Application of Nano Zero Valent Iron Coated Granular Activated Carbon for Pathogen Inactivation in Septic Tank Effluent

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Abstract
On-site sanitation systems, commonly used in most developing countries, usually generate effluents containing high concentrations of organic matters and pathogenic microorganisms, which need to be further treated before discharge into the environment. This study applied nano zero valent iron coated on granular activated carbon (NZVI/GAC) to inactivate some pathogenic indicators in the septic tank effluents. The synthesized NZVI/GAC were found to content 0.9% Fe and the surface area was 550 m^2/g. Batch experiments conducted with actual septic tank effluent and synthetic wastewater showed that the NZVI/GAC could reduce *E.coli* about 5 and 8 logs, respectively, after the operating time of 1 h. At the hydraulic retention times of 2 and 3 h, the continuous NZVI/GAC columns could reduce *E.coli* about 8 logs for the operating times of 6 and 9 h, respectively. The breakthrough time and regeneration method of NZVI/GAC column were conducted in order to study the applicability of the NZVI/GAC column for treating septic tank effluent.

Keywords
breakthrough point; *E.coli*; nano zero valent iron; on-site sanitation; regeneration

INTRODUCTION

In developing countries, on-site sanitation (OSS) systems such as septic tanks and cesspools are commonly used. Due to absence of drainage trenches, effluents from these OSS systems still contain high concentrations of organic matters and pathogenic microorganisms. According to Langergraber and Muellegger (2005), over 90% of these effluents are discharged into surrounding soils and nearby storm sewers or watercourses, causing water pollution and health problems.

Applications of nano zero valent iron (NZVI) for removing toxic substances and pathogenic enteric viruses in water and remediation of contaminated water have been previously reported (Cheng et al., 2014; Dickinson and Scott, 2010; Fu et al., 2014; Gosu and Gurjar, 2013; Zhu et al., 2009). Some literatures reported effective *E. coli* inactivation by NZVI (Kim et al., 2010; Lee et al., 2008). NZVI coated on solid porous materials such as bentonite, granular activated carbon, kaolinite and resin, have been synthesized to removing different contaminants such as heavy metals (Zhang et al., 2010; Liu et al., 2013) and dyes from wastewater (Shu et al., 2010; Chen et al., 2011). In this study, the application of the NZVI coated on granular activated carbon (NZVI/GAC) was investigated for post-treatment of the septic tank effluent. The specific objectives of the research were to: determine the efficiency of NZVI/GAC on *Escherichia coli* (*E. coli*) inactivation, study breakthrough time of NZVI/GAC column and, evaluate the potential regeneration method of the used NZVI/GAC.

MATERIAL AND METHODS

NZVI/GAC synthesis

NZVI/GAC was synthesized by a borohydride method using 3-Mercaptopropyltrimethoxysilane (MPTMS, ≥95%) as a binding agent. Ferrous sulfate ($FeSO_4.7H_2O$, ≥99%) and sodium borohydride ($NaBH_4$, ≥94%) were used as oxidizing and reducing agents, respectively, as shown in the following chemical reactions (Gosu and Gurjar, 2013; Wang and Zhang, 1997).

$$2Fe^{2+} + BH^{4-} + 2H_2O \rightarrow 2Fe^0 + BO_2^- + 2H_2 + 4H^+ \quad (1)$$

$$Fe^{2+}_{(aq)or(s)}/GAC + 2BH^{4-}_{(aq)} + 6H_2O_{(l)(aq)} \rightarrow Fe^0_{(s)} + Fe^0_{(s)}/GAC + 2B(OH)_{3(aq)} + 7H_{2(g)} \quad (2)$$

The mixture of GAC and MPTMS solution (0.5 mL MPTMS per 100 mL ethanol (C_2H_6O, 95%)), at the ratio of 1 g per 5 mL, was heated at 80 °C for 4 h to dry the GAC coated with MPTMS (Koottatep et al., 2015). The dried GAC coated with MPTMS were added into N_2-purged 0.11 M $FeSO_4$ at the ratio of 1 g per 30 mL and mixed continuously for 15 min, subsequently, 0.22 M $NaBH_4$ was added gradually into the solution and mixed further for 15 min. The synthesized NZVI/GAC were separated from the mixture by using a 1-mm wire mesh screen and rinsed with ethanol.

Batch operations

Batch experiments were conducted with synthetic wastewater samples (*E.coli* concentration of 10^8 CFU/mL) and actual septic tank effluent samples (*E.coli* concentrations of 10^4-10^5 CFU/mL) collected from households. The synthesized NZVI/GAC of 20 g were added to 20 mL of each sample in an Erlenmeyer flask and the mixture was mixed by a horizontal shaker at 100 rpm. Samples were collected for analysis at the operating times of 0.5, 1, 2, 3 and 4 h.

