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Phosphate removal from aqueous solution using ZVI/sand bed reactor: Behavior and mechanism

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A B S T R A C T

This research reports on phosphate removal from aqueous solution using ZVI/sand packed columns. The influence of column preconditioning, consisting of ZVI pre-oxidation before feeding the columns with phosphate solution, revealed that a column aged for 1 day was more efficient than un-conditioned column, 5-days and 10-days preconditioned columns. The distribution of phosphate trapped inside the columns was evaluated by measuring phosphate concentration in the solids at different levels (P1, P2 and P3) along the depth of the columns. The distribution of phosphate inside the columns was determined for a time period up to 46 days, corresponding to column saturation. Results showed heterogeneous trapping along the column before saturation and homogeneous distribution upon saturation. The maximum cumulative trapped phosphate after column dismantling was determined before saturation (after 17 days running) at 130, 68 and 31 mgP/gFe at the inlet-P1, P1-P2 and P2-P3 layers, respectively, whereas the homogeneous distribution of phosphate upon saturation was determined at 132 mgP/gFe throughout the column. Solid supports were characterized using SEM, XRD and XPS. Lepidocrocite and maghemite/magnetite were the only iron oxidation products identified at the different layers inside the columns. XPS results confirmed the sorption of phosphate at the surface of ZVI and its oxidation products and highlighted the formation of an iron phosphate complex.

1. Introduction

Many methods were developed for phosphate removal and recovery from water to mitigate eutrophication, where phosphate is the limiting nutrient. Phosphate recovery has become an important issue as it contributes to solving the depletion of phosphate resources (Tran et al., 2014; Zhang et al., 2013). Phosphate removal and recovery methods include sorption, precipitation, co precipitation and crystallization (Hauduc et al., 2015). Zero valent iron (ZVI) is one of the main sorbents investigated for contaminant removal as it is efficient, non-toxic and easy to handle (Guan et al., 2015). ZVI has been widely used for the removal of different organic and inorganic contaminants. It was recognized to be effective in the treatment of halogenated organic compounds (Matheson and Tratnyek, 1994), As(III) (Kanel et al., 2005), As(V) (Du et al., 2014) (Mak et al., 2011), Cr(VI) (Liu et al., 2009), Pb(II) (Ponder et al., 2000), Cu, Zn (Rangsivek and Jekel, 2005), NO_3^- (Huang and Zhang, 2005; Su and Puls, 2004), and PO_4^{3-} (Almeelbi and Bezbaruah, 2012; Wen et al., 2014).

The efficiency of ZVI to remove phosphate was reported previously in batch experiments in many studies. Results showed high phosphate removal (245.65 mgP/gFe) using NZVI (Nanoscale ZVI); more than 99% of phosphate (C_0 = 10 mg/L) can be removed in 5 min (Wen et al., 2014). Similarly, Almeelbi and Bezbaruah (2012) conducted batch studies to evaluate the effectiveness of NZVI to remove phosphate from water. Results showed that 97% of the initial phosphate (10 mgP/L) were removed after 60 min. However few data can be found in the literature concerning the removal of

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phosphate using ZVI packed columns. ZVI in packed columns can be used alone or accompanied by a support material such as carbon, resin, bentonite, kaolinite, zeolite or sand (Fu et al., 2014). Jeong et al. (2014) used ZVI/sand bed reactor with external electric potential of 600 V to remove phosphate from 150 mg/L phosphate solution. In general, researchers using ZVI packed columns especially focused on the removal of arsenic from water (Biterna et al., 2010; Nikolaidis et al., 2003; Wan et al., 2014).

As column experiments are long term studies, the effect of aging is worthwhile investigation. The effect of aging time on the efficiency of ZVI to remove contaminants was investigated in previous work only in batch experiments. Sarathy et al. (2008), Liu and Lowry (2006) and Du et al. (2014) showed a strong influence of aging time on the reactivity of Fe^0 to remove contaminants (CCl_4, TCE and As) in batch studies.

ZVI is unstable under oxic conditions, it undergoes spontaneous oxidative dissolution. This oxidation is initially manifested by the formation of a porousfilm of $Fe(OH)_2$ which covers the surface of the ZVI. This layer evolves in time (aging process) into a complex and thick film formed by a mixture of amorphous iron oxide, iron salts, and other mineral precipitates (Liu et al., 2015). In parallel when no air pumping is added inside the columns, dissolved oxygen (DO) will not be the same along the column and the surface reactive sites will not be also the same at different layers inside the column so the reactivity along the column may not be homogeneous. Then it is worthy to study the behavior of a ZVI/sand packed reactor at different layers along the column. Wan et al. (2014) reported that the removal rates of arsenic in aerated columns were as much as 2 times greater near the inlet end of the iron column than near the effluent end. Nikolaidis et al. (2003) reported that the arsenic retention mainly occurred near the inlet end of the iron column. The greater removal at the inlet end was attributed to rapid oxidation of Fe^0 by small amounts of dissolved oxygen (DO) in the influent (Mehta and Chaudhari, 2015).

