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Original Article

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The Use of Acid-Washed Iron/Aluminum Mixture in Permeable Reactive Barrier for the Elimination of Different Heavy Metal Ions From Water

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Abstract
In this experimental study, the performance of a fixed bed column containing a mixture of iron and aluminum modified with acid, as a reaction bed, was evaluated for the removal of heavy metals of cadmium, nickel, and copper. The tests were carried out by feeding the columns with aqueous solutions at the concentration of 100 mg/L using four iron/aluminum granular mixtures at various volume ratios (100/0, 50/50, 75/25, 25/75 and 0/100), and pH (3, 5, 7) for a total of 28 column tests. Results showed that metal ion removal was mainly accomplished via redox reactions that initiated the precipitation of mineral phases. At pH 5 and flow rate of 1 mL/min, the removal efficiency of cadmium, nickel, and copper at the 50/50 ratio of modified iron and aluminum was obtained higher than 99% and this removal efficiency could be kept about 50 hours. It seems that the column with the volume ratio of 75/25 of iron and aluminum mixture was the most efficient column for removing the heavy metals with the most suitable iron content and also high hydraulic performance due to the suitable aluminum content. It is therefore seen that the mixture of iron and aluminum can be used as an environmentally and economically viable remediation technology for the subsequent prevention of groundwater contamination.
Keywords: Acid-washed iron/aluminum mixture, Copper, Nickel, Cadmium

1. Introduction

Due to the widespread pollution of water resources with heavy metals which is caused by human or natural resources, the adequate access to safe and clean drinking water for human society is one of the serious challenges of global health (1,2). Exposure to some concentrations of heavy metals, even the concentrations below the allowable limits, can lead to cardiovascular, pulmonary, immune, neurological, and endocrine disruptions (3). Membranes for the removal of heavy metals promise high efficiency and low residual, but their widespread application have been confined due to the need for high energy, condensation of the waste materials, and the maintenance related problems (4). Ion exchange (IE) has been significantly limited by the interference of competitive ions and the problem of regeneration and disposal of condensed by-products (5). Permeable reactive barrier (PRB) is one of the recently developed methods, which has been designed to purify and eliminate the contaminants in underground water and has been known as a low-cost and successful method. In PRB technique, the contaminated water is treated by passing through the barrier while the contaminants react with the reactive medium used in this system. In fact, the PRB is not an obstacle to water, but the reactive medium acts as a medium to remove the contaminants. Zerovalent iron (ZVI) is detected to be a commonly used reactive medium in majority of the PRBs to remove various contaminants such as heavy metals (6). Heavy metals can reduce from the oxidized form to reduced form by producing Fe^{+2} and H/H_2 from the ZVI dissolution (7,8). Of course, there are still many challenges in the increasing use of ZVI. One of the serious issues of the ZVI is its passive corrosion or activity reduction; that is, the slow kinetic and non-linear corrosion of Fe^0 and consequently low efficiency to eliminate the target contaminants (8-10). Furthermore, the decrease of permeability with the accumulation of sediment between the initial holes as a result of sticking the locally produced factors is another problem of using the ZVI (8). In recent years, various modifications have been introduced to this method, including the ZVI nanoparticle strategy, bimetallic alloys and the creation of a magnetic field (11-13). ZVI nanoparticles are smaller in size compared to the ZVI and are relatively expensive due to the high cost of reagent precursors and the combination of their integration processes

(10,12). Coupling the precious metals such as platinum, palladium, and silver is also costly in bimetallic systems and may be toxic (12). Therefore, a simple, cost-effective, and eco-friendly method is required for the significant improvement of ZVI. To tackle this problem, one of the best ways is the use of a ZVI, mixed with other materials in various weight ratios which would be desirable. So far, in some studies, a mixture of ZVI granules and other reactive substances, such as Pumice in PRB, has been used (14-16). Aluminum is classified as a valuable electron donor with a standard electrode potential of -1.67 (Al^{+3}/Al), which is greatly lower than the standard electrode potential of Fe (-0.44) (Fe^{+2} / Fe) (17). Aluminum can be considered as a powerful reducer for the removal of heavy metals; however, the rapid formation of aluminum oxide would impose a higher cost, which reduces its efficiency. Therefore, some pre-treatment for commercial zerovalent aluminum (ZVAl) is required. Washing with acid is a good way to remove oxide layers (18,19). Hence, a mixture of acid-washed iron and aluminum in various ratios, as the reaction medium for the removal of heavy metals including the cadmium, nickel, and copper, which are commonly found in groundwater and sewage, were utilized. Moreover, the effect of the mixture ratio and pH were investigated.

