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Removal of hexavalent chromium by Fe doped zeolite

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ABSTRACT

Hexavalent chromium (Cr(VI)) has been known to be one of the frequently detected contaminants in soil and groundwater. Many technologies have been developed to remediate the Cr(VI)-contaminated soil and groundwater. Among them, Fe(0) mediated technologies have shown a great potential to be effectively applied in in-situ remediation of Cr(VI). However, rapid agglomeration of nanoscale Fe(0) caused by its high surface energy and magnetic property has limited the practical application in real sub-surface environment. In this study, we developed an natural zeolite-based Fe(0) (Fe@Pret.Z). The experimental results confirmed that NaOH pretreatment could enhance the dispersibility and mobility of Fe@Pret.Z in column test, whereas Fe(0) showed a clogging problem in the soil matrix. The results obtained from batch experiment and 3D box type reactor revealed almost 70% and 50% of Cr(VI) removal efficiencies, respectively, which were comparable to those of Fe(0) alone (99% and 15%).

1. INTRODUCTION

In soil and groundwater system, chromium usually exists in oxidative state of Cr(VI) and Cr(III). Compared to Cr(III), Cr(VI) is more soluble, mobile, and toxic. A variety remediation process have been developed to remove Cr(VI), but the most of process have technical or economical limits.

Nanoscale zerovalent iron (Fe(0)) has been successfully applied to in-situ remediation of Cr(VI)-contaminated soil and groundwater sites without any detrimental effect on the quality of groundwater. However, bare Fe(0) particle has shown a limitation in their mobility and efficiency due to tendency of agglomeration by magnetic attraction that can induce blockage of active site and hind movement of Fe(0) flow through the porous subsurface environment.

Zeolites are one of the most common and promising industrial minerals with broad application in environmental engineering. Moreover, certain zeolites i.e., clinoptilolite and mordernite) are known to be abundant in nature, and they are used as

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eco-friendly resources. Due to its large surface area and high cation exchange capacity, the zeolite have been used as a support material for Fe(0).

2. EXPERIMENTAL METHODS

2.1 Preparation of Fe@Pret.Z

To prepare the NaOH pretreated zeolite (Pret.Z), zeolite (Nat.Z) was dissolved in a NaOH solution and magnetically stirred for 24h. This suspension was then separated by centrifugation and washed with deionized water (DIW). The separated solid was dried and directly used as a support of Fe(0).

The Fe (III) precursor solution was added into the Pret.Z suspension. After sufficient stirring, $NaBH_4$ solution was added dropwise to the mixture solution to reduce Fe(III) to Fe(0) on the zeolite surface. Finally, synthesized Fe@Pret.Z was separated by vacuum-filtration, rinsed with ethanol, and dried in vacuum drying oven.

2.2 Experimental procedure of batch and 3D box reaction for Cr (VI) removal

To confirm the applicability of Fe@Pret.Z in field-relevant conditions, a three dimensional (3D) box type reactor was designed in this study (Fig.1). A comparative experiment for Cr (VI) removal was conducted through batch and a 3D box reactor.

Batch experiment was performed in 24 mL serum bottles. Exact amount of Fe@Pret.Z (0.02g) was dispersed serum bottle containing DIW (19.5 mL) to prepare the Fe@Pret.Z suspension with concentration of 1g/L. Cr(VI) removal reaction was initiated by injection of Cr(VI) stock solution into the suspension. After 2h reaction, 3 mL of sample was collected using a syringe and filtered 0.45μm polyvinylidene fluoride (PVDF) syringe filters (Whatman).

For the 3D box experiment, Cr(VI)-contaminated artificial groundwater were prepared. The 3D box reactor was filled with silica sand to create a porous environment. First, Cr(VI)-contaminated artificial groundwater was made to flow into the box reactor. Then, Fe@Pret.Z suspension was injected through the injection port using a peristaltic pump under a continuous flow of artificial groundwater. Finally, discharged samples were collected and concentration of Cr(VI) was monitored as function of time. The Cr(VI) concentration of all samples collected in batch and 3D box experiments was determined using UV-vis spectroscopy by the diphenyl carbazide method.

