Research Progress of Removal of Pollutants from Wastewater by Zero-valent Aluminum

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Abstract: In recent years, the use of zero-valent metals (ZVMs) to treat environmental pollutants has been a research hotspot in the field of environment. Zero valent aluminium (ZVAl) has attracted much attention due to its lower redox potential and amphoteric properties (reaction pH can be extended to alkaline) than other metals. In this paper, zero-valent aluminium and its composite materials are used to treat pollutants in wastewater, including phenols, organic halides, azo dyes organic pollutants and perchlorate, Cr(VI), As(III) inorganic pollutants. The removal effect and reaction mechanism were also clarified. The existing problems and bottlenecks of this method are further discussed, and the development direction and application prospect of zero-valent metal aluminium redox technology are prospected.

1. Introduction
Removal of pollutants from water by reducing zero-valent metals (ZVMs) has always been a research hotspot in the field of environmental control. ZVMs are widely used in many kinds of polluted wastewater treatment, groundwater remediation and contaminated soil treatment because of their strong reductive activity[1]. It is one of the most promising pollutant treatment technologies. At present, the commonly used zero-valent metals include iron, copper, zinc and aluminium, among which zero-valent iron (ZVI) is the most widely used. However, due to the limitation of pH range, high reduction potential and low driving force of reduction reaction in the process of removing pollutants by ZVI, the unique properties of ZVAl have attracted the attention of researchers. Aluminum is the most abundant metal element in the crust, and ZVAl is a strong reductant. Its redox potential (E0(Al3+/Al0) =-1.662V) is much lower than other common ZVMs such as ZVI (E0(Fe2+/Fe0)=-0.44V). It has stronger reductive activity and electron transfer ability. Its thermodynamic driving force for electron transfer is nearly four times that of ZVI. More importantly, because of the amphoteric chemical properties of aluminium, the applicable range of pH can be extended to alkaline[2].

2. Application of ZVAl Technology in Removal of Pollutants
At present, the research on ZVAl removal of pollutants in water mainly includes two types: oxidation of pollutants in water with zero-valent aluminium/oxygen/acid (ZVAl/O2/H+) and reduction of pollutants in water with zero-valent aluminium/anaerobic (ZVAl/anaerobic). For a long time, the former has attracted much attention for its in-situ production of H2O2 to form Fenton-like oxidation system. The reaction process of ZVAl/H+/O2 system is shown in Fig 1: First, the alumina on the
surface is dissolved under acidic conditions; three electrons are generated in the process of oxidation of $\text{Al}^0$ to $\text{Al}^{3+}$, and dissolved oxygen in water is combined with $\text{H}^+$ to form $\text{HO}_2^\cdot$, then $\text{HO}_2^\cdot$ forms $\text{H}_2\text{O}_2$ through its own rapid disproportionation reaction; finally, $\text{H}_2\text{O}_2$ obtains the electrons transferred on the surface of aluminium powder to form $\text{HO}^\cdot$. $\text{ZVAI/\text{O}_2/\text{H}^+}$ system is the oxidation of ZVAI to remove pollutants in water in the presence of strong acid and oxygen. In the reaction system, ZVAI induces Fenton-like reaction. It is well known that Fenton reaction is one of the most representative processes in advanced oxidation technology. The traditional Fenton reaction can produce hydroxyl radicals ($\cdot\text{OH}$) with strong oxidative properties through formula (3-1). It is very popular in the treatment of refractory organic pollutants. However, this process requires more $\text{H}_2\text{O}_2$, and $\text{ZVAI/\text{O}_2/\text{H}^+}$ is a new Fenton-like system, which has played a catalytic role. The effect of decomposition of $\text{H}_2\text{O}_2$, while molecular oxygen is reduced to $\text{H}_2\text{O}_2$ by ZVAI, so no additional $\text{H}_2\text{O}_2$ is needed.

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \quad (1-1)$$

Fig1 The mechanism of hydroxyl radical produced by ZVAI/\text{H}^+/\text{O}_2 system\textsuperscript{[1]}

In recent years, the study of direct reduction of pollutants in water by ZVAI/anaerobic system has also begun to attract attention. Some researchers began to attempt to directly use the reductive properties of ZVAI to reduce pollutants in water, such as reducing nitrobenzene and reducing azo dyes by hydrogenation breaking azo bond. Other researchers began to try to reduce pollutants in water based on different bimetallic systems of ZVAI. The specific research progress can be seen in the following 2.2, 2.4, 3.2, etc.

