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Removal of trichloroethylene (TCE) from groundwater by GAC and ZVI

Tie-hong Song[a], Yan-jiao Gao[b,*]

[a]*Key Laboratory of Songliao Aquatic Environment, Ministry of Education, Jilin Architectural and Civil Engineering Institute, 130118 Changchun, China*
[b]*College of Civil Engineering and Architecture, Liaoning University of Technology, 121001 Jinzhou, China Tel. +86 4164198022; email: yanjiaogao@163.com*

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ABSTRACT

Dynamic and static test methods were used to investigate the removal efficiency of trichloroethylene (TCE) from ground water by different media of zero-valent iron (ZVI), two kinds of granular activated carbon (GAC), and a mixture of ZVI and GAC. The test results showed that ZVI, GAC, and the mixture of ZVI and GAC could effectively remove TCE. Under static conditions, the TCE removal rate by ZVI was 68.32%, the TCE removal rate by coconut shell GAC was 55.2%, and the TCE removal rate by ZVI + GAC was 90%. Under dynamic station, the mass ratio of one mixture of ZVI and GAC had the best TCE removal rate of over 85% at a flow rate of 25 ml/min.

Keywords: Trichloroethylene (TCE); Granular activated carbon (GAC); Zero-valent iron (ZVI); Ground water

1. Introduction

Trichloroethylene (TCE) is one of the most abundant groundwater pollutants in industrialized countries all over the world. TCE is very stable, and in some aquifers it has persisted for decades. High levels of TCE have the potential to cause liver damage and malfunctions in the central nervous system, and it is considered likely to be a human carcinogen [1]. Different methods of TCE removal include permeable reactive barriers (PRB), bioremediation, and solvent extraction [2–7]. In drinking water supplies, TCE contamination is primarily removed by sorption on to granular activated carbon (GAC) [8, 9]. However, GAC only transfers TCE from liquid or gas phase to solid phase and does not decompose TCE into a harmless substance. Recent research shows that TCE can, however, be degraded very rapidly by zero-valent iron particles (ZVI) [10]. ZVI can be used to reduce TCE through redox reactions that ZVI reduces TCE to ethylene, a harmless organic matter. Therefore, when GAC + ZVI are placed in water containing TCE, GAC can use its larger specific surface area to absorb TCE for ZVI and the redox reactions rate can be accelerated. This project will investigate the TCE removal efficiency by GAC, ZVI, and GAC + ZVI in static and dynamic conditions and determine the optimum conditions of TCE removal. This GAC + ZVI method for TCE removal can be implemented in municipal systems or used commercially for emergency relief in disaster zones.

*Corresponding author.

2. Materials and methods

2.1. Test equipment

Static tests were conducted using several 250-ml glass volumetric flasks with lids. The media and ground water containing TCE were added into the volumetric flasks which were placed in the oscillating incubator for reaction. The dynamic test equipment were three same folded-plate reactors made of organic glass as shown in Fig. 1. The folded reactor was divided into two layers. The inner layer was a reactive tank including four small tanks and each small tank was provided with three sampling ports. All the sampling ports were hitched with rubber tubes clamped with tongs for convenient collection of water samples at any time. The outer layer was an insulating layer sealed with lid. The size of the reactive tank and the insulating layer was 600 mm × 500 mm × 200 mm (length × height × width) and 700 mm × 500 mm × 300 mm (length × height × width), respectively. The small organic glass baskets loaded on the medium were put into different positions of No.3 organic reactive tank for preventing jam, replacing, and cleaning the medium better. The baskets had two sizes. The big size of baskets were put on the top of the reactor and the small size of baskets were put on the bottom of the reactor for preventing bottom plug. ZVI (0.85 ~ 1.70 mm) and GAC (0.38 ~ 0.85 mm) were used as test media and the particle sizes were selected according to the research results of Aki S. and Matin [11]. The water to be treated contained 100 μg/L of synthetic TCE (with ground water and TCE) and the pH of the solution was adjusted to 5 using a solution of sodium hydroxide and hydrochloric acid. The synthetic TCE solutions were poured into the water tank, sealed, and a constant flow pump was used to control the flow of water to the reactor.

