



# Enhancement of Cr(VI) removal by mechanically activated micron-scale zero-valent aluminum (MA-mZVAL): Performance and mechanism especially at near-neutral pH



Yixuan Zhang<sup>a,c</sup>, Shiyang Yang<sup>a,b,c,\*</sup>, Yuqi Zhang<sup>c</sup>, Sui Wu<sup>c</sup>, Jia Xin<sup>a,b,c</sup>

<sup>a</sup> Key Laboratory of Marine Environment and Ecology, Ministry of Education, Qingdao 266100, China

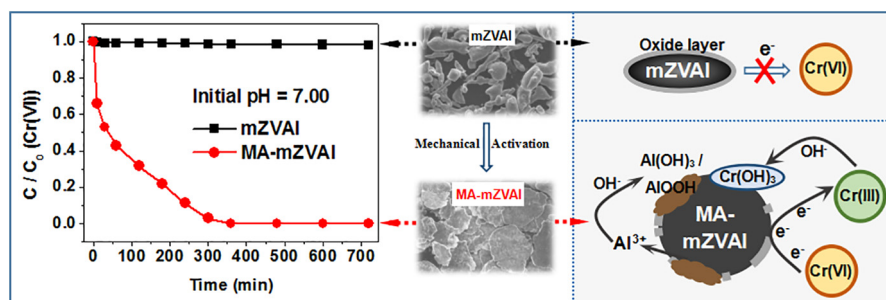
<sup>b</sup> Shandong Provincial Key Laboratory of Marine Environment and Geological Engineering (MEGE), Qingdao 266100, China

<sup>c</sup> College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

## HIGHLIGHTS

- Mechanically activated mZVAL was used for Cr(VI) removal for the first time.
- MA-mZVAL can remove Cr(VI) over a wide pH range (3.00–11.00), even at neutral pH.
- At pH 7.00,  $k_{obs}$  of MA-mZVAL was 292 times roughly of that of raw mZVAL.
- Cr(VI) was rapidly and completely reduced to Cr(III), and precipitated as  $\text{Cr}(\text{OH})_3$ .
- The dense film was destroyed by BM, and changed into a rough one after corrosion.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Micron-scale zero-valent aluminum (mZVAL)  
Mechanical activation  
Surface corrosion mechanism  
Oxide film destruction  
Cr(VI) reduction  
Reusability

## ABSTRACT

The dense oxide film greatly limits the strong reducibility of micron-scale zero-valent aluminum (mZVAL), especially at near-neutral pH. In this study, we found that the removal efficiency of Cr(VI) can be greatly enhanced over a wide pH range (3.00–11.00) by mechanically activated mZVAL (MA-mZVAL), which was prepared from mZVAL by ball milling (BM) in the presence of additive NaCl. Compared with mZVAL, at initial pH 7.00, MA-mZVAL removed Cr(VI) at a roughly 292-fold faster rate. The effects of BM parameters including the amount of additive NaCl, BM speed, BM time, and BM atmosphere on Cr(VI) removal were first evaluated. Then, the Cr(VI) removal mechanism was explored by measuring the concentration of different valent chromium, monitoring the changes of water chemical parameters including DO, pH, ORP, Al ions concentration, and by ascertaining the role of  $\text{Cl}^-$  in solution. Furthermore, the structure evolution of mZVAL after BM and the surface corrosion mechanism of MA-mZVAL during reaction with Cr(VI) were unveiled through the characterization by means of SEM-EDS, BET, XRD, and XPS. Based on above tests, we found that Cr(VI) was reductively removed by MA-mZVAL to form  $\text{Cr}(\text{OH})_3(\text{s})$  precipitated on the surface of MA-mZVAL. NaCl promoted the reactivity of MA-mZVAL not in corrosion process but in BM process. The dense oxide film was destroyed by BM, and changed into a rough Al-(hydr)oxide film after corrosion. The reusability of MA-mZVAL was hindered by the formation of Al and Cr (hydr)oxide, but can be easily and completely rejuvenated by BM. Overall, BM can not only break through the bottleneck of oxide film but recover the passivated MA-mZVAL. Therefore, MA-mZVAL particles are of considerable potential for pollutants removal.