2. Materials and Methods

2.1. Materials

In this study, all stock solutions were prepared using the distilled water. All containers were soaked in 15% nitric acid and washed by distilled water prior to the experiments. The stock solution containing nickel, cadmium, and magnesium were prepared by dissolving $NiSO_4.6H_2O$, $CdCl_2.H_2O$, $CuSO_4.6H_2O$ (Merck Co., Germany). Iron powder with a purity of 98.84% and aluminum powder with a purity of 98% were purchased from the Kavian Metal Coal Company, Persian Gulf. The percentage of the purity of the compounds in iron and aluminum powders was analyzed using the spectrophotometer (Foundry Master, Germany). The data are presented in Tables 1 and 2.

Table 1. The Percentage of Iron and Aluminum Powders

Elements (in powder)	Aluminum	Iron
Percentage	98	98.84

Table 2. Column Volume-Ratio Studies (volume = 18 cm^3 and Q = 1 mm/min)

Contaminant	Reactive Medium (Volume Ratio)	Weight of Fe and Al(g)	Total Weight (g)
Cu 100 mg/L	Fe-Al (100-0)	110.23 0	110.23
Cu 100 mg/L	Fe-Al (0-100)	0 43.52	43.52
Cu 100 mg/L	Fe-Al (50-50)	55.115 21.76	76.88
Cu 100 mg/L	Fe-Al (75-25)	82.67 10.55	93.485
Cu 100 mg/L	Fe-Al (25-75)	10.55 82.67	93.485
Ni 100 mg/L	Fe-Al (100-0)	110.23 0	110.23
Ni 100 mg/L	Fe-Al (0-100)	0 43.52	43.52
Ni 100 mg/L	Fe-Al (50-50)	55.115 21.76	76.88
Ni 100 mg/L	Fe-Al (75-25)	82.67 10.55	93.485
Ni 100 mg/L	Fe-Al (25-75)	10.55 82.67	93.485
Cd 100 mg/L	Fe-Al (100-0)	110.23 0	110.23
Cd 100 mg/L	Fe-Al (0-100)	0 43.52	43.52
Cd 100 mg/L	Fe-Al (50-50)	55.115 21.76	76.88
Cd 100 mg/L	Fe-Al (75-25)	82.67 10.55	93.485
Cd 100 mg/L	Fe-Al (25-75)	10.55 82.67	93.485

2.2. Washing the Iron and Aluminum With Acid

2.2.1. Washing Technique for Zerovalent Iron

Iron was soaked in 0.1 M sulfuric acid for 10 minutes, and then in acetone for 30 minutes. This process was performed for three times. Then, they were rinsed with distilled water and placed on an ice vacuum desiccator to dry completely.

2.2.2. Washing Technique for Zerovalent Aluminum

Ten milliliters of concentrated chloride acid was slowly added into a 1000 mL beaker containing 15 g of ZVI. After observation of the steam, 10 mL of distilled water and 0.5 mL of 0.5 M sulfuric acid were added for heat dissipation. This process was repeated twice 30 seconds after sampling and the aluminum suspension. After performing this process for three times, the sample was stirred in the stirrer by means of a magnet for 20 minutes, and then the sample was separated by a vacuum filter and washed by distilled water for several times. Finally, the sample was placed in the oven until it was completely dried. This test was carried out under aseptic conditions and at ambient temperature (20).

2. 3. Column Studies

Column experiments were designed using a plexiglass column with a dimension of 2.4 × 40 cm (Fig. 1). The middle part was filled with 10 cm of acid-washed iron and aluminum with the size of 20 mesh. Then, as the filler,

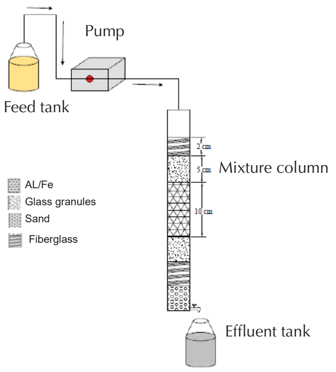

Fig 1. The Schematic Representation of the System Used in This Study.

5 cm of sandstone was applied to the top and bottom of the column, respectively. Moreover, the glass wool (length 2 cm) and glass granules were applied on the top and bottom of the columns, respectively. The prepared synthetic wastewater containing heavy metals was incessantly pumped into the column with downward flow. Samples were collected at predetermined time intervals. The tests were carried out by feeding the columns with aqueous solutions at concentrations of 100 mg/L using four iron/aluminum granular mixtures at various volume ratios (100/0, 50/50, 75/25, 25/75 and 0/100), and pH (3, 5, 7) for a total of 28 column tests. All experiments were performed in at least triplicate and the data obtained were presented as a mean value with a standard deviation.