2.2. Test procedure

Both the static and dynamic experiments followed the same reaction conditions that the original pH was 5 and the concentration was 100 μg/L (the TCE solution was prepared according to the national standard method), the swing speed of the oscillating incubator was 200 r/min, and the temperature was 13℃. The insulating layer of the dynamic reactor was controlled at 13℃. Before using, the iron particles were soaked with a 0.2 mol/L hydrochloric acid solution for 10 min and then flushed with distilled water to neutral state.

Under static conditions, the removal effects of TCE by ZVI were studied. 0, 5, 10, 15, and 20 g ZVI were added, respectively, into five 250 ml volumetric flasks filled with 150 ml of TCE solution, and immediately covered with lid seal. Then the flasks were placed into the oscillating incubator for reaction.

Under static conditions, the removal effects of TCE by two kinds of GAC were studied. Twenty grams of nut shell GAC and 20 g of coconut shell GAC were added, respectively, into three 250 ml volumetric flasks filled with 150 ml of TCE solution, and immediately covered with lid seal. Then the flasks were placed into the oscillating incubator for reaction.

Under static conditions, the removal effects of TCE by a different mixture ratio of ZVI and coconut shell GAC were studied. The mass ratio (iron and carbon) of 0.25, 0.33, 0.5, 1, 2, 3, and 4 of the mixture was added, respectively, into eight 250 ml volumetric flasks filled with 150 ml of TCE solution, and immediately covered with lid seal. Then the flasks were placed into the oscillating incubator for reaction.

Under static conditions, the removal effects of TCE by ZVI, GAC, and ZVI + GAC were studied. Twenty grams of ZVI, 20 g of GAC, and 20 g of ZVI + GAC were added, respectively, into three 250 ml volumetric flasks filled with 150 ml TCE solution, and immediately covered with lid seal. Then the flasks were placed into the oscillating incubator for reaction.

Under dynamic conditions of 25, 50, 100, and 200 ml/min flow velocity, the removal effects of TCE by ZVI, GAC, and ZVI + GAC were investigated. Twenty grams ZVI, 20 g GAC, and 20 g ZVI + GAC were wrapped with nylon and put into small baskets, respectively. The small baskets were placed into corresponding No. 3 room of folded-plate reactors according to the different sizes of small baskets. Flow velocity of dynamic reactors was controlled by peristaltic pump.

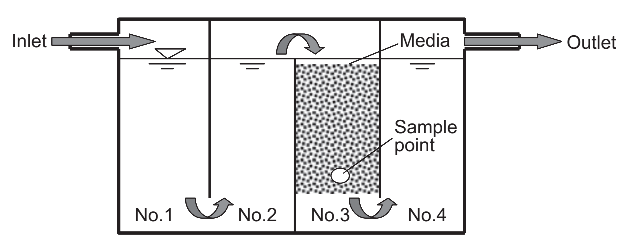

Fig. 1. Dynamic test equipment.

2.3. Analytic methods

TCE was determined by gas chromatography (SHIMADZU GC-14C) with the method of Hexane extraction. The repeated tests proved that hexane extraction method is stable and reliable, and the test error in 24 h is less than 1%. The conditions of gas chromatography are as follows: split injection, injection volume 1 μL, flow rate of carrier gas lml/min, split ratio 35:1, tail gas flow rate 62 ml/min, inlet temperature 210℃, detector temperature 280℃, column temperature 60℃, and 10 min keeping.

3. Results and discussion

3.1. Under static conditions TCE removal effects by ZVI

Fig. 2 shows the TCE removal rate curves for different qualities of iron. From the curve of 0 g ZVI, it is noticed that TCE content does not decrease, except few volatile to Air. With the increase of reaction time, other curves have varying degrees of decline which testifies ZVI could degrade TCE from solution. The removal rate of 20 g curve is big than others, which mentions that removal rate increases with increasing iron mass. When the reaction time is 16 h, TCE degradation rate by 5, 10, 15, and 20 g iron is 45.75, 53.64, 58.63, and 68.32%, respectively. After 16 h of reaction time, the reaction tends to be steady and the degradation rate of iron is reaching a steady state. The TCE removal rate of 20 g ZVI is the biggest which shows that the removal rate of TCE is increasing with the increasing ZVI quality. Due to the redox reaction, TCE was removed quickly. The complete chemical reduction of TCE to ethene can be described with the following equation [11]:

$$3Fe^0 + 3H_2O + C_2HCl_3 \rightarrow 3Fe^{2+} + C_2H_4 + 3OH^- + 3Cl^- \quad (1)$$

