Perchlorate degradation in aqueous solution using chitosan-stabilized zero-valent iron nanoparticles

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ABSTRACT

As an emerging contaminant, perchlorate has been detected in groundwater, surface water, soil and food worldwide. Perchlorate has good solubility and chemical stability, thus its degradation in water is challenging. Chitosan-stabilized nano Zero-valent Iron (CS-nZVI) was synthesized and tested to degrade perchlorate in water. Chitosan could improve the dispersive property of nZVI, and thus improve its reactivity. Compared with ZVI and nZVI, CS-nZVI exhibited better and faster removal of perchlorate. CS-nZVI exhibited excellent degradation of perchlorate, especially in high-concentration ($\sim$200 mg L^{-1}) perchlorate polluted water. The initial solution pH (3–11) and salinity (0.1–30 g L^{-1}) of the solution did not have a significant influence on perchlorate degradation by CS-nZVI after 8 h reaction. Increasing the temperature could enhance the removal efficiency of perchlorate, and the removal rate reached to 96.1% at 92 °C with the initial perchlorate of 10 mg L^{-1}. A low activation energy (E_a) of 41.55 ± 1.93 kJ mol^{-1} in the reaction was observed, which was lower than that in other relevant studies. The degradation of perchlorate by CS-nZVI was completed by the interaction of initial adsorption and subsequent reduction. After 8 h reaction, most of the perchlorate (>73%) was completely reduced to chloride with very little byproduct at relatively high reaction temperatures (>85 °C). Therefore, this research provides an effective method for perchlorate degradation in contaminated water with high concentrations or high salinity.

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1. Introduction

Perchlorate is both a natural and man-made environmental contaminant, and the major source of perchlorate is from man-made products [1]. Perchlorate can enter the human body and interfere with thyroid functions caused by inhibition of the sodium iodide symporter [2]. To protect human health, the US EPA set a reference dose of 15 μg L^{-1} for drinking water in 2008, and different states have different action levels ranging from 1 to 18 μg L^{-1} of perchlorate [3]. Liuyang city, the largest firework production district in China, was found to have perchlorate pollution, and the residents are exposed to high doses of perchlorate [4]. Huge amounts of perchlorate have been found in dust samples, ranging from 0.132 to 5300 mg kg^{-1} in Northern China and from 0.270 to 3700 mg kg^{-1} in Southern China [5]. Perchlorate contamination was detected in drinking water, groundwater, surface water, and soil by the Department of Defense (DOD) and other federal facilities in the USA, and the highest reported concentrations of perchlo-

rate were 118 μg L^{-1}, 3700 mg L^{-1}, 120 mg L^{-1} and 2000 mg kg^{-1}, respectively [3]. One report showed that the concentration of perchlorate ranged from 0.23 to 2300 μg L^{-1} in the Usui River in Japan [6]. In Southern India, perchlorate concentrations were 0.005–7690 μg L^{-1} in groundwater, and the prime sources of perchlorate pollution in this area were from the fireworks and safety match industries [7].

Perchlorate has good solubility, strong mobility, low adsorption to natural solids, and sluggish reactivity. Due to its unique chemical nature, various treatment technologies have been developed for perchlorate remediation in water. IX is regarded as the most effective technology for the removal of perchlorate in water. However, this method produces large volumes of spent regenerant brine which has high concentrations of perchlorate [8]. Similarly, adsorption and membrane filtration require the disposal of regenerative brine and reject streams concentrated with perchlorate [9]. Biodegradation is an effective method to detoxify water contaminated by perchlorate. However, it may be limited by second-pollution, long treatment time and a slow degradation rate [10]. Chemical reduction can also degrade perchlorate completely, however, the common reduction process is slow, and the use of

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metal catalysts may lead to secondary pollution [11]. Consequently, more cost-effective technologies, which can reduce perchlorate to chloride rapidly and thoroughly, are urgently needed.

In the last decade or two, increasing interest has been paid to the new reducing metals. Zero-valent iron (ZVI) has been used to remove a wide variety of contaminants from water by a mixture of reduction, adsorption, and co-precipitation processes [12]. However, the reaction rate was slow for traditional iron powder or iron filings. Studies indicate that ZVI-based reactions are surface-medicated processes, and increasing the surface area of the ZVI can enhance the reaction rate [13]. Thus, nanoparticle ZVI (nZVI) was developed and used for contaminant reduction, which greatly increased the reaction rate [14]. The nZVI has proved effective for the removal/degradation of a wide range of pollutants, including halohydrocarbon, azo dyes, aromatic compounds, nitrate, and heavy metals [15,16]. ZVI and nZVI were also used to reduce perchlorate from water. For instance, Moore and Young [17,18] studied perchlorate removal by commercial iron filings (size = 20–100 mesh, surface area = 0.08–5.65 $m^2 g^{-1}$), and about 66% of perchlorate (0.1 mM) was removed after 336 h at an iron dosage of 1.25 g mL^{-1}. Oh et al. [19] found that elevating reaction temperature could enhance the reduction rate of perchlorate by ZVI. Heating by microwave to 200 °C, up to 98% of aqueous perchlorate (0.5 mM) could be removed by cast iron (surface area = 1.29 $m^2 g^{-1}$) in 1 h at pH 7.4. Oh et al. [20] also reported that perchlorate in water could be completely removed by iron at 150 °C in 6 h without pH control. Im et al. [21] reported that oxic conditions were beneficial for perchlorate removal by iron powder, and perchlorate (0.016 mM) was removed completely within 9 h via adsorption or co-precipitation processes. Cao et al. [16] investigated perchlorate removal by nZVI and found that 59.1% of perchlorate (200 mg L^{-1}) at nZVI dosage of 20 g L^{-1} after 28 d at 25 °C, and elevating temperature could accelerate reaction rate.