2. 4. Analysis Method

The concentration of heavy metals was measured using atomic absorption spectrometer (Thermo Scientific™) and the samples containing heavy metals were pumped using Thomas's peristaltic pump.

3. Results and Discussion

This study was performed to evaluate the ability of the PRB system, filled with a mixture of acid-washed iron and aluminum at various volume ratios (100 aluminum, 100 iron, 75/25 and 50/50 iron and aluminum) and at various pH values (3, 5 and 7). The obtained results, based on the effect of the variables studied, are presented as follows:

3.1. Effect of Inlet pH On Heavy Metal Removal Efficiency

pH has been introduced as the most effective variable in heavy metal removal in previous studies (16,21,22); thus the effect of pH was studied in this study. As shown in Figs. 2-4, in this system, increasing the pH had a positive significant effect on increasing the heavy metal removal efficiency. The obtained results were not in agreement with most of previous studies; for instance, Liu et al conducted a study on treating the Cr(VI)-contaminated groundwater with simulated PRB filled with natural pyrite as a reactive material. They observed that increasing the pH caused the decrease of heavy metal removal to such an extent that the best results in their study were observed at pH 5.4 (23). However, the study of Han et al confirmed our results (24). Similar results were also observed in another study conducted by Ahn et al on the ability of the steel manufacturing by-products as permeable reactive materials for Arsenic removal in mine tailing containment systems and described that the increase of pH increased the heavy metal removal (25).

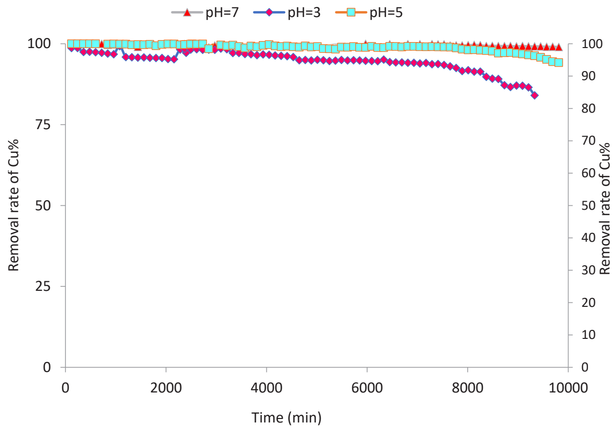

Fig 2. Variation of Copper Removal Efficiency at Different pH (Iron/Aluminum Ratios of 50/50, Copper Concentration of 100 mg/L).

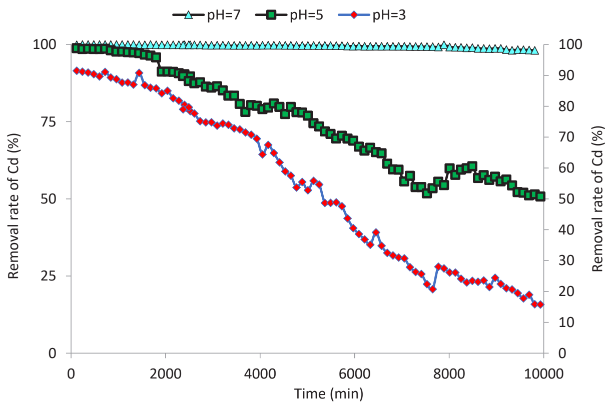

Fig 3. Variation of Cadmium Removal Efficiency at Different pH (Iron/Aluminum Ratios of 50/50, Cadmium Concentration of 100 mg/L).

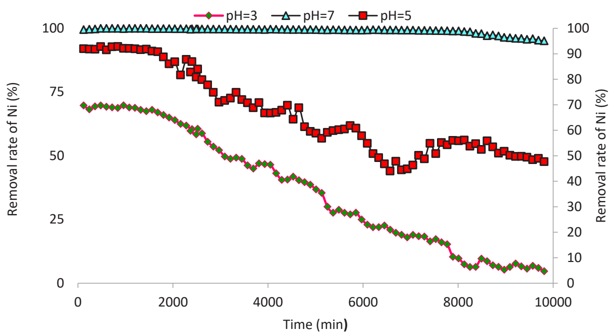

Fig 4. Variation of Nickel Removal Efficiency at Different pH (Iron/Aluminum Ratios of 50/50, Nickel Concentration of 100 mg/L).