Continuous operations

Continuous operations were conducted using two NZVI/GAC columns (Figure 1) fed with the synthetic wastewater (*E.coli* concentration of 10^8 CFU/mL) at various hydraulic retention times (HRT) of 0.5, 1, 2 and 3 h. To avoid frequent clogging, the up-flow system was employed for the continuous operations.

NZVI/GAC regeneration

The used NZVI/GAC were washed by deionized water, heated at 50 °C in an oven at least 12 h to remove remaining moisture and then slowly mixed with the reducing agent (0.22 M $NaBH_4$) to convert iron oxide (Fe_2O_3) to zero valent iron (Fe^0). To verify the potential of this regeneration method, the regenerated NZVI/GAC were tested for *E.coli* inactivation efficiency in the synthetic wastewater samples by batch operation as explained above.

Analytic methods

Surface morphology of the synthesized NZVI/GAC was analyzed using a scanning electron microscope (SEM) (S-3400N, Hitachi, Japan). The specific surface area was analyzed by using Brunauer-Emmett-Teller (BET) analysis with adsorption isotherm data in a relative pressure (p/p_0) range of 0.05-0.3. The amount of the NZVI attached on GAC was measured by an inductively coupled plasma with mass spectrometry (7900 ICP-MS, Agilent Technologies, USA). *E. coil* concentration was analyzed using a plate count standard method (APHA/AWWA/WEF, 2005).

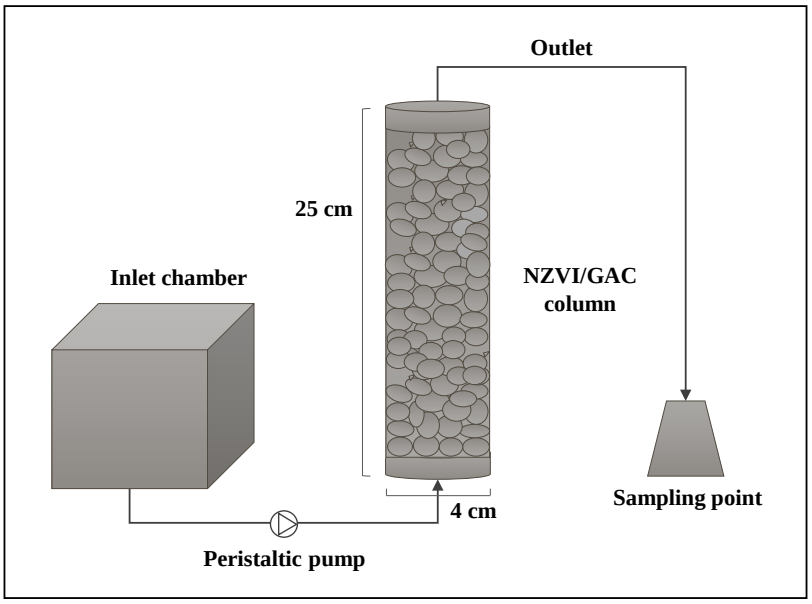
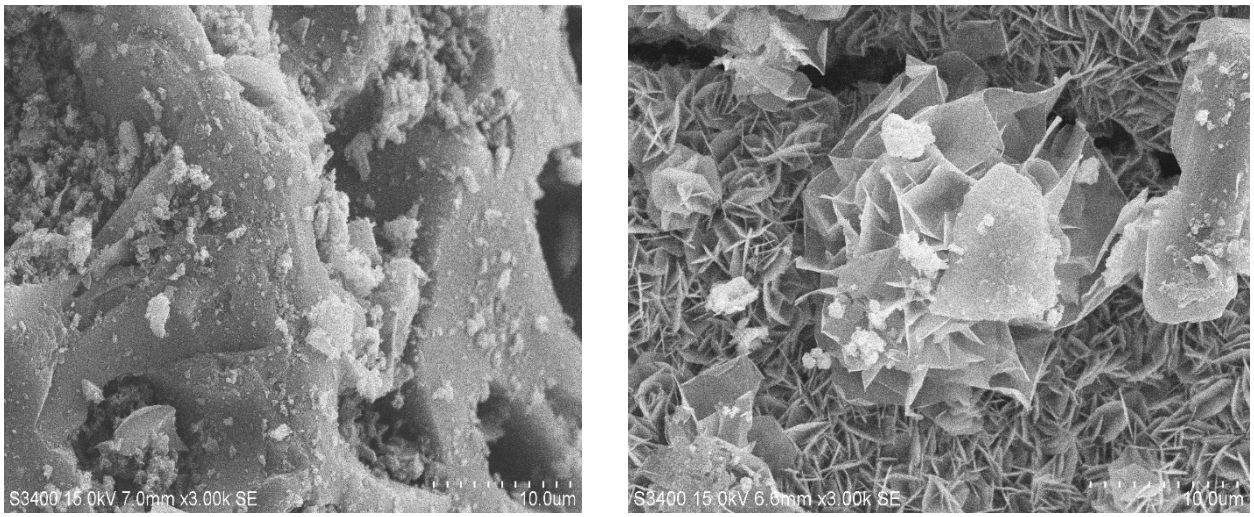