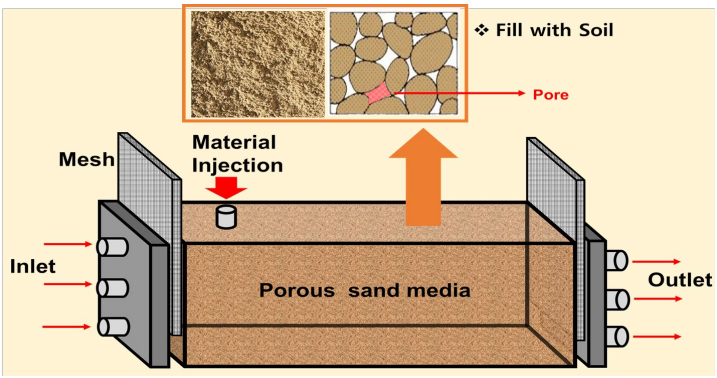

Fig.1 Designed 3D box type reactor

3. RESULTS AND DISCUSSION

Fig.2 (a) illustrate the Cr(VI) removal efficiency in batch and 3D box experiments of bare Fe(0), Fe@Nat.Z and Fe@Pret.Z. From the batch experiment, Fe(0) showed the highest removal efficiency (99%), followed by Fe@Nat.Z (91%) and Fe@Pret.Z (70%). On the other hand, we obtained almost opposite results in the 3D box experiment compared with the batch reaction. As a results, Fe@Pret.Z revealed the almost 50% of Cr(VI) removal efficiency, and both Fe(0) and Fe@Nat.Z exhibited a low Cr(VI) removal efficiency less than 20%.

Fig.2 (b) and (c) show the particle mobility of bare Fe(0) and Fe(0) materials (Fe@Nat.Z and Fe@Pret.Z) in 2D column and 3D box reactor, respectively. In column and box tests, Fe(0) did not pass through the soil matrix due to clogging problems. Indeed, we visually observed some blackening of the soil after Fe(0) injection, indicating Fe(0) agglomeration within the soil pores. While, Fe@Pret.Z and Fe@Nat.Z showed increased mobility. However, when using a zeolite support, the particle mobility did not significantly increase. The tendency of column and box test results for mobility were consistent. These findings suggest that pretreatment for zeolite is an important factor in enhancement of mobility.

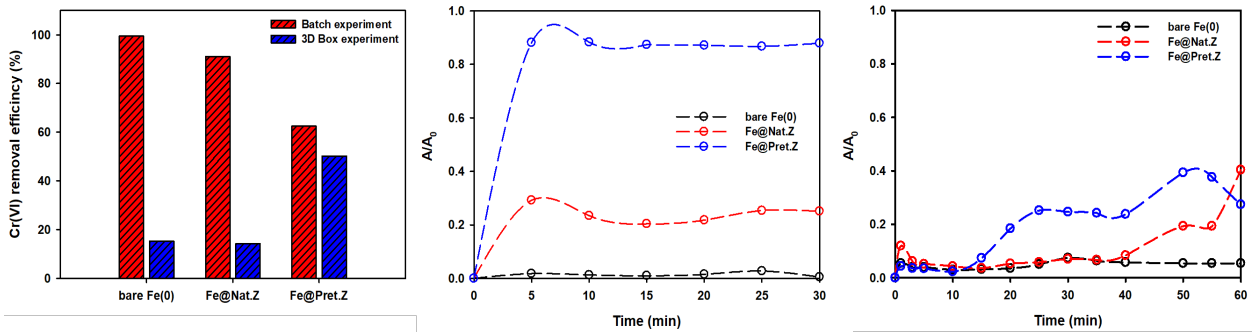

Fig.2 (a) Comparison result of Cr(VI) removal efficiency for each materials (bare Fe(0), Fe@Nat.Z and Fe@Pret.Z) in batch and 3D box experiment. (b) Column mobility test and (c) box mobility test results

