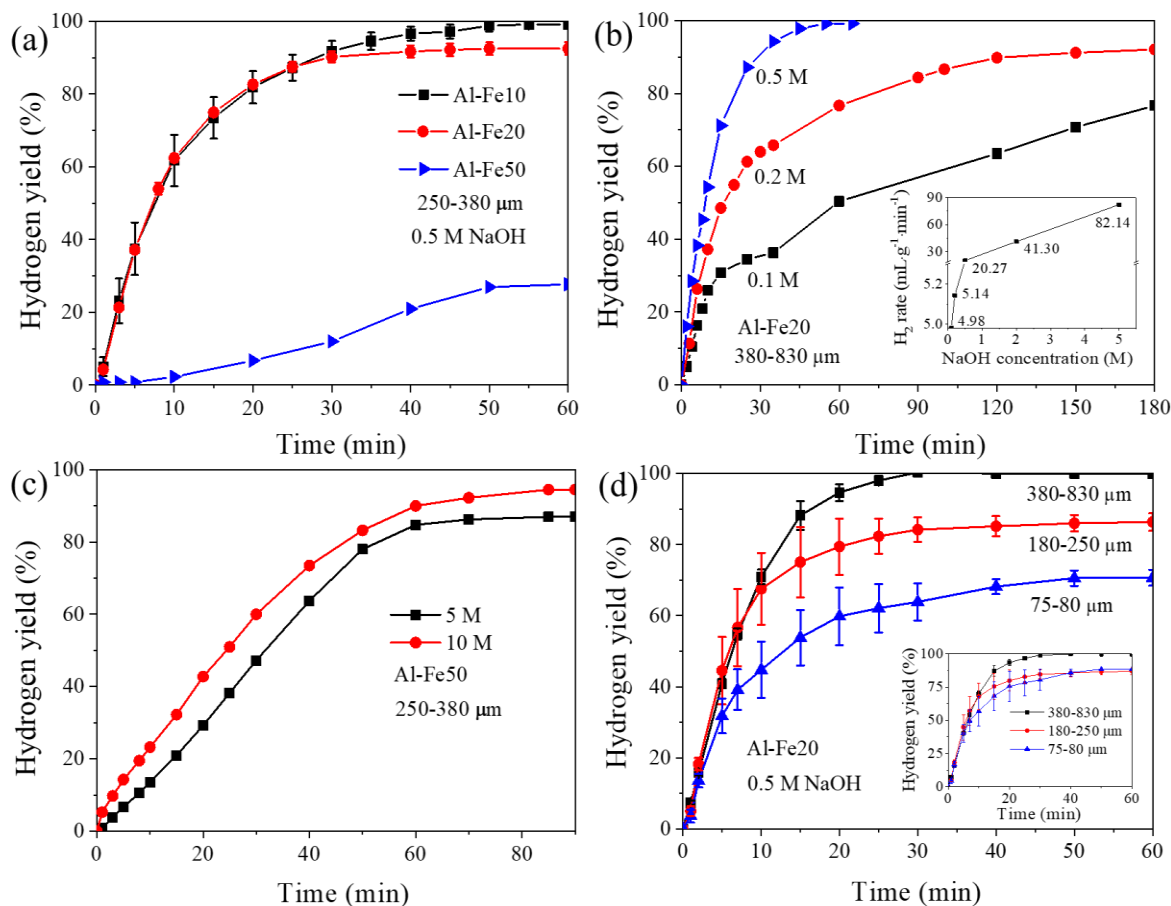


Fig. 1. Hydrogen generation yield by the hydrolysis of Al-Fe alloys in NaOH solution. Temperature: 25 °C, alloy dosage: 10 g/L. (a) Effect of iron concentration; (b) Effect of NaOH concentration on Al-Fe20 alloy, the inserted graph is the average hydrogen production rate as a function of NaOH concentration (0.1-5 M); (c) Effect of NaOH concentration (5 M and 10 M) on Al-Fe50 alloy; (d) Effect of Al-Fe20 alloy particle size; the inserted graph is re-calculated hydrogen yield on the corrected Fe concentration in the alloys.