Figure 1 Experiment set-up of NZVI/GAC column

RESULTS AND DISCUSSION

Characteristics of NZVI/GAC

From the SEM analysis, the particle sizes of the synthesized NZVI/GAC were found to be approximately 100 nm with platy crystal growth and botryoidal textures (Figure 2). The ICP analysis revealed about 0.9% Fe coated on the NZVI/GAC particles. However, due to NZVI coating on the GAC surface, BET surface area of the NZVI/GAC was found to be 550 m^2/g, less than the GAC of 836 m^2/g (Figure 2).



(a) (b)

Figure 2 SEM images of (a) GAC and (b) NZVI/GAC

Batch operation

The results of the batch operation using the NZVI/GAC and GAC for inactivating the pathogens at various operating times are shown in Figure 3. The *E.coli* reductions by the NZVI/GAC in the

actual septic tank effluent and synthetic wastewater samples were found to be about 5 and 8 logs, respectively, after the operating time of 1 h. The GAC could not reduce or inactivate the *E. coil* at any operating times.

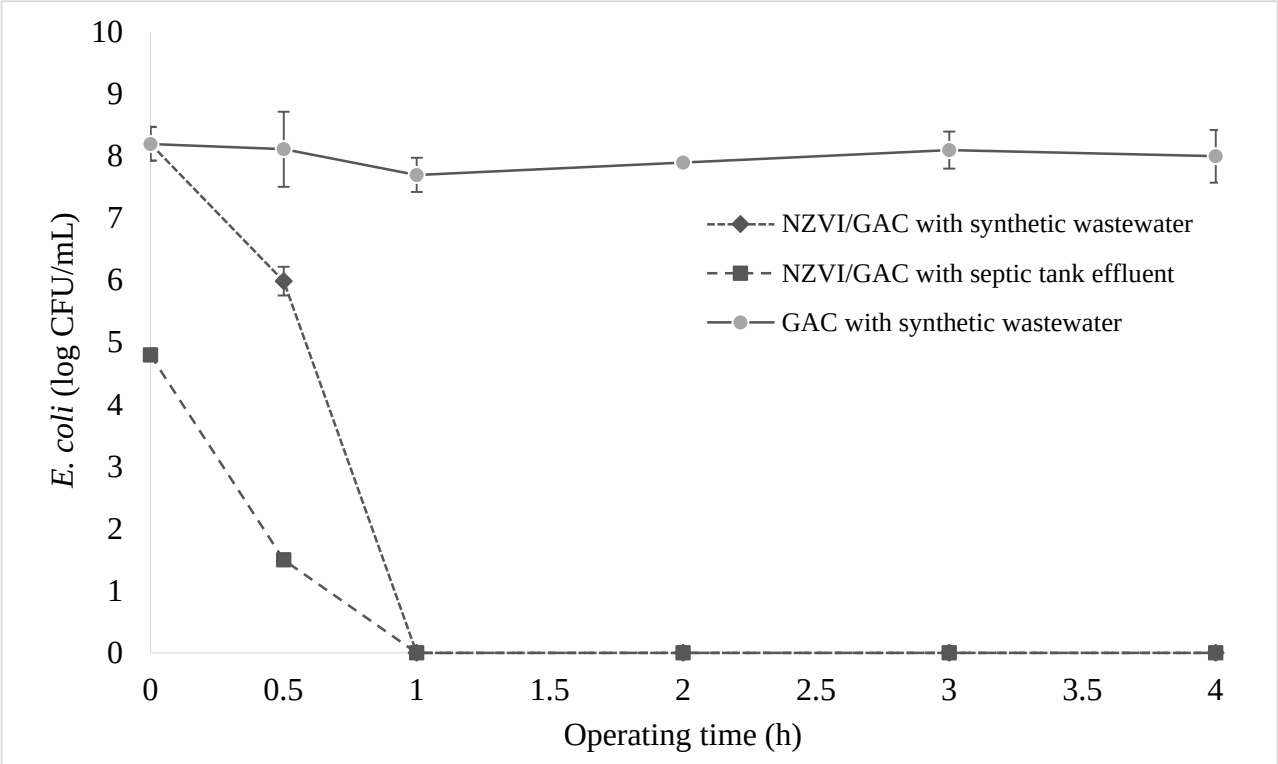


Figure 3 *E. coli* inactivation using NZVI/GAC and GAC for treating synthetic wastewater and septic tank effluent