\* Corresponding author at: Key Laboratory of Marine Environment and Ecology, Ministry of Education, Qingdao 266100, China.

E-mail address: [ysy@ouc.edu.cn](mailto:ysy@ouc.edu.cn) (S. Yang).

<https://doi.org/10.1016/j.cej.2018.07.174>

Received 12 May 2018; Received in revised form 11 July 2018; Accepted 26 July 2018

Available online 27 July 2018

1385-8947/ © 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

Aluminum, one amphoteric metal, is the most abundant metallic element in the earth's crust. Zero-valent aluminum (ZVAL) exhibits an extremely negative standard reduction potential ( $E^0(\text{Al}^{3+}/\text{Al}^0) = -1.662\text{ V}$ ), and is also an excellent electronic donor [1,2]. So, ZVAL was more and more widely used to remove the toxic contaminants in water environment [3,4].

However, ZVAL is prone to be oxidized under ambient conditions, and then the surface is covered with a passive oxide film [5]. This passive oxide film hinders the release of electrons from ZVAL, which greatly limits and even hides the reductive capacity of ZVAL, especially at near-neutral pH (4.00–9.00) [1]. Until now, the reducibility of ZVAL under either acidic or alkaline condition ( $\text{pH} < 4.00$  or  $\text{pH} > 9.00$ ) has been confirmed, because its surface oxide and hydroxide are both amphoteric [1,6–9]. However, it is usually extremely difficult for the oxide film to be broken under near-neutral condition [10]. Though nano-scale ZVAL (nZVAL) has been found to remove nitrobenzene [10] and trichloroethylene [11] at near-neutral pH in our previous studies, micron-scale ZVAL (mZVAL) can hardly be used for removing pollutants from aqueous solution at near-neutral pH [1,12]. Considering that mZVAL is more readily available, inexpensive, and environment-friendly than nZVAL [13], the reducibility of mZVAL especially at near-neutral pH is urgent to be excavated for application.

As stated above, the surface oxide layer becomes the biggest bottleneck for application of mZVAL. In order to break through the bottleneck of oxide layer, scholars are looking for various methods to remove, transform or destroy surface oxide film to activate or enhance the reactivity of mZVAL [14], including acidic or alkaline washing [1,2,8,9,15–19], preparation of Al-based bimetal [20–25] or aluminum alloys [26,27]. All these researches confirmed that it is indispensable to activate the reactivity of mZVAL when mZVAL was used for pollutants removal from aqueous solution.

High-energy mechanical ball milling (BM) is an easy-to-operate, low-cost and efficient solid-state powder processing technique involving repeated welding and fracturing of powder particles [28]. BM process may efficiently activate the reactivity of mZVAL, because it can change the microstructure of ZVAL, eliminate or destroy the oxide film, and then create fresh Al surface [29]. BM of pure ZVAL alone is not feasible because agglomeration phenomenon of ductile metal ZVAL would take place [30]. So addition of BM additive is needed. At present, mechanically activated mZVAL (MA-mZVAL) with the help of additive NaCl has been studied for hydrogen generation [31,32].

We can not help thinking that whether MA-mZVAL is able to realize the removal of pollutant from aqueous solution. In the Al/H<sub>2</sub>O system, electrons transfer from MA-mZVAL to the main acceptor H<sub>2</sub>O and hydrogen was generated. However, in the system of Al/H<sub>2</sub>O/contaminant, there is a process of electron competition between H<sub>2</sub>O and contaminant. Until now, it is still unknown whether contaminant can successfully capture electrons released from the surface corrosion of MA-mZVAL against other electron competitors to realize its reductive removal. Then, the roles of NaCl in both BM and Al corrosion processes are required to be investigated and identified. Furthermore, whether the surface oxide film of mZVAL is completely eliminated or simply destroyed after BM is not well confirmed, and the surface corrosion mechanism of MA-mZVAL in removing pollutant is also unclear. Finally, the reusability of MA-mZVAL is of particular importance for its application.