However, due to magnetic interactions and van der Waals attractive forces, bare nZVI formed large particles by agglomeration within a few minutes, resulting in a decline in its specific surface area and eventually a decrease in its dispersibility and reaction efficiencies [22]. To prevent aggregation of nZVI, particle stabilization has been commonly practiced by attaching a stabilizer onto the nanoparticles, including "green" biopolymers [23,24], resins [25,26], clay minerals [27,28]. Considering the potential problems and toxicities associated with the application of a stabilizer for nZVI, the easily biodegradable biopolymers are more suitable to degrade pollutants from water. Xiong et al. [29] used sodium carboxymethyl cellulose (CMC) stabilized nZVI for complete destruction of perchlorate in water and ion-exchange brine (NaCl = 6% (w/w)), up to 90% of perchlorate in both water were removed within 7 h at 90–95 °C. Besides, the CMC stabilized ZVI nanoparticles could remain dispersed in water for more than 1 week.

Chitosan is one of the most important natural polymers due to its excellent biocompatibility and biodegradability. It has been successfully used as a stabilizer to enhance the dispersibility and stability of nZVI, and the stabilized nZVI can effectively remove organics and heavy metals from water. Most previous reports used chitosan as the stabilizer for the preparation of a bimetallic nZVI system [23,30–32]. However, the second catalytic metals caused an increase in treatment cost and secondary contamination. Furthermore, chitosan is a cationic polyelectrolyte, which is attractive for anion separation in water. Our previous studies showed that raw chitosan solution and protonated cross-linked chitosan exhibited relatively high efficiency in perchlorate adsorption [33].

Therefore, in this study, chitosan was used as a stabilizer for nZVI preparations due to its dispersibility characteristics and good affinity for perchlorate. Meanwhile, the chitosan stabilized nZVI (CS-nZVI) was tested to degrade perchlorate in water. The rate and extent of perchlorate degradation by CS-nZVI was investigated. Furthermore, the influences of temperature, salinity, initial perchlorate concentration and pH on the reactivity of CS-nZVI were examined. Finally, the main mechanism of perchlorate degradation by CS-nZVI was discussed.

2. Materials and methods

2.1. Chemicals

All reagents used in this study, including $FeSO_4 \cdot 7H_2O$, $NaClO_4 \cdot H_2O$, $NaClO_3$, $NaClO_3$, $NaClO_2$, $NaClO$, $NaCl$, $NaBH_4$ and CH_3COOH, were of analytic grade and supplied by Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). Anhydrous ethyl alcohol and ZVI powders ($Fe^0 \geqslant 98\%$, size = 100 mesh) were acquired from Cheng Du Kelong Chemical Co., Ltd., (Sichuan, China). Chitosan powder was purchased from Golden-shell Biochemical Co. (Zhejiang, China), with the molecular weight of 10^5 Da and the deacetylation degree of 95.38%.

2.2. Preparation of chitosan stabilized nZVI

The CS-stabilized nZVI was prepared by reducing ferrous ions with borohydride in the aqueous phase. The synthesis of CS-stabilized nZVI used in this study was changed based on previous research [24,32]. The reaction was carried out in a 1 L three-necked flask with mechanical stirring under the protection of nitrogen gas. The flask was immersed in a water bath at a constant temperature of 22 ± 1 °C. Firstly, chitosan powder was dissolved in 2% (v/v) acetic acid solution, and 2% w/w chitosan solution was obtained. The solution was degassed by ultrasound for 5 min and dissolved completely by standing overnight. Secondly, in a typical preparation, 60 mL of $FeSO_4 \cdot 7H_2O$ solution was mixed with 67.5 mL of chitosan solution. The mixture was agitated at a speed of 180 rpm for 15 min to ensure a complete mix. Thirdly, 135 mL anhydrous ethanol was added to the mixture under constant stirring for 5 min. The $NaBH_4$ solution at the concentration of 0.8 M was then dropped into the system at a slow speed of 0.15 mL s^{-1}. As a result, ferrous iron was reduced and nZVI nanoparticles were successfully formed. The suspension was stirred for another 20 min until hydrogen gas eventually ceased. Lastly, the CS-nZVI particles were separated using a magnet and washed with deoxygenated water several times to get rid of the excess chemicals. The freshly prepared CS-nZVI was used for perchlorate reduction without drying. The nZVI was prepared in the same steps without chitosan addition.

2.3. Degradation of perchlorate

The degradation of perchlorate was examined in a series of duplicated batch experiments. The batch tests were carried out in 150 mL serum bottles capped with a Teflon/silicone mininert valve. Firstly, 100 mL of perchlorate solution at the desired concentration was added to the serum bottle. Then, the ZVI, nZVI or CS-nZVI particles at a concentration of 15 g L^{-1} were rapidly mixed with the perchlorate solution. To ensure thorough mixing, a 50 mL headspace was left in the serum bottle. Secondly, the prepared serum bottle containing the aqueous solution was purged with nitrogen gas for 3 min to exclude air and obtain an anaerobic atmosphere. The bottle was then sealed by the Teflon/silicone mininert valve. Lastly, the sealed bottle was placed in a water-bath shaker at a speed of 160 rpm, which was set at the desired temperature for the reduction reaction. At a given reaction interval, duplicate samples were collected with glass syringes. The samples were centrifuged to separate suspended solids, and then filtered through