Continuous operation

The results of the continuous operation using the NZVI/GAC columns with the synthetic wastewater at various HRTs are shown in Figure 4. Probably due to short circuiting effects, *E. coli* reductions at low HRTs of 0.5 and 1 h were found to be approximately 1 log. *E.coli* reduction at the HRT of 2 h was found to be 8 logs during the operating times of 2-6 h and later decreased to about 1 log after the operating time of 48 h. At the HRT of 3 h, the *E.coli* reduction was found to be 8 logs during the operating times of 3-9 h and later decreased to about 3 logs after the operating time of 45 h. During operation of the NZVI/GAC columns, the Fe^0 on the surface of the NZVI/GAC particles reacted with the influent wastewater and formed Fe_2O_3 and FeOOH (Khatikarn, 2009) which could cause reduced *E. coli* inactivation efficiency after certain periods of operation, resulting in *E.coli* breakthrough in the NZVI/GAC column effluents.

Breakthrough time

The performance of the NZVI/GAC columns on *E. coli* inactivation in the septic tank effluent was investigated and the results are shown in Figure 5. The *E.coli* breakthrough times of the NZVI/GAC column operated at the HRTs of 3, 6 and 12 h were found to be 1, 4 and 7 days, respectively, which increased with increasing HRTs. Suspended solids in the actual septic tank effluent might adsorb on the NZVI/GAC surface and hindered the contact of active NZVI and *E. coli*, resulting in reduction of *E. coli* inactivation efficiency at long operation times.