In this study, the effectiveness of ZVI for the removal of phosphate in an upflow ZVI/sand packed columns was assessed along with the determination of the maximum ZVI phosphate trapping capacity. ZVI and its oxidation products may change over time along with their reactivity. In order to assess the evolution of ZVI oxidation products reactivity, phosphate removal was investigated in column reactors with different preconditioning durations. Phosphate removal was also investigated along the various depths of the columns. To attain this goal, phosphate concentration was measured at different sampling ports along the column and the results were assessed in relation to the corresponding phosphate amounts trapped inside the column. Phosphate retention capacities were confirmed through analyzing total phosphorus and iron in the ZVI/sand support collected at the end of the experiment. Solid samples were also characterized in order to understand the mechanism of phosphate removal.

2. Materials and methods

2.1. Pilot unit

Column experiments were conducted using column reactors with a length of 40 cm and an internal diameter of 8 cm. The columns were pumped with an upflow mode. Four sampling valves were affixed along the length of the reactor located at different distances from the inlet. The valves allow for water sampling at P1 (10 cm from the inlet), P2 (18 cm), P3 (27 cm) and P4 (35 cm) (Fig. 1). The reactors were comprised of three layers; the first layer at the bottom (5 cm long) containing only sand; the second layer containing a homogenous mixture of Sand/ZVI (1% W_{Fe}/W_{Sand}; 17 g of ZVI) (22 cm long) and the third layer containing only sand (8 cm long). ZVI particles (purity > 99%) with an average diameter of 250 μm were obtained from Jeulin. The sand was sieved to yield size between 2 and 4 mm then it was washed and dried at ambient temperature. The sand layers at the inlet and the outlet were used in order to prevent iron loss from the reactor. The mixture of sand and ZVI was wetted to permit homogeneous ZVI repartition in the support.

Throughout the experiments, the reactors were pumped with phosphorus synthetic water from a 300 L tank. Flow rate was set to 10 mL/min using peristaltic pumps, the residence time was thus 72 min and the velocity was 0.12 m/h. Experiments were carried out at room temperature (20 ± 3 °C).

Phosphorus synthetic water (20 mgP/L) was prepared from a phosphorus stock solution buffer (10 gP/L) containing KH_2PO_4 (purity > 99%) and K_2HPO_4 (purity > 99%) supplied from Sigma Aldrich whereas NaCl (0.01 M) was purchased from Fluka. NaCl was used in order to fix the ionic strength in all experiments. The pH of the solution was fixed at 7.0 ± 0.2 in order to simulate natural water. The synthetic water was analyzed for phosphorus concentration when renewed. The values of pH and dissolved oxygen were measured at the outlet and in the feeding tank throughout the experiment using a Professional Plus Ysi pH meter and a HQ-30d flexi oximeter, respectively. In addition, oxygen probes obtained from Firesting O_2 were fixed inside one column at sampling point P1 and P3 for continuous monitoring.

2.2. Effect of preconditioning conditions

In order to study the effects of iron oxidation and the synthesis of ZVI products in the column on the efficiency of ZVI to remove phosphate, different preconditioning times were applied. The preconditioning time was set as the duration in which the columns were pumped only with the background electrolytes NaCl 0.01 M at 100 mL/min flow rate in closed circuit. During these periods of time, different ZVI oxidation products were formed in the columns. After preconditioning time, the columns were pumped with phosphate synthetic water (20 mgP/L) and the flow rate was set to 10 mL/min corresponding to a velocity of 0.12 m/h. Four different preconditioning times were tested (1) fresh column pumped directly with phosphate synthetic water, (2) column preconditioned for 1 day, (3) column preconditioned for 5 days and (4) column preconditioned for 10 days. Experiments were conducted under the same experimental conditions cited above (Section 2.1). Phosphate monitoring was done at the outlet of the columns as a function of time and at the different ports as applicable.

2.3. Phosphorus and Fe analysis

Samples were filtered using 0.45 μm acetate syringe filters for phosphate and dissolved/colloidal iron analyzes. Phosphate was analyzed using a colorimetric method, with the formation of an antimonyl/phosphomolybdate complex (Murphy and Riley, 1962). The absorbance of the blue complex was measured at 880 nm in 1 cm cells with an Agilent 8453 UV–visible spectrometer; the limit of quantification was 100 μg/L.

Iron concentration was measured with flame atomic absorption spectroscopy (AAS) using Varian SpectrAA220; quantification limit was 0.1 mg/L. Total iron was obtained by acidifying samples for 3 h at 90 °C by adding 2 mL of HNO_3 65% and 1 mL HCl 37% for 10 mL of each sample. After acidification, samples were filtered using 0.45 μm syringe filter and then analyzed by AAS.

At the end of the experiment, columns were dismantled and solid samples were collected at different lengths (P1, P2 and P3) in the column in order to measure phosphorus and iron. Samples were subjected to microwave assisted acid digestion. 2 g of solid