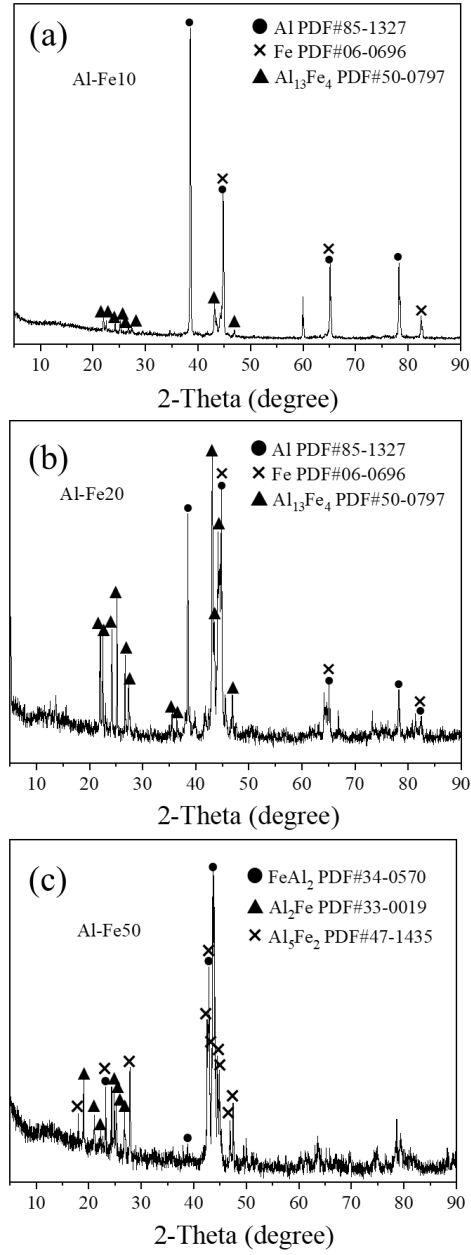


Fig. 2. XRD characterization of Al-Fe alloys. (a) Al-Fe10, (b) Al-Fe20, (c) Al-Fe50.