3.2. Under static conditions TCE removal effects by two kinds of GAC

Fig. 3 shows the TCE removal rate curves of two kinds of GAC (nut shell GAC and coconut shell GAC). The removal rate of coconut shell GAC on TCE in a short period of time is faster than nut shell GAC.

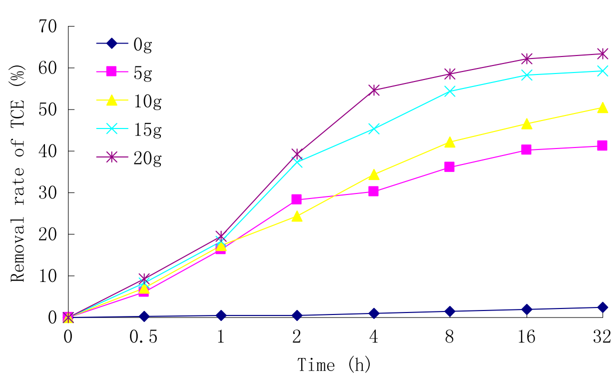

Fig. 2. TCE removal rate of different quality of ZVI.

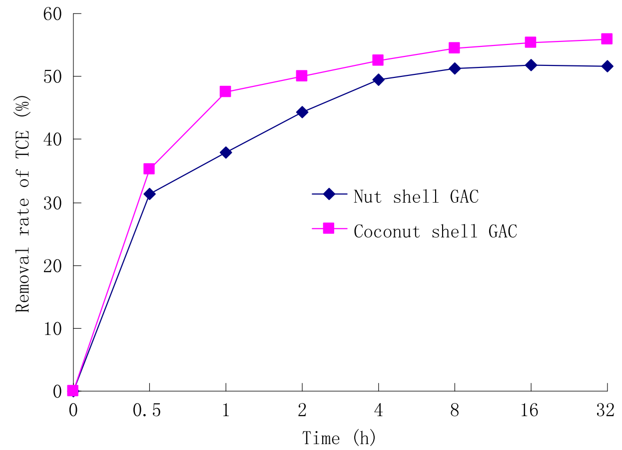

Fig. 3. TCE removal rate of different GAC.

When the reaction time is 8 h, reaction tends to be steady, and the removal rate of coconut shell GAC on TCE is 55.2%, and the coconut GAC is better than nut shell GAC. Coconut shell GAC has more pore structure and the larger specific surface area. It is believed that the pore structure of GAC is more developed that its adsorption capacity is more stronger [12].

3.3. Under static conditions TCE removal effects of different mass ratio of ZVI and coconut shell GAC

Fig. 4 shows the TCE removal rate of different mass ratios of ZVI and coconut shell GAC. Large mass ratio is better than small mass ratio to remove TCE and the mass ratio of 1 of mixture is best for the removal of TCE. The removal rate of TCE by mass ratio 1 of a mixture of ZVI and GAC is 93% higher than the results of single GAC or ZVI. When GAC + ZVI are placed in water including TCE, GAC can use its larger specific surface area to absorb TCE for ZVI and redox reactions rate can be accelerated. Mass ratio 1 of mixture of ZVI and GAC fits the need of reaction speed.

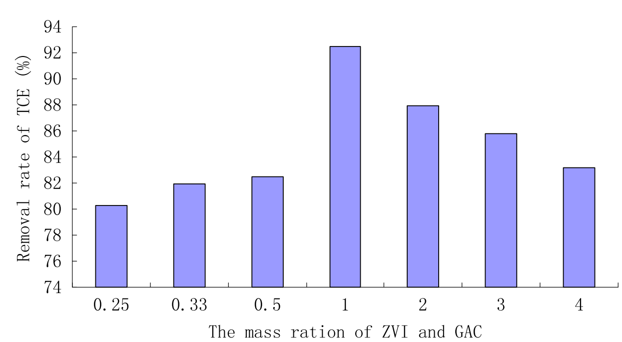

Fig. 4. TCE removal rate of different mass ratio of ZVI and GAC.

