Performance enhancement of zero valent iron based systems using depassivators: Optimization and kinetic mechanisms

Karim Vayalunkal Karottu Ansaf, Selvaraj Ambika, Indumathi Manivannan Nambi[*]

Environmental and Water Resources Division, Department of Civil Engineering, Indian Institute of Technology Madras, Chennai, India

ABSTRACT

The long-term ability of Zero-Valent Iron (ZVI) in contaminant removal relies on the effectiveness of iron to serve as electron donor, which makes it a versatile remediation material. However, the formation of oxide and hydroxide layers results in passive layer on ZVI surface during contaminant removal hinders its reactivity. The focus of this research was to evaluate the performance of corrosive agents such as acetic acid (HAc), aluminium sulphate (Alum) and potassium chloride (KCl) as depassivators to overcome passivation for sustainability and longevity. Batch experiments using seven combinations of the above chemicals were conducted to optimize the dosage of depassivators based on passive layer removal. The influence of depassivators in catalytic activity of ZVI in removing Cr^{6+} was evaluated. The passive layer on ZVI particles was characterized using Scanning Electron Microscopy (SEM) and confirmed by Energy-Dispersive X-ray spectroscopy (EDAX) analysis. The major mechanisms in passive layer removal was found to be H^+ ion embrittlement followed by uniform depassivation when [HAc] was used and pitting corrosion when [Alum] and [KCl] were used. All the seven sets of chemicals enabled depassivation, but considering the criteria of maximum depassivation, catalytic activity and long term reactivity the depassivation treatments were effective in order as [HAc-Alum] > [HAc-Alum-KCl] > [HAc] > [Alum] > [HAc-KCl] > [KCl] > [Alum-KCl]. The kinetic rate of ZVI using [HAc-Alum] and [Alum] was relatively unchanged over the pH range of 4–10, made it suitable for ex-situ remediation. This insignificant influence of initial pH in catalytic activity of ZVI along with the improvement in longevity and sustainability makes it suitable for effective water treatment applications. The present work has successfully demonstrated that chemical depassivation can restore considerable reactivity of ZVI in the existing permeable reactive barriers.

1. Introduction

Iron is a promising tool for a variety of applications including contaminant removal in ground and surface water, electrodes, conveyance, solar cells, clean up membranes and filters in the field of electrical, transportation and renewable energy (Ambika et al., 2016; Cundy et al., 2008; Shin et al., 2014; Georgiou et al., 2015). Zero-valent Iron (ZVI) is an excellent agent for chemically reducing various pollutants such as organic compounds (Ambika et al., 2015; Su et al., 2013; Dries et al., 2005), heavy metals (Kanel et al., 2005; Liu et al., 2013; Gheju and Iovi, 2006), pesticides (Cao et al., 2013; Bezbaruah et al., 2009) and inorganic anions (Westerhoff and James, 2003). The absorptive capability and reductive activity towards an extensive range of contaminants along with its cheap and wide accessibility made ZVI as a versatile material for contaminant removal (Stumm and Morgan, 1996; Gheju, 2011; Sparisa et al., 2013). In-situ PRB using ZVI as reactive material is a widely accepted technique for the remediation of contaminated groundwater (Obiri-Nyarko et al., 2014). The service life of PRB relies on the effectiveness of filling material viz. ZVI to serve as an electron donor for reduction reactions in subsurface systems (Jeen et al., 2007). However, during these applications, the products and by products such as oxides and hydroxides of iron and toxic heavy metals are precipitated on the surface of ZVI and acts as a passive layer (Guan et al., 2015; Prasad et al., 2011). The surface passive layer formation not only diminishes the performance of ZVI, but also results in incomplete utilization of ZVI. The troubles due to passive layer formation restrain the smooth functioning of PRB, decrease its active life, and make ZVI not feasible for long-term uses, as it requires more maintenance and operation cost

(Henderson and Demond, 2007; Keith and Irene, 2008; Puls, 2006; Puls et al., 1999). Hence, it is of utmost importance to either prevent the formation or remove the passive layer (depassivation) to make the applications of iron based technology sustainable (Guo et al., 2015; Luo et al., 2010; Ching-Yao et al., 2010). Various counter measures such as pretreatment of ZVI, bimetallic concept, nano sized ZVI, coupling with other materials, chemical enhancement of ZVI etc, were practiced to overcome the limitations of ZVI technology (Oh et al., 2005; Lee et al., 2009; Jiang et al., 2015). The electrochemical depassivation evidenced a significant level of restoration in the reactivity of passivated ZVI in PRB for the contaminant removal (Chen et al., 2012; Lu et al., 2012). Researchers on iron corrosion have established that certain chemicals can be used to strongly activate the surface reactivity of ZVI. Watlow corrosion guide shows that acetic acid, $Al_2(SO_4)_3 \cdot 18H_2O$, lead acetate, copper sulphate, ammonium chloride, sodium hydroxide, H_2O_2, sodium and potassium chlorides can act as corrosion promoters that can create new reactive sites on the surface (Gaber et al., 2002; Hernandez et al., 2004; Nazari and Allahkaram, 2010; Comfort et al., 2001; Devlin and Allin, 2005; Lakshmipathiraj et al., 2008). For sustainable environment applications, in this study acetic acid [HAc], aluminium sulphate [Alum] and potassium chloride [KCl] were selected and experimented as depassivators because of their easy availability, eco-friendliness, economical and non-toxic nature. Nevertheless, it is necessary to know the actual composition of passive layer to choose the appropriate depassivators and to discover the mechanism of depassivation. These facts make chemical speciation study essential in conducting research on depassivation. In addition, chemical speciation study enables the quantitative and qualitative information on the transformed iron in both soluble and precipitated form during detoxification process (Ambika et al., 2015). Cr^{6+} is considered as the model pollutant for the study, because of being a highly toxic compound which is carcinogenic and having high mobility and solubility in water which can cause serious health effects and should be converted to less mobile, less soluble and 10–100 times less toxic Cr^{3+} (Ambika and Nambi, 2014; Keith and Irene, 2008; Blowes et al., 1997; Wei et al., 1993). These redox reaction sends with Fe and Cr (oxy)hydroxides and resulted with passivation on the surface of ZVI (Mitra et al., 2011; Nambi and Ambika, 2012; Gheju and Balcu, 2011). The systematic stepwise passive layer formation on ZVI which is reported in this study, to conduct effective research on depassivation, is first of its kind.