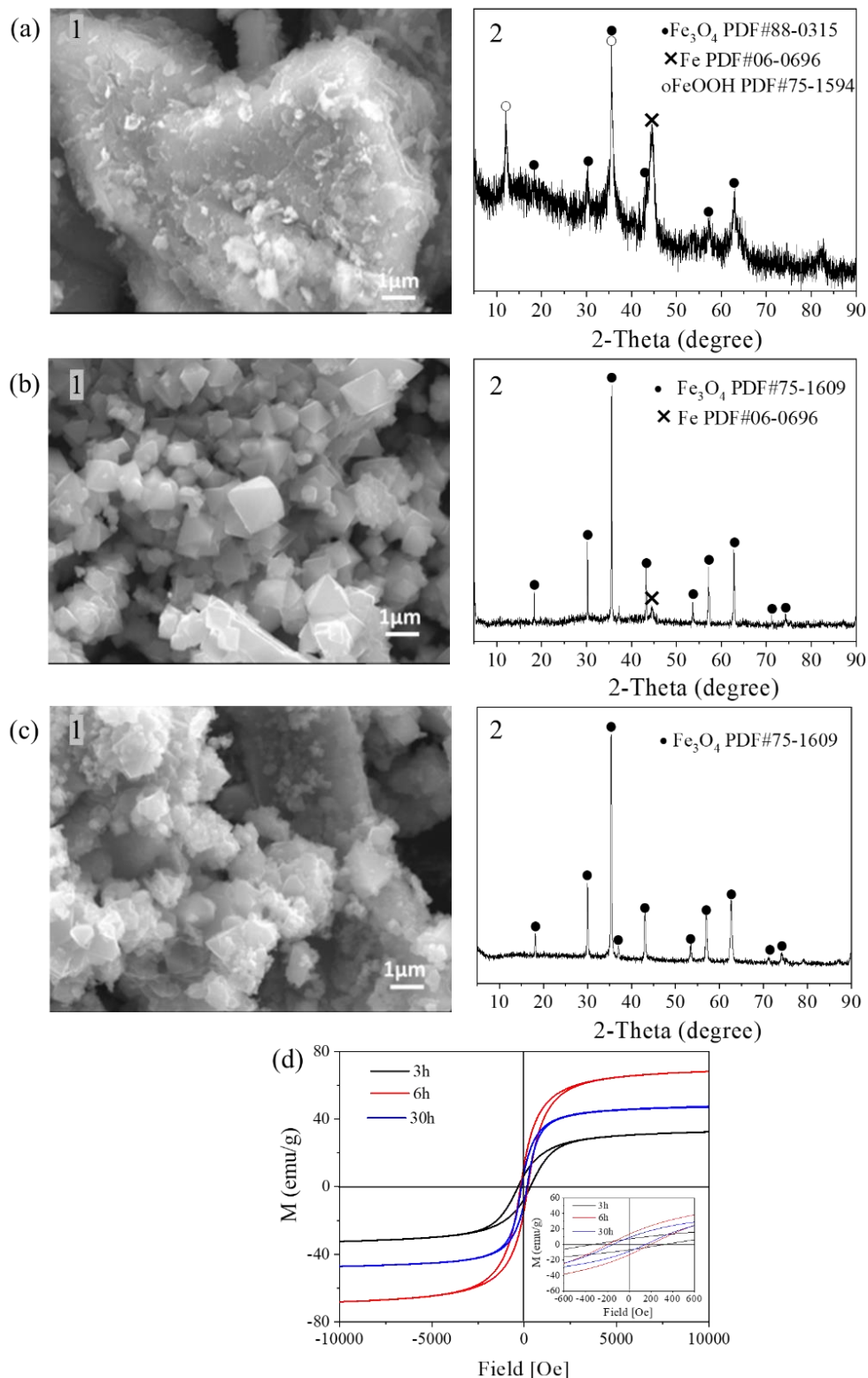


Fig. 3. SEM image and XRD characterization of magnetic iron oxide (Fe_3O_4) at different ageing time (a) 3 h, (b) 6 h, (c) 30 h and the ambient temperature magnetic hysteresis (M-H) curves of Fe_3O_4 (d). Hydrolysis condition: Al-Fe20 alloy (380-830 μm), 2 M NaOH, temperature: 90 $^\circ\text{C}$.

