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The enhancement methods for the degradation of TCE by zero-valent metals

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Abstract

Batch tests were performed to compare the degradation rates of TCE on Fe^0 and Zn^0. Our results indicated that the degrading capability of Zn^0 to TCE was nearly 10 times higher than that of Fe^0. On the other hand, the degradation rates of Fe^0 or Zn^0 in conjunction with other metals for reduction of TCE was investigated. The selected metals were nickel (Ni^0) and palladium (Pd^0) both of which have a strong enhancement effect. The reduction rates of Zn^0/Pd^0 and Zn^0/Ni^0 for TCE were the fastest. Fe^0 that had lost its surface activity could be activated again by the addition of Pd^0 or Ni^0.

Keywords: Chlorinated organic compound; Zero-valent metal; Bimetallics; Chloroethylene

1. Introduction

In Taiwan, chlorinated organic compounds, such as PCE, TCE, CCl_4, $CHCl_3$ and CH_2Cl_2, are widely used in industry. They are mainly used as solvents in degreasing, washing, extraction, foaming, spraying and manufacturing, etc. In recent years, the underground water of many sites in Taiwan has been heavily contaminated by chlorinated organic compounds. For example, the RCA site in Taoyuan is contaminated by PCE and TCE, the Philips site in Hsinchu is contaminated by PCE, and the An-Shuenn site in Tainan is contaminated by pentachlorophenol (PCP). There is, therefore, considerable interest in the remediation technique of sites contaminated by chlorinated organic compounds. The reduction power of zero-valent iron to chlorinated organic compounds has been a focus of investigation in recent years among the techniques that are used in the remediation of sites contaminated by chlorinated organic compounds (Matheson and Tratnyek, 1994; Gillham and Stephanie, 1994; Smyth et al., 1995; Orth and Gillham, 1996; Agrawal and Tratnyek, 1996; Weber, 1996; O'Hannesin and Gillham, 1998).

The research on the zero-valent iron technique in recent years has shown that zero-valent iron has many drawbacks in practical applications. Firstly, after a short period of reactions zero-valent iron is liable to form an oxide film on the surface, which subsequently reduces the reaction activity (Wang and Zhang, 1997). Secondly, the retention of the surface activity of zero-valent iron is difficult to maintain. Once Fe^0 is in contact with air, even under proper storage, its reactivity towards chlorinated organic compounds is inevitably reduced (Cheng and Wu, 1998). Thirdly, there is considerable variation in the reactivity towards chlorinated organic compounds of Fe^0 of different origins. The reaction rates can differ by up to three orders of magnitude (Su and Puls, 1999). Matheson and Tratnyek (1994) proposed that if Fe^0 received an HCl acid washing process prior to its use, this could increase the surface reaction activity. However, according to the research of Su and Puls (1999) on the effects of the acid prewashing and our previous research results, the acid-washing process not only tends

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to cause many fine particles of Fe^0 powder to be lost, but also causes the Fe^0 to have a faster oxidation rate in the processes of washing and drying. The above factors cause the zero-valent iron technique to be largely restricted in its application to in situ remediation.

In recent years, a great deal of research has concentrated on the improvement of the zero-valent iron technique. This research has included the use of ultrasonic oscillation to remove the oxide film on the Fe^0 surface (Ruiz et al., 1998), the use of external voltage to maintain the surface activity of Fe^0 (Cheng and Wu, 1998), the use of the bimetallics technique (Appleton, 1996; Siantar et al., 1996), the use of palladized iron (Muftikian et al., 1995) and the use of synthesized nanoscale palladized iron (Wang and Zhang, 1997), etc.