FE-SEM images of Fe@Nat.Z and Fe@Pret.Z are shown in Fig.3. The FE-SEM image of Fe@Nat.Z showed that the Fe(0) particles are agglomerated on natural zeolite support to form a chain-like structure (Fig.3 (a)) (Yan, Weile, et al. 2010). In addition, we observed that some Fe(0) particles did not doped on the zeolite surface and aggregated outside the support matrix (Fig.3 (a-1)). While, Fe@Pret.Z exhibited more uniform dispersion of spherical Fe nanoparticles on pretreated zeolite surface without any aggregation phenomenon (Fig.3 (b) and (b-1)). From these results, we can expected that particle mobility in porous media depends on the minimization of Fe(0)

aggregation through the alkaline pretreatment. Thus, we suggest that Pret.Z provides adequate support to compensate for the shortcomings of bare Fe(0).

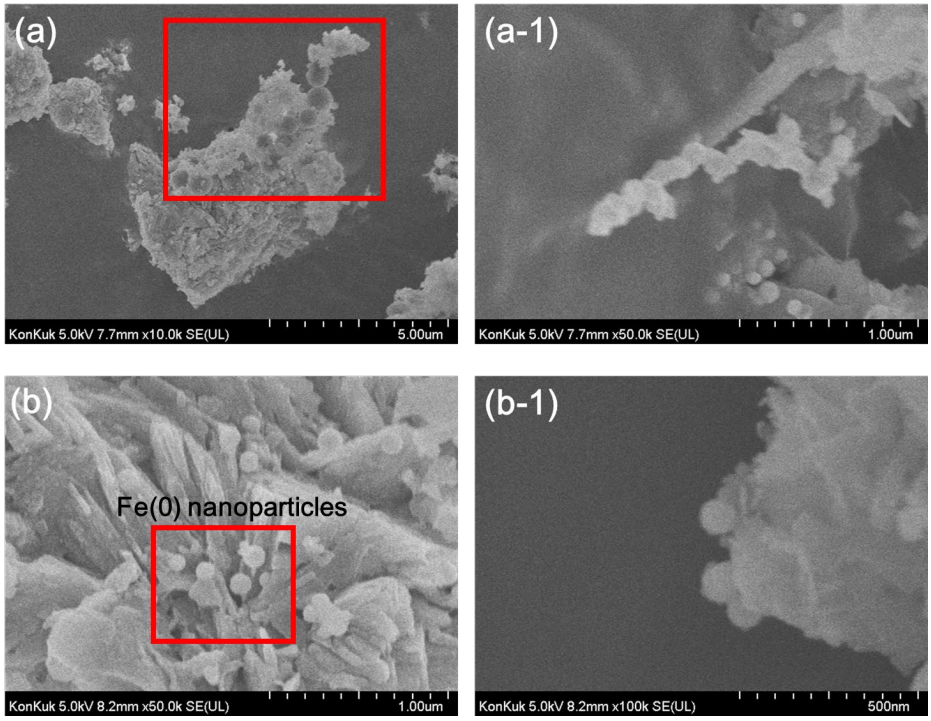

Fig 3. FE-SEM images of (a and a-1) Fe@Nat.Z and (b and b-1) Fe@Pret.Z

4. CONCLUSIONS

In this study, Fe(0) material supported by pretreated zeolite was synthesized for remediation of Cr(VI)-contaminated soil and groundwater. The Cr(VI) removal efficiency in the 3D box reaction was obtained in the order of Fe@Pret.Z > Fe@Nat.Z > bare Fe(0), which showed the opposite result of batch experiment. Similarly, the mobility test results using 2D column and 3D box showed the high particle mobility in the order of Fe@Pret.Z > Fe@Nat.Z > bare Fe(0). FE-SEM analysis demonstrated that NaOH pretreatment on natural zeolite could more strongly prevent Fe(0) agglomeration, which contributed to the increase in mobility. From the comparison of the box Cr(VI) removal reaction and the mobility test, it can be seen that the highly mobile material has good Cr(VI) removal activity.

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