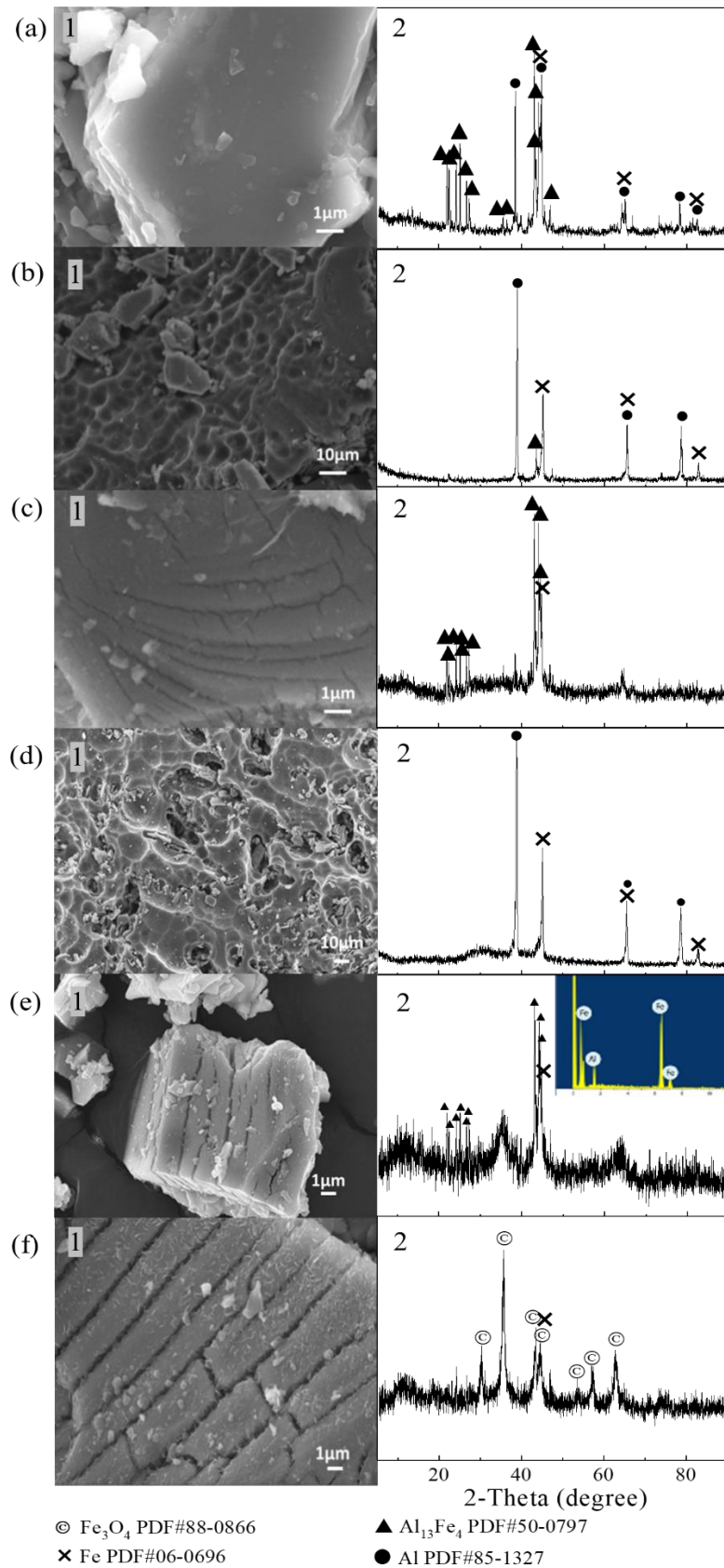


Fig. 4. SEM image and XRD characterization of Al-Fe₂₀ alloy (380-830 μm) before etching and at different degrees of etching in 0.5 M NaOH at 25°C. (a) before etching, (b) 25% etched alloy, (c) 25% etching product, (d) 75% etched alloy, (e) 75% etching product (the insert graph is EDS characterization). (f) 100% etching product. The degree of etching is defined by the hydrogen yield relative to its theoretical value in accordance with the Al concentration.

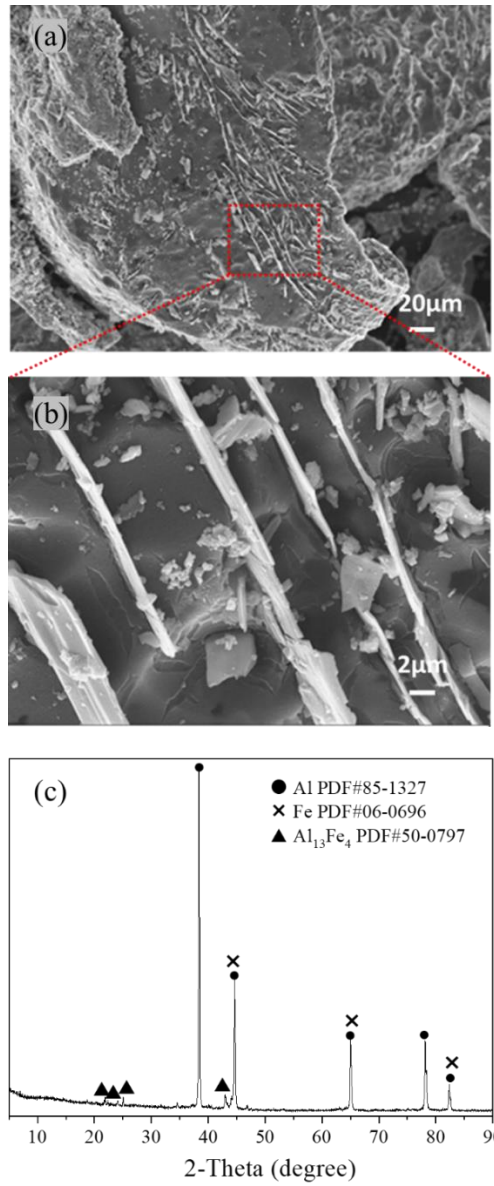


Fig. 5. (a, b) SEM images at the scales of 20 μm and 2 μm and (c) XRD characterization of the 75% etched Al-Fe₂₀ alloy in 0.1 M NaOH at 25 °C.