3.4. Under static conditions TCE removal effects by ZVI, coconut shell GAC, and the mixture of ZVI and coconut shell GAC

Fig. 5 shows the TCE removal rate by ZVI, coconut shell GAC, and the mixture of coconut shell GAC and ZVI. From Fig. 5, with the increase of reaction time, the removal rate of TCE by the three kinds of medium are all rising. In the first 0.5 h, the TCE removal rate of coconut shell GAC is the best, which is attributed to the strong adsorption. At the reaction time of 4 h, the adsorption of coconut shell GAC on TCE reaches a basic balance and the TCE removal rate maintains stable. At the beginning, TCE removal rate by ZVI is relatively slow, but the removal rate gradually increases. After 8 h, the TCE removal rate by ZVI is higher than by coconut shell GAC, because the reaction of ZVI and TCE is a redox reaction, and the response curve of the redox reaction is different from adsorption curves. In the initial 2 h, removal rate of TCE by the mixture of ZVI and coconut shell GAC is in the middle, but after 2 h, the removal rate is higher than that of ZVI and the coconut shell GAC treatment. A mixture of ZVI and coconut shell GAC plays a complementary advantage on the TCE removal, because after adsorption, coconut shell GAC transfers the mass of ZVI to the reduced TCE, and this accelerates the reaction process.

3.5. Under dynamic conditions TCE removal effects of different velocity by ZVI, coconut shell GAC and the mixture of ZVI and coconut shell GAC

Fig. 6 shows the removal rate of TCE under different velocity by ZVI, coconut shell GAC, and the mixture of ZVI and coconut shell GAC. From Fig. 6, when the flow velocity is 25 ml/min, the three TCE removal effect by their medium are higher than other velocity condition. The flow velocity is the smallest at

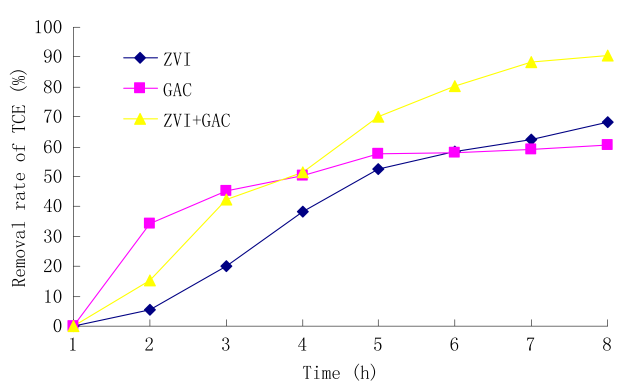

Fig. 5. TCE removal rate of different medium.

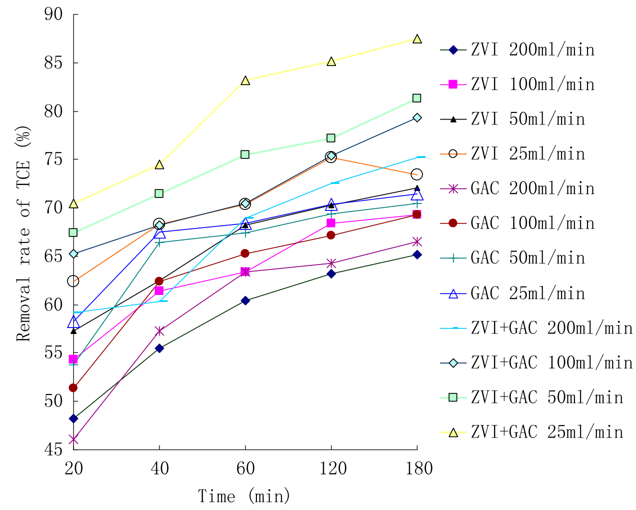

Fig. 6. The removal rate of TCE under different velocity by ZVI, coconut shell GAC and the mixture of ZVI and coconut shell GAC.