2.1. Removal of phenols

Phenolic compounds are a kind of serious environmental pollutants. Phenolic wastewater is one of the most harmful and widely polluted industrial wastewater in the world. ZVAI/\text{H}^+/\text{O}_2 system is an efficient, inexpensive, compatible and operable advanced oxidation treatment method for organic wastewater, which can effectively remove phenolic pollutants. Cheng\textsuperscript{[3]} et al. studied the characteristics of pickling zero-valent aluminium (AW-ZVAI) and the mechanism of phenolic removal in the presence of $\text{H}_2\text{O}_2$ using AW-ZVAI/\text{O}_2/\text{H}^+$. They found that AW-ZVAI had larger capacity to remove phenols than ZVAI. In the presence of 4.002 mM $\text{H}_2\text{O}_2$, the dosage of ZVAI was 6 g/L, and the initial concentration of phenol was reduced from 20 mg/L to 0.3 mg/L after pickling for 3 hours at 2.7 pH. $\text{H}_2\text{O}_2$ promotes the reaction in AW-ZVAI/\text{O}_2/\text{H}^+$, because it enhances the formation of hydroxyl radicals. Liu\textsuperscript{[4]} took bisphenol A, a common phenolic compound in the environment, as a model compound, and studied a new method for the degradation of phenolic compounds. The degradation efficiency and reaction mechanism of zero-valent aluminium-acid system (ZVAI/\text{H}^+) for bisphenol A under aerobic conditions were studied. The results showed that the removal efficiency of bisphenol A by aluminium powder was obvious when pH <3.5. The removal rate of BPA with initial concentration of 4.0 g/L can reach more than 75% in 12 hours when the temperature is 25\degree C and the pH is 1.5.
2.2. Removal of Azo Dyes

Zero-valent aluminium reduction treatment of azo dye wastewater has the advantages of: (1) Zero-valent aluminium can be used to treat azo dye wastewater in alkaline condition. (2) Although zero-valent aluminium can also increase the pH of the system in the reaction process, it can form soluble metal-luminate under strong alkaline condition, which does not affect the activity of zero-valent aluminium. (3) The reduction potential of zero-valent aluminium is lower than that of zero-valent iron, which makes the reaction driving force greater. Wang et al. [5] studied the degradation of azo dye Acid Orange 7 (AO7) by zero valent aluminium (ZVAl) combined with ultrasound. They found that ultrasound-assisted ZVAl could promote decolorization of AO7, and its degradation effect was better than that of single ultrasound or single ZVAl/O2/H+ system. The removal rate of AO7 could reach 96% after 30 minutes when the pH value was 2.5, the dosage of aluminium was 2 g/L and the initial concentration of AO7 was 20 mg/L. The research shows that the decolorization of azo dye wastewater can be effectively treated by ultrasound+ZVAl process. Yuan et al. [6] treated alkaline azo dye wastewater which was difficult to be biodegraded. The typical azo dye RB222 (reactive blue 222) was used as the treatment object. ZVAl was directly used to reduce the wastewater under alkaline conditions. The effects of solution pH, reaction temperature and the dosage of zero-valent aluminium powder on the molecular degradation of azo dyes are systematically evaluated. The results showed that with the increase of pH from 7.00 to 12.00, the decolorization rate increased from 62.6% to 98.4%, the dosage of ZVAl powder increased from 5 g/L to 50 g/L, and the decolorization rate increased from 90.8% to 98.8%.

2.3. Removal of Perchlorate

Perchlorate is a persistent toxic substance with extremely stable physical and chemical properties, which makes it difficult to biodegrade under aerobic conditions. In recent years, the degradation of perchlorate by zero-valent metals as reducing agents has provided a new way for the remediation of perchlorate pollution in the environment [7]. Zhang et al. [8] investigated the influencing factors and mechanism of perchlorate removal by zero-valent aluminium. The results showed that high purity of zero-valent aluminium was obtained by acid pickling pretreatment, and the removal efficiency of perchlorate was high. Range analysis of orthogonal experiment showed that the optimum reaction level was 25℃, pH 4.5, 35 g/L dosage and 2 mg/L initial perchlorate concentration. The main mechanism of removing perchlorate by zero-valent aluminium is not the reduction of zero-valent aluminium, but the adsorption process on the solid surface of aged aluminium powder. Lien et al. [8] remove perchlorate in batch reactor by pickling zero-valent aluminium and aluminium hydroxide. Within 24 hours, 35 g/L aluminium powder, acidic pH value (4.5±0.2), perchlorate removal rate was 90-95%. Although aluminium is a strong reductant, this study shows that there is no evident evidence to support the reduction of perchlorate by aluminium, and it is found that the removal of perchlorate involves the adsorption process. Using 1.0 g/L MgSO4 solution to adsorb and desorb perchlorate ions has a good effect.

