Factors affecting TCE reduction by ZVI

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Abstract. Zero valent iron (Fe(0)) was used to reduce trichloroethylene (TCE). Some influence factors of TCE removal including Fe(0) purity, Fe(0) size, Fe(0) quality, solution pH, reaction temperature, oscillation rate and initial concentration of TCE were investigated in the batch experiments. The optimum experimental conditions were determined as: Fe(0) purity of 92%, Fe(0) size of 30 mesh, Fe(0) quality of 30mg/L, solution initial pH of 6.0 and reaction temperature of 25°C. Oscillation rate and initial concentration of TCE had little effects on TCE removal. The 5-day TCE removal rate was 90.4% under the optimum conditions.

1. Introduction

The industrial solvent trichloroethylene (TCE) is among the most widespread chlorinated compounds found in groundwater contamination^{[1].} High levels of TCE is considered a likely human carcinogen^[2]. The technology chosen for remediation is typically pump-and-treat. Although pump-and-treat can be effective in controlling plume migration, in-situ treatment approaches are required to better remediate and reduce risk at chlorinated solvent contamination sites. The typical technology used for TCE removal is in-situ permeable reactive walls. The main advantage of a reactive barrier is the passive nature of the treatment. Reactive barriers containing iron metals are currently being developed for in situ treatment technology ^[3]. In 1981, Sweeny utilized iron powders to degrade various hydrocarbons, such as trichloroethylene^[4].In 1994 Gillham and Matheson used (Fe0) for treating contaminated groundwater in-situ, demonstrating the identification of (Fe0) as a remediation constituent ^[5]. A use of (Fe0) as reactive medium for TCE treatment is one of the most promising techniques because the iron metal is of low-cost, is easy-to-obtain, and has good effectiveness and ability of degrading contaminants. In addition, iron waste particles from industrial filings can be used as a zero-valent iron. Although significant progress has been made, much need to be done for studying various mechanisms of TCE removal by (Fe0). In this paper some batch tests were performed to examine the application of (Fe0) for TCE removal. The optimum parameters were indentified.

2. Materials and methods

The Fe(0) filings (97% of purity, 30 mesh; 85% of purity, 30 mesh; 92% of purity, 30 and 50 mesh) were obtained from iron processing factory. Trichloroethylene (C_2HCl_3), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from chemical reagent store. All chemicals used were of analytical reagent grade.

Batch experiments were performed using 300-mL glass conical flasks containing a certain quality of Fe(0) and a certain concentration of TCE solution. The solution pH was adjusted by the addition of sodium hydroxide and hydrochloric acid. The flasks were sealed with rubber plugs and aluminum covers. The solutions were shaken in oscillation boxes at a certain rotation speed and temperature the experiment required. Every five flasks with the same reaction conditions were divided into a group, and one flask was taken out from box every one day to be measured concentration of trichloroethylene using gas chromatograph. The pH was measured by a pH meter.

3. Results and discussion

3.1 Effect of Fe(0) purity

Figure 1 shows the relationship between reaction time and TCE removal rate under different solution pH. With the increase of reaction time removal rate of TCE all increased by different purity of Fe(0). After 5 day, TCE removal rate of Fe(0) purity of 97%, 92% and 85% was 82.4%, 73.7% and 65.4% respectively. TCE removal rate of Fe(0) purity of 97% was the highest, reached 85.2%. The higher purity but higher were removal rate. High purity of Fe(0) could offer more effective reaction medium and more closely contact with the TCE solution. Therefore, reactions between Fe(0) and TCE were more strongly and the better effects on removing TCE were acquired The higher the Fe(0) purity was, the more expensive the Fe(0) was. Fe(0) purity of 92% was the best for this experiment.

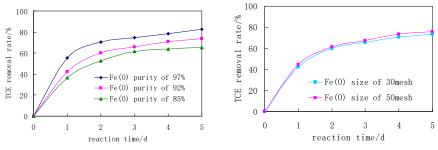


Fig. 1 Fe(0) purity and TCE removal

Fig. 2 Fe(0) size and TCE removal

3.2 Effect of Fe(0) size

Figure 2 shows the relationship between reaction time and TCE removal rate under different size of Fe(0). After 5 day, TCE removal rate of Fe(0) size of 50mesh was 75.8% higher than that of size of 50 mesh 2.1 percentage points. The bigger the Fe(0) particle size was, the higher the TCE removal rate was. The reductive dechlorination reaction of chlorinated hydrocarbons in water of iron system was typical of the solid-liquid mass transfer reaction, the reaction was carried out mainly depending on the iron surface.Big Mesh of Fe(0) with small particle size and large specific surface area could effectively collide with TCE.

3.3 Effect of Fe(0) quality

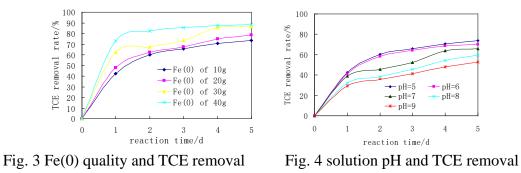


Figure 3 shows the relationship between reaction time and TCE removal rate under different quality of Fe(0). With the increase of reaction time removal rate of TCE all increased under different quality of Fe(0). After 5 day, TCE removal rate of Fe(0) quality of 10g,20g,30g and 40g was 73.7%,78.4%,86.4% and 88.2% respectively. TCE removal rate of Fe(0) quality of 40g was the highest, reached 88.2%. The higher quality but higher was removal rate. More dosage of Fe(0) had more surface area in reductive dechlorination reactions of iron and had more chances to reduce TCE. In this experiment, the removal rate of TCE by 40g Fe(0) was higher than that of TCE by 30g Fe(0) only 1.6%. When the Fe(0) quality increased to critical value of 30g, the reaction sites were so excessive that brought Fe(0) into good contact with the TCE.