25 ml/L and TCE removal rate by ZVI and coconut shell GAC can reach 70%, respectively, and TCE removal rate by the mixture of ZVI and coconut shell GAC is over 85%. The test shows that the better removal efficiency on TCE is acquired under smaller velocity of the water. The three kinds of media under the dynamic conditions and the removal effect of the mixture of ZVI and coconut shell GAC is still the best, which verifies that the mass ratio of one mixture of ZVI and coconut shell GAC is a good medium to treat TCE of groundwater.

4. Conclusions

(1) In static conditions, when the quality of ZVI increase, the removal rate of TCE was greater, and the removal rate of TCE by coconut shell GAC was higher than nut GAC. TCE removal rate by ZVI was 68.32%, TCE removal rate by coconut shell GAC was 55.2% and TCE removal rate by ZVI + GAC was 90%. The TCE removal efficiency of ZVI, GAC, and the mixture of ZVI and coconut shell GAC shows that the mixture of ZVI and coconut shell GAC (mass ratio was 1) was the best choice for TCE removal.

(2) In dynamic conditions, the smaller the velocity of the water, the better removal of TCE was reached by ZVI, GAC, and the mixture of ZVI and coconut shell GAC. When the minimum flow velocity was 25 ml/min, TCE removal rate by ZVI and coconut shell GAC could reach 70%, respectively, and the TCE removal rate by the

mixture of ZVI and coconut shell GAC was over 85% which showed that under dynamic conditions, ZVI and coconut shell GAC (mass ratio was 1) was also the best choice for TCE removal.

References

[1] Y. Bae, J.-W. Park, TCE reduction modeling in soil column: Effect of zero-valent iron, ferrous iron, and iron-reducing bacteria, Desal. Water Treat. 4 (2009) 229–232.

[2] Y.C. Kuo, S.F. Cheng, P.W.G Liu, H.Y. Chiou, C.M. Khao, Application of enhanced bioremediation for TCE-contaminated groundwater: a pilot-scale study, Desal. Water Treat. 41 (2012) 364–371.

[3] Q. Guo, D.W. Blowes, Biogeochemistry of two types of permeable reactive barriers, organic carbon and iron-bearing organic carbon for mine drainage treatment: Column experiments, J. Contam. Hydrol. 107 (2009) 128–139.

[4] R. Thiruvenkatachari, S. Vigneswaran, R. Naidu, Permeable reactive barrier for groundwater remediation, J. Indust. and Eng. Chem. 14 (2008) 145–156.

[5] J. Yang, Y. Guo, D. Xu, A controllable Fe0–C permeable reactive barrier for 1,4-dichlorobenzene dechlorination, Chem. Eng. J. 203 (2012) 166–173.

[6] J. Yang, L. Cao, R. Guo, Permeable reactive barrier of surface hydrophobic granular activated carbon coupled with elemental iron for the removal of 2,4-dichlorophenol in water, J. Hazard. Mat. 184 (2010) 782–787.

[7] A.S. Ruhl, N. Ünal, M. Jekel, Combination of Fe(0) with additional reactive materials in fixed bed reactors for TCE removal, Chem. Eng. J. 222 (2013) 180–185.

[8] Y. Nakano, L.Q. Hua, W. Nishijima, Biodegradation of trichloroethylene (TCE) adsorbed on granular activated carbon (GAC), Water Res. 34 (2000) 4139–4142.

[9] Y. Miyake, A. Sakoda, H. Yamanashi, H. Kaneda, M. Suzukid, Activated carbon adsorption of trichloroethylene (TCE) vapor stripped from TCE-contaminated water, Water Res. 37 (2003) 1852–1858.

[10] S.-F. Cheng, S.-C. Wu, The enhancement methods for the degradation of TCE by zero-valent metals, Chemosphere 41 (2000) 1263–1270.

[11] A.S. Ruhl, M. Jekel, Impacts of Fe(0) grain sizes and grain size distributions in permeable reactive barriers, Chem. Eng. J. 213 (2012) 245–250.

[12] J.E. Kilduff, T. Karanfil, Trichloroethylene adsorption by activated carbon preloaded with humic substances: Effects of solution chemistry, Water Res. 36 (2002) 1685–1698.