Matheson and Tratnyek (1994) proposed three pathways for the reduction dechlorination reactions of Fe^0 to chlorinated organic compounds: (1) to direct electrons transfer from iron metal at the metal surface; (2) to catalyze hydrogenolysis by the H_2 that is formed by reduction of H_2O during anaerobic corrosion; (3) to reduction by the Fe^{+2}, which results from corrosion of the metal. From the viewpoint of electrochemical theory, the first pathway means that a metal with a stronger reducing power is advantageous to the dechlorination reactions of the chlorinated organic compounds. According to electrochemical corrosion theory, in an oxygen-free $Zn–H_2O$ or $Fe–H_2O$ system containing H^+, the surface of the metal (such as Zn^0) will generate the following reaction:

$$Zn^0 + 2H^+ \rightarrow Zn^{+2} + H_2 \uparrow$$

According to electrolysis chemical theory, the reduction power of a cathode in an electrolysis system is mainly derived from the function of hydrogen atoms. Once the hydrogen atoms, through the reaction of $H + H \rightarrow H_2 \uparrow$, combine together and form a hydrogen gas in a bubble form, they no longer participate in the reduction reaction. Furthermore, the accumulation of H_2 gas bubbles on the metal surface will hinder the progress of the reaction (Matheson and Tratnyek, 1994; Ballapragada et al., 1997). Due to the different characteristics of metals, the formation rate of hydrogen gas on the surface of each metal varies; this is called the hydrogen overvoltage of the metal. The second pathway means that a metal with a higher hydrogen overvoltage is advantageous to the reduction of the chlorinated organic compounds. The reduction potential of Zn^0 is stronger than that of Fe^0, and Zn^0 is a metal with a high hydrogen overvoltage, second only to that of mercury. Hence, from the above two points of view, Zn^0 should be the better selection in degradation of chlorinated organic compounds.

Recent studies pointed out that where zero-valent iron was used in conjunction with another metal for the degradation of chlorinated organic compounds, the second metal primarily has the following functions: (1) as a catalyst (Wang and Zhang, 1997), (2) preventing the formation of the oxide film on the surface of Fe^0 (Wang and Zhang, 1997), and (3) inducing Fe^0 to release electrons at a faster rate due to the difference of electric potentials between Fe^0 and the second metal to reduce the chlorinated organic compounds (Gavaskar et al., 1998). Appleton (1996) proposed that nickel has the effect of accelerating the degradation of TCE by Fe^0. Wang and Zhang (1997) synthesized nanoscale palladized iron to degradation of TCE and PCBs. Muftikian et al. (1995) used palladized iron to reduction of CCl_4 and TCE. All these studies showed a significant promotional effect.

The objectives of our study were to: (1) compare the degradation rates of different Fe^0 and Zn^0 to TCE in order to further evaluate the feasibility of using Zn^0 to replace Fe^0; (2) investigate the promotional effects of a combination Fe^0 or Zn^0 with a second metal Ni^0 or Pd^0 for degradation of TCE.

2. Experimental

2.1. Chemicals and materials

Chlorinated compound, trichloroethylene (TCE) was obtained from Merck (99.5+%, GR grade). TCE stock solution was prepared by weighting 0.0695 g of pure TCE solvent to dissolve in 100 ml of methanol. Methanol was obtained from Acros (99.8+%, PA grade). TCE aqueous solutions were made by diluting the stock solution with Milli-Q water. The Milli-Q water was sparged with Argon gas.

Two kinds of iron were used: one was obtained from Riedel-deHaen, powdered Fe^0 (99+%, RG, made by reduction), the other was obtained from Aldrich, granular Fe^0 (10–40 mesh, 99.999%, stored under nitrogen). Zincs were obtained from three different companies: Aldrich granular Zn^0 ($-10 + 50$ mesh, 99.8%, ACS reagent), Acros granular Zn^0 (30 mesh, 99.7%, PA grade), and Hanawa powdered Zn^0 (90.0%, guaranteed reagent). Nickel was obtained from Aldrich powdered Ni^0 (-100 mesh, 99.99%). Palladium was obtained from Acros powdered Pd^0 (99.99%, ACS reagent).