In the present study, the highest removal efficiency of the heavy metals including cadmium, nickel, and copper were obtained at pH 7 and this removal efficiency could be kept constant for longer period of time compared to the length of time at pH 3 and 5. This duration was much higher at pH 7 due to the fact that the hydroxide precipitation, in addition to the reduction and adsorption processes, also played a role in the removal of heavy metal ions at higher pH (24). The reaction shown at Equation 1 was done at acidic pH (3) indicating no hydroxide precipitates, while the reduction and adsorption played main roles in the heavy metal removal at this pH; so decreasing the heavy metal removal was expected at pH 3.

$$M^{n+} + n\,OH^- \rightarrow M(OH)_n \downarrow \; (M^{n+} \text{ represents } Cd^{2+}, Ni^{2+}, Cu^{2+}) \quad (1)$$

In the present work, various ratios of ZVI/ZVAl were used. Therefore, the formation of Fe $(OH)_3$ and $Al(OH)_3$ at higher pH was expected (Equations 2-5). These hydroxides have been introduced as good adsorbents for dissolved species (26,27). Hence, these precipitates, at higher pH, could act as an adsorbent to remove the residual heavy metals. Moreover, increasing the concentration of OH increased the number of negative sites on the surface of iron and aluminum which led to an increase in the adsorption between heavy metals and iron and aluminum (28).

Furthermore, our results showed that copper was removed much easier than other studied heavy metals. This phenomenon is described by different redox potential of copper (Cu^{+2}/Cu, 0.34), which is greater than that of cadmium (-0.40Cd^{+2}/Cd) and nickel (0.20Ni^{-2}/Ni). Hun et al observed similar results in their study (24).

$$2Al + 3M^{2+} \rightarrow 2Al^{3+} + 3M \; (M \text{ represents Ni, Cu, and Cd}) \quad (2)$$

$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu \quad (3)$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \downarrow \quad (4)$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \downarrow \quad (5)$$

3.2. The Effect of Various Elements Constituting the Media on the Column Properties

Based on previous studies, although the use of various zerovalent metals such as iron, aluminum, zinc, and so on has been found more interesting, there have been some limitations in the use of these metals alone (29). In a study conducted by Basu et al, the performance of As(V) adsorption of calcined (250°C) synthetic iron(III)–aluminum(III) mixed oxide in the presence of some groundwater ions was evaluated and observed that mixed metal oxides showed greater ability in As (V) removal compared to individual metal oxide (30).

Therefore, in the present work, the mixture of ZVI/ZVAl in various volume ratios was applied. In this study, it was observed that there was low efficiency when the column was filled with acid-washed iron or aluminum alone; so that, the concentration of heavy metals in the wastewater could be hardly decreased to the maximum allowable concentration (MCL) for heavy metals in drinking water determined by the United States Environmental Protection Agency (USEPA), and the concentration of copper present in the effluent showed 100% removal for a short time using 100% ratio of iron or aluminum. It was also observed that the highest removal efficiency for nickel using the columns with 100% ratio of iron was 85.74%, while the highest removal efficiency of this metal using the column filled with 100% aluminum was 80.9%. For the cadmium, the highest removal efficiency using the column filled with 100% iron was 98.8% and the removal efficiency using the column filled with 100% aluminum was 94.1%, which these achieved removal efficiencies did not meet the standard allowable concentrations existed for discharge into the groundwater (Fig. 5). Since the aluminum or iron alone are easily oxidized, an oxide layer is formed on the aluminum or iron particles that reduces their reactivity. In addition, it has been observed that the performance of the column filled with acid-washed aluminum was not better than the column filled with acid-washed iron which can be due to the faster formation of aluminum oxide.

However, for removal efficiency, the column filled with the volume ratios of 50/50 or 25/75 of iron and aluminum was used which showed that the use of bimetallic mixture could be more successful in removing the heavy metals. It was found that the cadmium, nickel, and copper removal efficiency (more than 99.5%) using 50/50 ratio of iron and aluminum mixture was observed for 50 hours, which was much higher than the efficiency level achieved by the use of iron or aluminum alone. Furthermore, the column with a volume ratio of 75/25 of the acid-washed iron and aluminum represented higher removal efficiency and this efficiency was kept constant for longer period of time (more than 100 hours) compared to other conditions applied in this study. Therefore, in this study, the column with a volume ratio of 75/25 of the acid-washed iron and aluminum was chosen as the most efficient and suitable medium for the reaction (Figs. 5-7). This result corroborated the results of previous studies (31,32).