Researchers have not yet focused on depassivation mechanisms in the aspects of speciation study and reusability of ZVI. In summary, the objectives of this study are to 1) explore the feasibility of employing [HAc], [Alum], [KCl] for the depassivation of ZVI 2) evaluate the mechanism of depassivation based on systematic chemical speciation study at every stage of experiment 3) assess the performance of depassivators in the reactivity and longevity of both ZVI using Cr^{6+} as model pollutant due to its toxicity towards human beings, plants, animals and micro-organisms and 4) investigate the influence of pH on the reactivity of ZVI towards Cr^{6+} reduction in the presence of depassivators. In this study, the key to improve the long-term reactivity of ZVI in practical cases with inexpensive, sustainable and highly effective way was proposed.

2. Materials and methods

The ZVI particles (99.8% metal basis) of 1–2 mm in size used in this study were purchased from Alfa Aesar, United States. All the chemicals were of analytical grade, purchased from Rankem, India. All the reagents used in the study were freshly prepared at the time of experiment using deionized water.

2.1. Formation of passivated ZVI

The formation of passivated ZVI(pZVI) was initiated by adding 2000 mg/L of fresh ZVI (fZVI) into 100 mL aqueous solution containing 2 mg/L of Cr^{6+} in glass serum bottles closed with rubber septa at various pH conditions (4–10). The bottles were agitated at 100 rpm in an orbital shaker (Remi Instruments Ltd., India) at room temperature to get the homogenous reactor set up. After stabilization of Cr^{6+} reduction, second series of reactions were started with adding same concentrations of Cr^{6+} into the aqueous solution to understand the formation passive layer on ZVI. The series of Cr^{6+} addition were repeated until no further reduction reaction was found. Later the bottles were kept undisturbed for 3 weeks to avoid the deterioration of passive layer due to agitation action and enhance the complete passive layer formation on the surface of ZVI. The resultant passivated ZVI (pZVI) were filtered using 0.45 μm nylon filter followed by washing with deionized water without disturbing the passive layer and used for further experiments. To quantify total iron (TFe_p) and total chromium (TCr_p) in passive layer, 15 mL of 1 N nitric acid (HNO_3) was added drop wise on the ZVI's surface to convert the solid phase of passive layer into solution. Further addition of HNO_3 did not account for passive layer removal whereas it initiated the iron corrosion. The resultant total iron (TFe_{aq}) and total chromium in aqueous solution (TCr_{aq}) were considered as the utmost amount of passive layer that can be removed from the pZVI.

2.2. Optimization of depassivators

Controlled batch experiments were conducted to optimize the concentration of depassivators for the removal of passive layer from pZVI. In this study, seven sets of depassivators with different combinations of [HAc], [Alum] and [KCl] were used in different concentrations as presented in Table 1 and Supplementary Table S1. Depassivation experiments were started by adding one among the seven sets of depassivators with 5–10 different concentrations into a 100 mL solution containing 2034 mg/L of pZVI (equivalent to 2000 mg/L of fZVI). A blank experiment was also conducted without adding any of the depassivators, hereafter denoted as blank. At regular intervals, the supernatant was collected and filtered immediately using 0.45 μm nylon filter and the filtrate was analyzed for total iron (TFe_{aq}) and total chromium (TCr_{aq}) in aqueous solution. The presence of Fe and Cr in solution were due to the removal of passive layer on pZVI surface due to the action of depassivators. Retained pZVI on the filter was washed with deionized water followed by acid washing with HNO_3 to remove the residual passive layer from the surface of ZVI and analyzed for TFe_p and TCr_p on pZVI. Mass balance was done for passive layer on the pZVI as in supplementary material. Surface analysis of ZVI at every stage of the experiment quantified the amount of Fe and Cr coming out from passive layer. Mass balance was checked by comparing the measured total Fe/Cr in passive layer with calculated total Fe/Cr in passive layer by subtracting the Fe/Cr concentration in solution with the initial Fe/Cr concentrations. The minimum concentration of any particular depassivator, which results in maximum passive layer removal viz depassivation was considered as the optimum concentration of that particular depassivator. During the optimization experiment, physical observations like ZVI disintegration, change in color of solution, formation of flocs, precipitate settling at the bottom/ZVI's surface were documented.

2.3. Effect of depassivators in the reactivity of ZVI

The influence of depassivators in the catalytic activity of both fZVI and pZVI was assessed at its optimum concentration through