2.2. Experimental methods

Batch tests were conducted to investigate the degradation of TCE. TCE aqueous solutions were prepared by diluting the stock solution with Ar-sparged Milli-Q water to 3 mg TCE l^{-1}.

2.3. Single metal tests

Three grams of each metal (Fe^0, Zn^0, Ni^0) were added to each brown serum vial (with measured internal volumes of 15 ml). Each vial was filled with TCE aqueous solution with no headspace, and was then sealed immediately with aluminum crimp caps with Teflon faced septum. For each test, 10 vials containing TCE and metal and 10 controls containing TCE only were prepared for different reaction times. All the vials were put on a shaker (oscillated frequency 130 rpm, at 25°C). At each sampling time, 5 ml of subsamples were transferred via a syringe from the sample to the other clean vials, and then were sealed immediately with aluminum crimp caps with Teflon faced septum. Before analysis, all the subsamples were stored in the oven (set at 25°C) for more than 0.5 h to let the TCE reach the equilibrium between the headspace and the aqueous phase.

2.4. Bimetallics tests

For the combination-with-palladium tests, 50 mg of palladium and 3 g of tested metal were added to each vial. For the combination with nickel tests, 3 g of nickel and 3 g of tested metal were added to each vial. The remaining steps were the same as for the single metal tests.

2.5. Analytical methods

The concentrations of TCE and its chlorinated products were determined by using the gas chromatography headspace equilibration method. For each sample, 5 μl of the headspace gas was taken by using a glass gas syringe, and then was injected into the chromatograph.

Analyses for TCE and its chlorinated products were conducted using a 5890II Hewlett Packard gas chromatograph equipped with a 30 m × 0.53 mm (ID) × 3.0 μm (thickness), DB624 analytical column (J & W) and an electron capture detector (ECD). The temperature was set as follows: oven temperature: 60°C, injection port temperature: 220°C, detector temperature: 250°C. Nitrogen was used as the carrier gas at a flow rate of about 4.5 ml/min. The method detection limit (MDL) for TCE was 0.005 mg/l.

3. Results and discussion

3.1. The effects of Fe^0 characteristics

Many research results lead to an unanimous conclusion that the degradation rate of Fe^0 to the chlorinated organic compounds is influenced by the magnitude of the "clean specific surface area" of zero-valent iron (Matheson and Tratnyek, 1994; Weber, 1996). In the past, most studies emphasized the study of the effect of the specific surface area of Fe^0. However, according to this research and recent research results (Cheng and Wu, 1998; Su and Puls, 1999), the influence of "cleanness" on the reaction rate is much greater than the influence of the magnitude of the specific surface area of Fe^0. The source, quality, purity and freshness of Fe^0 have a significant influence on the reaction rate. This research used two types of Fe^0 of different sources, different particle sizes, and different unsealed time. One was a granular iron of 10–40 mesh, produced by Aldrich, with a purity of 99.999%, stored in N_2, and never unsealed prior to its use. The other was a powdered iron, produced by Riedel-deHaen, with a purity of 99%, made by reduction, and unsealed for a few months under proper sealing and storage and showing no oxidation. The research results showed that the Riedel-deHaen powdered Fe^0 has almost no promotional effect on the degradation of TCE after nearly 250 h of reaction, as shown in Fig. 1. On the other hand, the Aldrich granular Fe^0 has a significant effect. Under the system used in our research, the degradation reaction of TCE indicated a half-life of 239 h, about 10 days.