The reduction potential of the aluminum is much lower than that of iron, so the use of ZVAl alone cannot reduce the heavy metals, but can reduce the iron ions. Iron ions are important in two aspects: on the one hand, in acidic conditions, ZVI reacts with H^+ and produces Fe^{+2}; on the other hand, ZVI can reduce the heavy metals such as copper. Therefore, the iron ions were created in the column and could reduce the aluminum, and small iron particles were formed on the aluminum surface. Hence, the acid-modified iron and aluminum had greater efficacy compared to iron and aluminum which were not modified. In the bimetallic system of iron and aluminum, aluminum is an electron source that can prevent the formation of iron corrosion by-products on its surface and thereby inhibiting the activity of iron. It is better

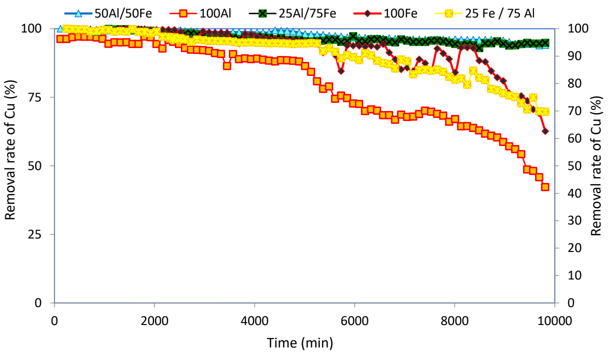

Fig 5. Variation in Copper Removal Efficiency in Different Volume Ratios (pH=5, Copper Concentration of 100 mg/L).

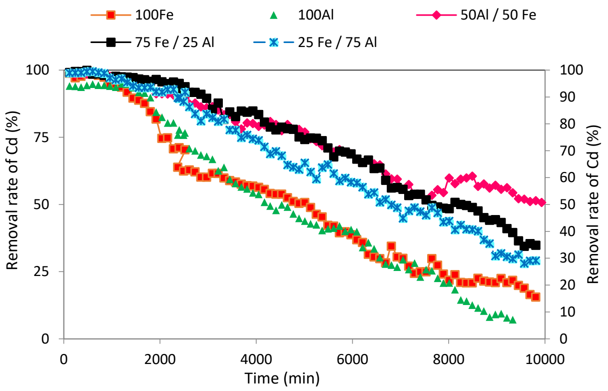

Fig 6. Variation in Cadmium Removal Efficiency in Different Volume Ratios (pH=5, Cadmium Concentration of 100 mg/L).

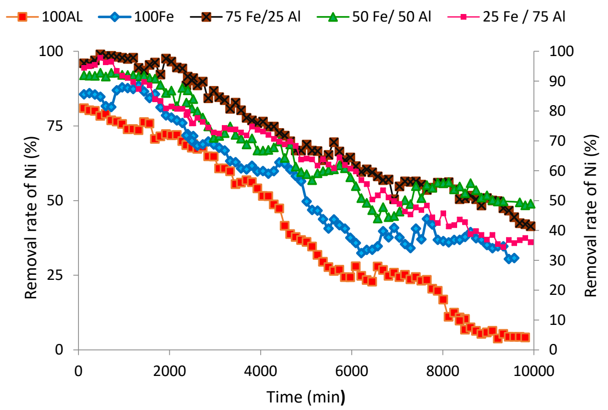

Fig 7. Variation in Nickel Removal Efficiency in Different Volume Ratios (pH=5, Nickel Concentration of 100 mg/L).

the ratio of iron to aluminum not to be lower. A part of ZVAl can be in standby mode with a ZVI/ZVAl mass ratio (22). This result is in agreement with the obtained results from previous studies (24,33). Moraci and Calabro conducted a study to estimate the optimum weight ratio in ZVI/Pumice granular mixtures used in PRBs for the remediation of nickel and found that the most successful compromise between reactivity (higher ZVI content) and long-term hydraulic performance (higher Pumice content) was achievable in the ZVI/Pumice granular mixture of 30/70 weight ratio which confirmed the results of the present work (9).

4. Conclusion

The acid-washed iron and aluminum was utilized as the reaction medium to treat the wastewater containing cadmium, nickel, and copper. The performance of the column increased in the mixed state so that the cadmium, copper, and nickel removal efficiency were higher than 99% using 50/50 ratio of iron and aluminum mixture. This efficiency was kept for 50 hours at the volume ratio of 50/50 of iron and aluminum. In addition, the efficiency of the column increased with increasing the pH. It was also observed that the cadmium was removed easier than nickel and copper. Heavy metals could be removed through the adsorption, reduction and co-precipitation mechanisms. Further studies on the hydraulic behavior of the reaction medium are needed to ensure the operation of the column.

Conflict of Interest Disclosures

The authors declare that they have no conflict of interests.

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