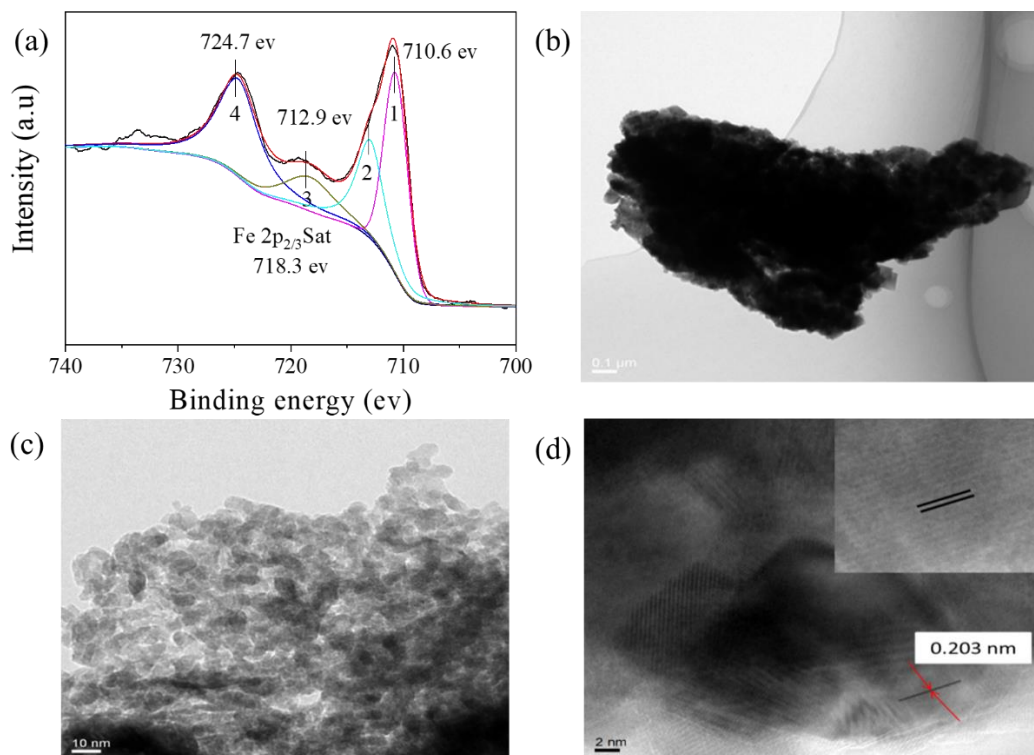


Fig. 6. Characterization of the 100% etching product of Al-Fe20 alloy. (a) XPS, Fe 2p spectra, peaks 1 and 2 are Fe³⁺ on Fe 2p_{3/2}, peak 3 is a satellite peak associated with Fe 2p_{3/2}, peak 4 is Fe²⁺ on Fe 2p_{1/2}. (b), (c) and (d) are TEM images at different scales, 100, 10 and 2 nm. The lattice fringes of 0.203 nm are the crystallographic planes (110) of iron.

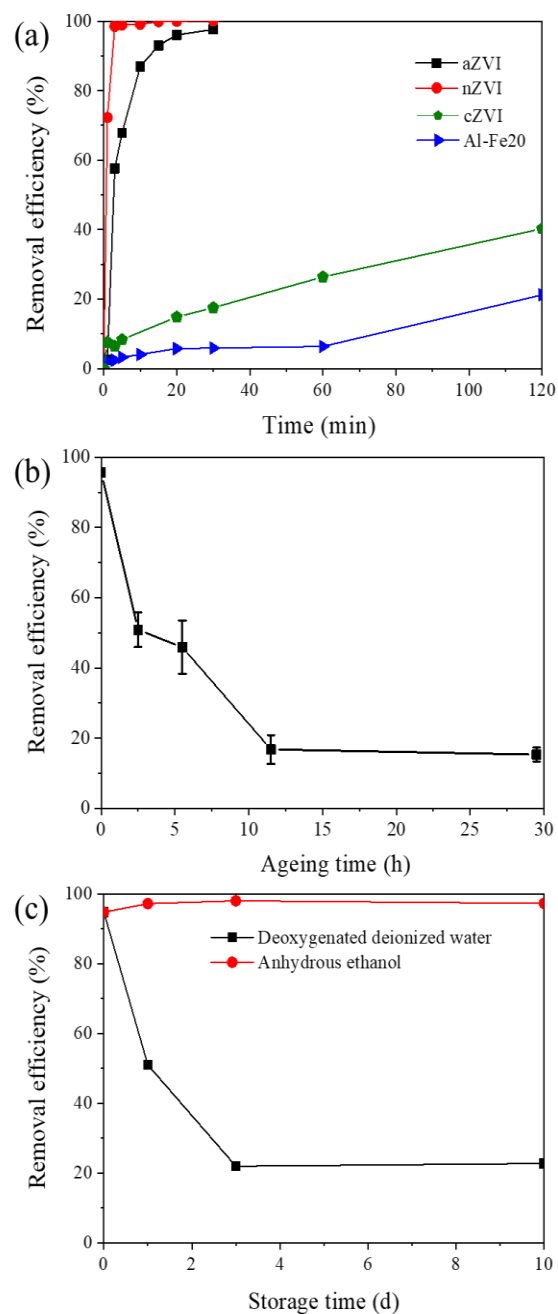


Fig. 7. Removal efficiency of AO7 from water by (a) aZVI, nZVI, cZVI and Al-Fe20 alloy, (b) aZVI at different ageing times in 2 M NaOH solution, (c) aZVI stored in deoxygenated deionized water and anhydrous ethanol. Initial AO7 concentration: 200 mg/L, aZVI, nZVI, cZVI and Al-Fe20 alloy dosage: 1 g/L, temperature: 25 °C, AO7 contaminated water pH = 7.32.