Although the magnitude of the specific surface area of Fe^0 is proportional to the degradation rate of TCE, the purity and the freshness of Fe^0 affect whether or not the degradation of TCE proceeds. In our past study, the Riedel-deHaen powdered Fe^0 that was used in this research had been used in experiments on the reduction of CCl_4 and $CHCl_3$ (Cheng and Wu, 1998). During the initial stage of unsealing, it has a conspicuous promotional effect on the degradation of CCl_4 and $CHCl_3$. Meanwhile, the powdered Fe^0 (325 mesh, purity 97%, hydrogen reduced, Cat. No. 20930-9) was obtained from Aldrich was used in the same tests; after more than 100 h of test, there were no indication of any promotional

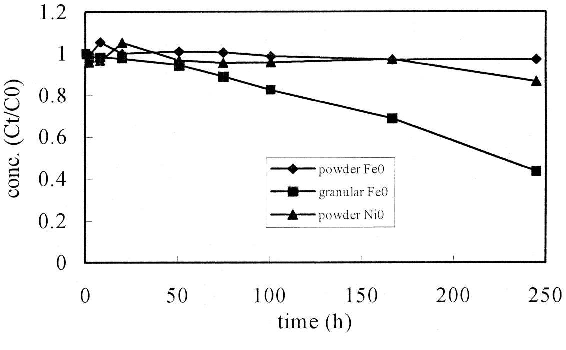

Fig. 1. TCE degradation by using Fe^0 and Ni^0. Conditions: batch tests were performed by using 3 g of Fe^0 or Ni^0 in serum vials (15 ml by volume) in contact with 3 mg TCE l^{-1} solution at 25°C, and mixed with the shaker at 130 rpm.

effect by the Aldrich Fe^0 on the degradation of CCl_4. Su and Puls (1999) also used the same Fe^0 in the degradation tests of TCE. Their results indicated that the reaction rate thereof can differ from that of Fe^0 from other manufacturers by up to three orders of magnitude.

Matheson and Tratnyek (1994) proposed that subjecting Fe^0 to an acid washing of HCl aqueous prior to reaction can remove the oxide film on the surface of iron, thereby increasing the available reactive sites and increasing the rate of the degradation. However, our research indicated that iron washed by aqueous HCl was oxidized into brown oxide at a high speed upon coming into contact with air during the washing, rinsing and drying processes. The acid washing of aqueous HCl in this way not only causes many fine Fe^0 particles to be lost, but also accelerated the oxidation rate of Fe^0. The research on the HCl pretreatment effects done by Su and Puls (1999) also indicated that the acid pretreatment processes may have generated more non-reactive sites relative to the reactive sites, and caused a decrease in the reaction rate constant. Therefore, acid prewashing may not be an effective and convenient method for improving the drawbacks of Fe^0 unless the contact of iron surfaces with air can be completely avoided.

3.2. TCE degradation by Zn^0

With electrochemical theory, not only can the degradation mechanism proposed by Matheson and Tratnyek be explained, but also Zn^0 can be considered to be the best metal in reduction of chlorinated organic compounds. For the first pathway in which the metal is directly used for reduction of the chlorinated organic compounds (Matheson and Tratnyek, 1994; Vogel et al., 1987; Criddle and McCarty, 1991; Gold et al., 1997; Roberts et al., 1996), the standard reduction potential of iron is −0.44 V, and the standard reduction potential of zinc is −0.763 V. Conspicuously, zinc more easily releases an electron to reduce the chlorinated organic compounds than iron does. The second pathway can be explained in greater detail by using the electrochemical theory. Metals with a higher hydrogen voltage are less liable to form hydrogen gas in the system. Therefore, most hydrogen exists in the atomic state, thereby generating a strong reduction potential. In the second pathway, H_2 designates hydrogen in its atomic state, and a metal with a high hydrogen overvoltage shall be the best selection of a catalyst. Zn^0 has a hydrogen overvoltage of 0.7 V, which is a metal with the second highest hydrogen overvoltage, second only to mercury. For the above two reaction pathways, Zn^0 not only can be used as a strong reducing agent, but also as a good catalyst.