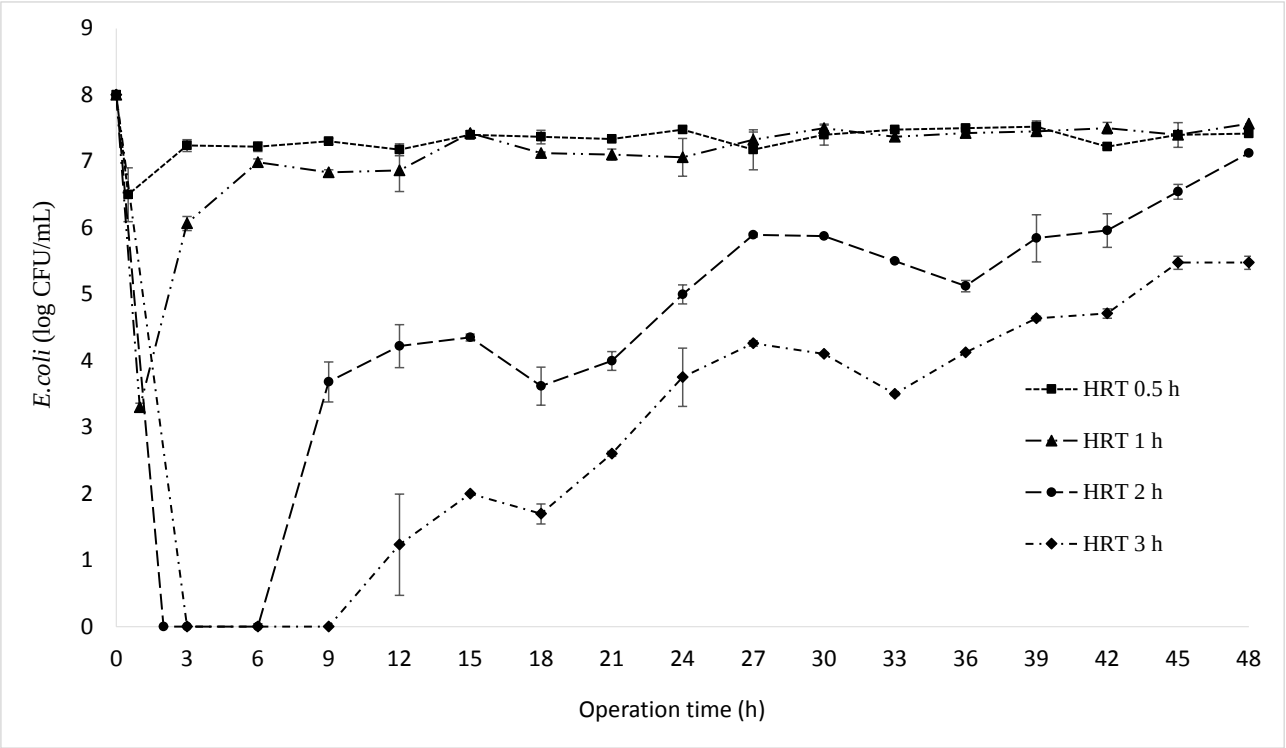


Figure 4 *E. coli* inactivation using NZVI/GAC columns at various HRTs

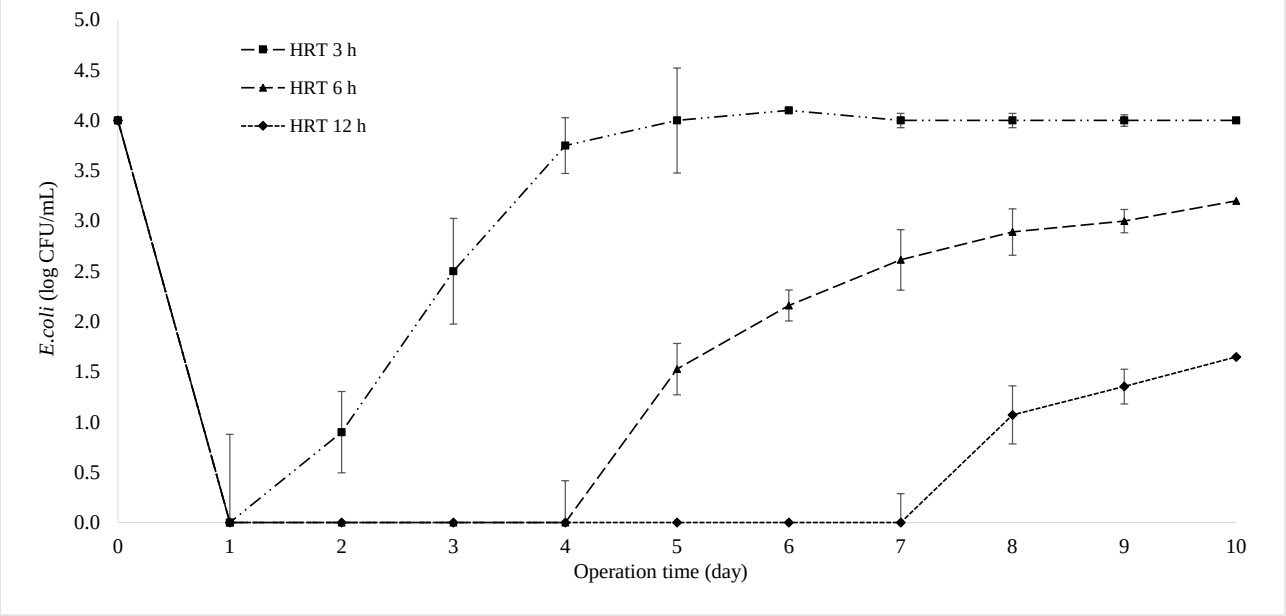


Figure 5 Breakthrough time of NZVI/GAC columns at various HRTs

Regeneration

To minimize operation costs, a method for NZVI/GAC regeneration was investigated. The used NZVI/GAC were regenerated by heating at 50 °C and then reacting with the reducing agent ($NaBH_4$). The BET surface area of the regenerated NZVI/GAC was found to be 650 m^2/g, relatively higher than initial NZVI/GAC. The Fe_2O_3 formed on the surface of the used NZVI/GAC particles was reduced by $NaBH_4$ to be Fe^0. The regenerated NZVI/GAC were found to be able to inactivate

E.coli in the synthetic wastewater samples about 6 logs at the operating time of 1 h. Further studies on long-term performance of the NZVI/GAC particles on *E.coli* inactivation efficiency and related costs are recommended.

CONCLUSIONS

The synthesized NZVI/GAC could be used for pathogen inactivation in the septic tank effluent. Batch experiments conducted with the actual septic tank effluent and synthetic wastewater samples showed that the NZVI/GAC could reduce *E. coli* about 5 and 8 logs, respectively, after the operating time of 1 h. At the HRTs of 2 and 3 h, the continuous NZVI/GAC columns could reduce *E.coli* about 8 logs for the operating times of 6 and 9 h, respectively. At HRT of 12 h, the *E.coli* breakthrough time occurred after 7 days of operation. The NZVI/GAC could be regenerated and able to inactivate *E.coli* about 6 logs.

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