Table 1. Concentration of iron in Al-Fe alloys at different particle sizes

Al-Fe alloys	Particle size (μm)	Fe (wt.%)
Al-Fe10	250-380	10.4 $\pm$ 0.3
Al-Fe20	380-830	19.0 $\pm$ 0.6
Al-Fe20	250-380	19.2 $\pm$ 0.8
Al-Fe20	180-250	20.5 $\pm$ 1.3
Al-Fe20	75-80	35.0 $\pm$ 0.3
Al-Fe50	250-380	51.0 $\pm$ 0.5

Table 2. Magnetic parameters of the magnetic Fe_3O_4 samples obtained from Al-Fe20 alloy at different ageing time in 2 M NaOH and at 90 °C

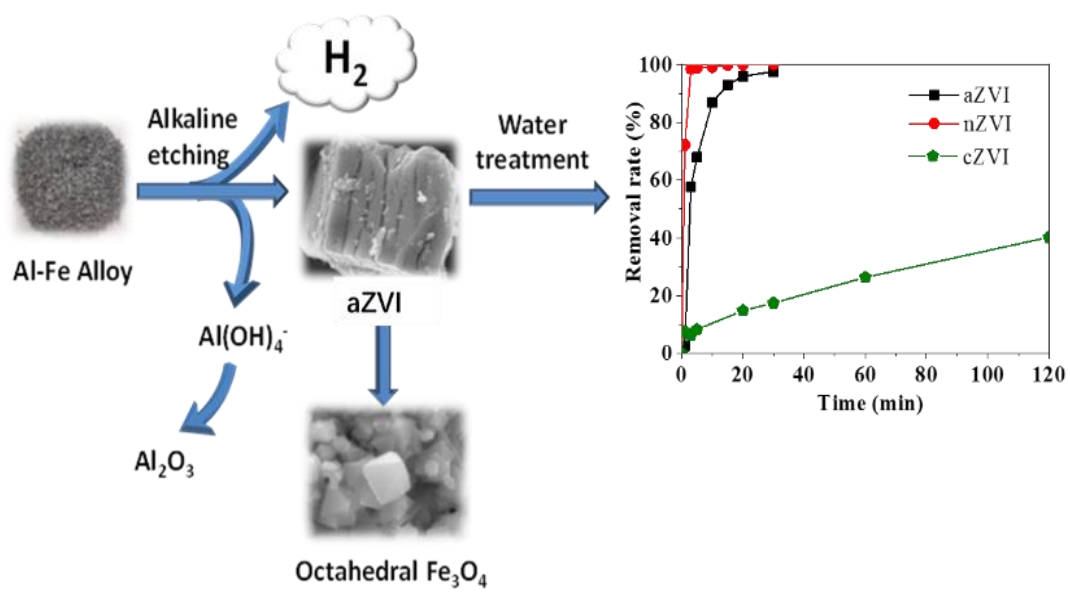
Ageing time (h)	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
3	32.4	7.1	330.2
6	68.2	13.2	200.4
30	47.5	8.9	150.2

Table 3. Removal of AO7 using ZVI materials

ZVI materials	C_0 (mg/L)	Dosage (g/L)	pH	Removal efficiency (%)	Reaction time (min)	References
B-nZVI ^a	20	2	2	98.3	10	[56]
PN-ZVI ^b	100	0.2	5.96	88	60	[58]
nZVI-R ^c	70	2	Neutral	100	10	[57]
aZVI	10	1	Neutral	98.3	5	This work
aZVI	200	1	Neutral	97.6	30	This work
aZVI	500	1	Neutral	98.6	30	This work

^a biochar-supported nanoparticle ZVI (B-nZVI), ^b hydroxypropylmethyl cellulose modified ZVI (PN-ZVI), ^c nZVI-rectorite (nZVI-R)

Graphical abstract



Highlights

- Hydrolysis of Al-Fe alloys produces hydrogen and active zero valent iron (aZVI) particles;
- aZVI particles have specific surface areas of 30-70 m²/g;
- aZVI outperforms conventional nano-ZVI for pollutant removal from water;
- Ageing aZVI in the hydrolysis solution generates octahedral Fe₃O₄ crystals;

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Production of hydrogen, active zerovalent iron and ferroferric oxide octahedron by alkaline etching Al–Fe alloys

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