2.4. Removal of heavy metal pollution

Generally speaking, heavy metals refer to metals whose specific gravity is equal to or greater than 5, such as Cu, Cr, Cd and so on. They also include metalloids with significant toxicity such as As, Pb. These heavy metals can not be decomposed in water. They migrate and transform between water and organisms in different valence states. They may combine with other toxins in water to form more toxic substances, endangering the whole aquatic ecosystem and endangering human health. Lin et al. [9] treated Cr (VI) wastewater with the activity of ZVAl catalyzed by POM. The results showed that in acidic solution, ZVAl greatly improved the treatment effect of Cr (VI) wastewater under the catalysis of POM; in aerobic condition, the treatment effect of Cr (VI) wastewater could be further enhanced. In addition, Lin et al. proposed that the used aluminium sheets and pots could be used instead of ZVAl to treat Cr (VI) wastewater, which would make the method more economical and effective and more environmentally feasible. Fu et al. [10] found that Al/Fe bimetallic can reduce and remove Cr
(VI) in water in a wider range of pH. ZVAl can provide electrons as an electronic source, transfer ZVI to Cr (VI) for reduction through zero-valent iron, and also directly transfer electrons to Cr (VI). They also found that Al/Fe bimetallics can effectively remove As(III) from water by surface adsorption, oxidation and internal reduction. They also use acid pickled ZVAl and ZVI as the media of permeable reaction wall (PRBs). Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Cr(VI) are removed by reduction, chemical precipitation, adsorption and co-precipitation.

3. Application of Aluminum Nanomaterials and Composites in Removal of Pollutants

3.1. Nano-scale Aluminum Oxide Hydroxide
ZVAl produces Al (OH)₃ or AlOOH during corrosion oxidation, and Al(OH)₃ or AlOOH is an excellent adsorbent. Wang et al. [11] Mixed the prepared aluminium hydroxide aggregate with alumina hydrate, added dilute Na₂SO₄ solution, controlled the acidity of solution pH, filtered with a filter, put in a temperature control instrument, heated, constant temperature, cooled, and obtained nano-AlOOH. The adsorption mechanism of As (III) on nano-iron-aluminium materials was studied by observing the scanning electron microscopic structure of the adsorbent, analyzing the adsorption kinetics, isotherm and desorption regeneration. It was found that the adsorption effect was the best under neutral conditions, and the equilibrium removal rate of As (III) by nano-AlOOH was 70%. Luo et al. [12] prepared magnetic nano-hydroxyalumina by hydrothermal method and characterized its morphology and structure. The effects of pH, initial concentration of Cu²⁺, contact time and temperature on the adsorption of Cu²⁺ by magnetic hydroxyalumina in water were studied. The maximum adsorption capacity was 284.77 mg/g. Nie et al. [13] prepared alumina hydroxide from alumina hydrate and alumina hydroxide aggregate microspheres as precursors, and studied the adsorption properties of self-made nano-alumina hydroxide for Cr(VI) in water. The maximum removal rate of Cr(VI) was 97.6% at pH=7, temperature 25℃, adsorbent dosage 2g/L, initial concentration 10 mg/L, and adsorption equilibrium time 60 min.

3.2. Al/M Composites
Bimetallic method is based on electrochemical oxidation-reduction reaction and utilizes the potential difference between two metals. It is a new development of Al/C micro-electrolysis. Compared with the limitation of ZVAl direct reduction technology in the range of pH (generally requiring pH > 10.5 or pH < 3.5), its application range of pH can be extended to recent neutrality. In recent years, researchers have been trying to use different bimetallic systems based on ZVAl to treat pollutants in water. Reduction is mainly concentrated in Al/Fe, Al/Pb and Al/Cu systems. There are relatively more studies on Al/Fe bimetals. Chen et al. [14] reduced carbon tetrachloride (CT) with Al/Fe bimetal. SEM showed that Fe was concentrated on the surface of Al. The molar ratio of Fe to Al was about 2:3, and the removal rate was 0.75 mL/min. Furthermore, the reduction products were further analyzed, and the action process of Al/Fe bimetallic system was explained. Electrons were produced by ZVAl reduction, and the target pollutants were reduced by ZVI transmission. Fu et al. [10] found that Al/Fe bimetallic can effectively remove As(III) from water by surface adsorption, oxidation and internal reduction. They also mix pickled ZVAl and ZVI as media for permeable reactive walls (PRBs).

4. Conclusions and prospect
ZVAl has extensive application prospects in the field of environmental water pollution treatment because of its strong reduction performance. In recent years, there are more and more studies on ZVAl in the two major fields (ZVAl/O₂/H⁺ and ZVAl/anaerobic), but the mechanism of its surface action is not fully clear, and there are still many problems to be further explored. Such as, Aluminum is a potential pollutant in water. Aluminum ions produced in the reaction process may cause secondary pollution to the water. The concentration of residual aluminum ions in treated water is an important factor in assessing its biological toxicity. The direct reduction of some refractory pollutants such as
nitrobenzene and azo dyes by ZVAI system will result in new reduction products, which can not be mineralized, and subsequent removal of mineralization requires a combination of other reactors.

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