This research used Zn^0 from different sources, with different particle sizes and different purities, to carry out the degradation tests on TCE, in order to study the feasibility of using Zn^0 for remediation of sites contaminated by chlorinated organic compounds. The research results indicated that the degradation reaction of Zn^0 to TCE approximates to a first-order degradation reaction model ($R^2 > 0.99$). The reaction rate thereof can be shown by the following equation:

$$\frac{C_t}{C_0} = e^{-kt}, \tag{1}$$

where C_0 is the initial TCE concentration (mg/l), C_t the TCE concentration (mg/l) at a reaction time t (h), and k is the degradation rate constant (h^{-1}). The research results are shown in Fig. 2. The Hanawa powdered Zn^0 has a degradation rate constant, k, of 0.0278 (h^{-1}) and a half-life, $t_{1/2}$, of 26.8 h. The Aldrich granular Zn^0 has a degradation rate constant, k, of 0.013 (h^{-1}) and a half-life of 56.8 h. The Acros granular Zn^0 forms a degradation reaction to TCE less conspicuous than that of the previous two Zn^0. Among the three kinds of Zn^0, the Aldrich granular Zn^0 reagent has been unsealed for more than one year, and yet the degradation rate thereof to TCE was quite fast in comparison with other Zn^0. Therefore, the activity of Zn^0 lasted longer and the decreasing rate of the surface activity was slower than that of iron. In other words, the storage method of Zn^0 is easier than Fe^0 when used in a remediation technique. Table 1 lists the half-lives for TCE degradation by Fe^0, Zn^0, Ni^0 and bimetallics.

In the degradation tests of Zn^0 to TCE, this research also investigated the influence of the amount of Zn^0 added on the reaction rate. Three grams and 5 g of Aldrich granular Zn^0, respectively, were separately added into 15 ml of aqueous TCE. The results indicated that the run with 3 g of Zn^0 had a degradation rate constant, k, of 0.013 (h^{-1}) and a half-life of 56.8 h; while the run with 5 g of Zn^0 had a degradation rate constant, k, of 0.0255 (h^{-1}) and a half-life of 35.7 h. The rela-

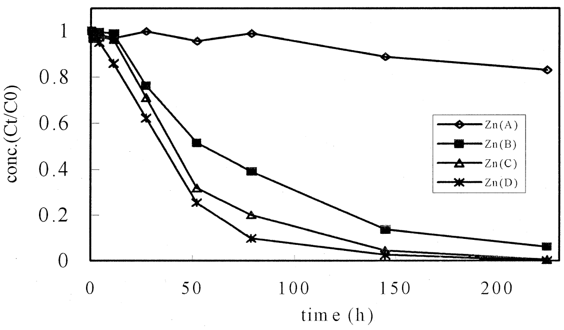

Fig. 2. TCE degradation by using Zn^0. Conditions: batch tests were performed by using different mass and sources of Zn^0 in serum vials (15 ml by volume) in contact with 3 mg TCE l^{-1} solution at 25°C, 130 rpm. Curve Zn(A): Acros, granular, 3 g. Curve Zn(B) and Zn(C): Aldrich, granular. Zn(B): 3 g; Zn(C): 5 g. Curve Zn(D): Hanawa, powdered, 3 g.

Table 1
The half-lives ($t_{1/2}$, for 3 mg TCE l^{-1}, 15 ml) for TCE degradation by Fe^0, Zn^0, Ni^0 and bimetallics