Therefore, the objectives of this work are (i) to verify the enhancement of removal of chromate (Cr(VI)), a typical heavy metal contaminant, by MA-mZVAL over a wide range of pH (3.00–11.00), and evaluate the effects of BM parameters including the amount of additive NaCl, BM speed, BM time, and BM atmosphere on Cr(VI) removal; (ii) to explore the removal mechanism of Cr(VI) by MA-mZVAL by measuring the concentration of different valent chromium, monitoring the changes of water chemical parameters including dissolved oxygen

(DO), pH, oxidation reduction potential (ORP), Al ions concentration, and by ascertaining the role of Cl<sup>-</sup> in solution; (iii) and to elucidate both the structure change of mZVAL after BM and the surface corrosion mechanism of MA-mZVAL after reaction with Cr(VI) through the characterizations by means of scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS); (iv) to evaluate the reusability of MA-mZVAL for Cr(VI) removal at initial pH 7.00.

## 2. Experimental

### 2.1. Materials and reagents

Chemicals used in this study were purchased from commercial reagent suppliers. Zero-valent aluminum particles (ZVAL, 100–200 mesh, i.e. 75–150 μm, 99% purity), sodium chloride (NaCl, 99% purity), potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), H<sub>2</sub>SO<sub>4</sub> and NaOH all were obtained from Shanghai Chemical Reagent Company. All chemicals were of analytical reagent grade. All solutions were prepared using distilled water.

### 2.2. Mechanical activation of mZVAL particles

The mZVAL particles were mechanically activated by high-energy BM, which was performed in a planetary ball miller (YXQM-4L, Mitr, China), equipped with stainless steel milling jars (500 mL capacity) and zirconia balls with 5 mm- and 8 mm- and 10 mm-diameter at a number ratio of 6:3:1 in a BM atmosphere. Usually, the jars were filled with nitrogen, if not specifically stated. The mass ratio of ball to powder was kept at 30:1 approximately. The mZVAL with different weight of NaCl added (0–10 wt% NaCl) were used to study the effect of NaCl. BM speed varied from 150 to 300 rpm and BM time varied from 0.5 to 5.0 h. To evaluate the effect of BM atmosphere, mZVAL particles were ball milled in the atmosphere of N<sub>2</sub>, air or O<sub>2</sub>, respectively. The other BM parameters were fixed when studying the effects of specific BM parameter. The MA-mZVAL particles obtained were used for Cr(VI) removal.

### 2.3. Cr(VI) removal experiments

The Cr(VI) removal experiments were carried out in a batch system using the MA-mZVAL particles. The reactions were performed in sealed serum bottles that were stirred on a thermostatic shaker at 180 rpm to keep the MA-mZVAL suspending evenly under ambient conditions (25 ± 2 °C). All the solutions were bubbled by nitrogen for 15 min to exhaust the oxygen before the reaction. In a typical reaction system, 250 mL of 0.2 mM deoxygenated Cr(VI) solution was reduced by 4.0 g L<sup>-1</sup> MA-mZVAL particles. The initial pHs were adjusted to desired value with 0.1 M H<sub>2</sub>SO<sub>4</sub> or 0.1 M NaOH. And 2.0 mL solution was withdrawn from one of the bottles at time intervals and filtered through a 0.45 μm PTFE filter for analysis. All experiments were carried out at least in duplicate, and average values were presented.

### 2.4. Analytical methods

#### 2.4.1. Analysis of chromium and hydrogen

The concentration of Cr(VI) in aqueous solution was analyzed in a visible spectrophotometer at 540 nm after forming a complex with 1,5-diphenylcarbazide in sulfuric and phosphoric acidic solution. The concentration of total chromium was obtained using the flame atomic absorbance spectrometer (M6, Thermo Co., USA). And the Cr(III) concentration in aqueous solution was calculated by subtracting Cr(VI) from total chromium.

H<sub>2</sub> was measured by a gas chromatograph (GC7900, Tianmei Shanghai, China) equipped with thermal conductivity detector (TCD) and a packed column (PORAPAK Q 80–100, 2.0 m × 2.0 mm).

Download English Version:

<https://daneshyari.com/en/article/6578075>

Download Persian Version:

<https://daneshyari.com/article/6578075>

[Daneshyari.com](https://daneshyari.com)