3.4 Effect of solution pH

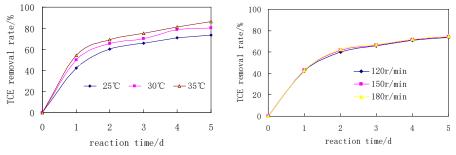
Figure 4 shows the relationship between reaction time and TCE removal rate under different solution pH. TCE removal rate of solution pH 5 was the highest, reached 73.7%. In this

experimental when pH was $5 \sim 6$,TCE removal rate could reach 70% above which illustrated the acidic environment was favorable to TCE removal. Reducing dechlorination of chlorinated hydrocarbons by Fe(0) was the process of oxidized dissolution of metal ions. The reaction equation was following.

$Fe^{0}+RCl+H^{+}\rightarrow Fe^{2+}+RH+Cl^{-}$

In this dechlorination reaction, if hydrogen ion concentration increased acidic conditions caused the increase of reaction rate. With hydrogen ion concentration decreased alkaline conditions caused the surface of Fe(0) forming iron deposit such as Ferrous hydroxide(Fe(OH)₂), ferric hydroxide (Fe(OH)₃)and iron carbonate (FeCO₃).These deposit attached on the surface of Fe(0) particles formed a protective layer and hindered the further reaction of Fe(0) with TCE. Therefore the pH value increased, the removal effect declined.

3.5 Effect of solution reaction temperature



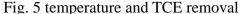


Fig. 6 oscillation rate and TCE removal

(1)

Figure 5 shows the relationship between reaction time and TCE removal rate under different reaction temperature. With the increase of reaction time removal rate of TCE all increased under different reaction temperature. After 5 day, TCE removal rate of 25°C,30°C and 35°Cwas 73.7%,

80.3%, 86.2% respectively. TCE removal rate of $35^{\circ}C$ was the highest, reached 86.2%. The higher temperature but higher was removal rate. With temperature increasing the mass transfer rate between the reaction media accelerated and chemical reaction rate accelerated. Considering the general laboratory room temperature was $25^{\circ}C$ optimal temperature of this experiment was determines at $25^{\circ}C$.

3.6 Effect of oscillation rate

Figure 6 shows the relationship between reaction time and TCE removal rate under different oscillation rate. With the increase of reaction time removal rate of TCE all increased under different oscillation rate. After 5 day, TCE removal rate of oscillation rate 120r/min, 150r/min and 180r/min was 73.7%,74% and 74.5% respectively. With the increase of oscillation rate, the removal rate of TCE increased slightly, which had little effect on the experiment. Fe(0) had characteristics of very small size and large surface area, and can be evenly distributed in the solution on the condition of 120r/min. Oscillation rate of 120r/min was the best for this experiment.

3.7 Effect of initial TCE concentration

Figure 7 shows the relationship between reaction time and TCE removal rate under different initial TCE concentration. With the increase of reaction time removal rate of TCE all increased under different initial TCE concentration. After 5 day, TCE removal rate of initial TCE concentration 150mg/L was the highest, reached77.6%. With the increase of initial TCE concentration, the removal rate of TCE increased slightly, which had little effect on the experiment. Dechlorination reaction of Granular iron and chlorinated hydrocarbons dechlorination was the surface reaction which includes mass transfer, adsorption, electron transfer and desorption processes. These reaction processed was not be changed by increase of initial concentration of TCE.

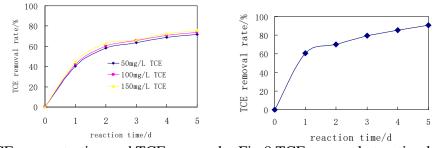


Fig.7 TCE concentration and TCE removal F

Fig.8 TCE removal at optimal conditions

3.8 The optimum conditions of the experiments

The optimum conditions for the batch experiments were as follow: Fe(0) purity of 92%, Fe(0)size of 30 mesh, Fe(0) quality of 30mg/L, pH=6.0, temperature of 25 citeration rate of 120r/min.The experimental results under optimum conditions is shown in Fig.8. The 5- day TCE removal rate of was 90.4%, which testified that using Fe(0) to dispose TCE was feasible, and could achieve good results.

4. Conclusions

The main influence factors of Fe(0) reduction of TCE were Fe(0) purity, Fe(0) size, ZVI Fe(0) quality, solution pH, reaction temperature. Oscillation rate and initial concentration of TCE had little effects on TCE removal. The optimum conditions for the batch experiments were as follow: Fe(0) purity of 92%, Fe(0)size of 30 mesh, Fe(0) quality of 30mg/L, pH of 6.0, temperature of 25 °C and oscillation rate of 120r/min. The 5-day TCE removal rate of was 90.4%, which testified that using Fe(0) to dispose TCE was feasible under the optimum conditions.

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