Materials	$t_{1/2}$ (h)
Riedel powdered Fe^0 (3 g)	2589
Aldrich granular Fe^0 (3 g)	239
Hanawa powdered Zn^0 (3 g)	26.8
Acros granular Zn^0 (3 g)	716
Aldrich granular Zn^0 (3 g)	56.8
Aldrich granular Zn^0 (5 g)	35.7
Aldrich powdered Ni^0 (3 g)	1226
Riedel powdered Fe^0 (3 g)/Aldrich powdered Ni^0 (3 g)	14.3
Aldrich granular Fe^0 (3 g)/Aldrich powdered Ni^0 (3 g)	3.9–5.0
Riedel powdered Fe^0 (3 g)/Acros powdered Pd^0 (50 mg)	32.8
Aldrich granular Fe^0 (3 g)/Acros powdered Pd^0 (50 mg)	1.3
Riedel powdered Fe^0 (3 g)/Aldrich granular Zn^0 (3 g)	84.1
Hanawa powdered Zn^0 (3 g)/Aldrich powdered Ni^0 (3 g)	0.86
Aldrich granular Zn^0 (3 g)/Aldrich powdered Ni^0 (3 g)	1.69
Acros granular Zn^0 (3 g)/Aldrich powdered Ni^0 (3 g)	0.98
Acros granular Zn^0 (3 g)/Acros powdered Pd^0 (50 mg)	0.46

tionship between the degradation rate of TCE and the amount of addition of Zn^0, within the scope of this study, seemed to be in a proportional relationship.

The comparison results in the system of this research indicated that the degrading rate of Zn^0 to TCE was much faster than that of Fe^0 under the same reaction conditions. There can be a difference of nearly 10 times between TCE half-lives. The research results also indicated that the method of using Zn^0 to decompose TCE was quite an effective method. In the future, studies can be carried out to further investigate the degradation process of Zn^0 on chlorinated organic compounds in order to evaluate the feasibility of using it to replace Fe^0.

4. The promotional effects of bimetallics on TCE degradation

4.1. The promotional effects of Pd^0 and Ni^0 on degradation of TCE by Fe^0

This research first investigated the effects of combining Fe^0 with a second metal of Ni^0 or Pd^0 on the reaction rate of decomposing TCE. The research results indicated that Ni^0 and Pd^0 all have a rather strong promotional effect on the degradation reaction of TCE by Fe^0. The degradation reaction of TCE by using Riedel-deHaen powdered iron singly was not very significant. However, the TCE conspicuously decomposed in a linear attenuation model when Aldrich powdered Ni^0 or Acros powdered Pd^0 was added to the reaction system. The degradation rate of TCE by combining Riedel-deHaen powdered Fe^0 with 3 g of Ni^0 had a half-life of 14.3 h; while by combining with 50 mg of Pd^0 the half-life was 32.8 h. The half-life of TCE was 239 h for Aldrich granular Fe^0 alone; it was 3.9–5 h for combination of the Aldrich granular Fe^0 with Ni^0, and 1.3 h for the combination of the Aldrich granular Fe^0 with Pd^0. Figs. 3 and 4 show the variation of TCE concentration to the reaction time in a degradation reaction system of TCE where Fe^0 in conjunction with Ni^0 or Pd^0 was used. The degradation process of granular iron in conjunction with Ni^0 approximates a linear slow attenuation model at the initial stage. After a short period of reaction, however, the degradation reaction model

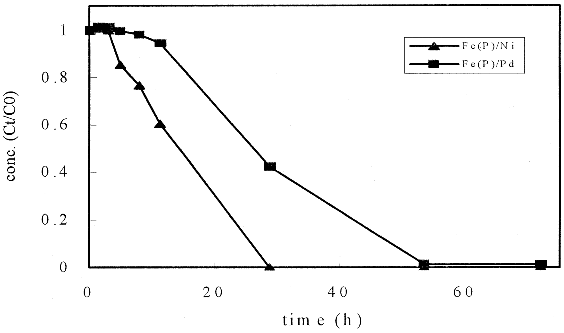

Fig. 3. TCE degradation by using powdered Fe^0 combination with Pd^0 and Ni^0. Conditions: batch tests were performed in serum vials (15 ml by volume) in contact with 3 mg TCE l^{-1} at 25°C, 130 rpm. Curve Fe(P)/Pd used 3 g of Fe^0 and 50 mg of Pd^0. Curve Fe(P)/Ni used 3 g of Fe^0 and 3 g of Ni^0.

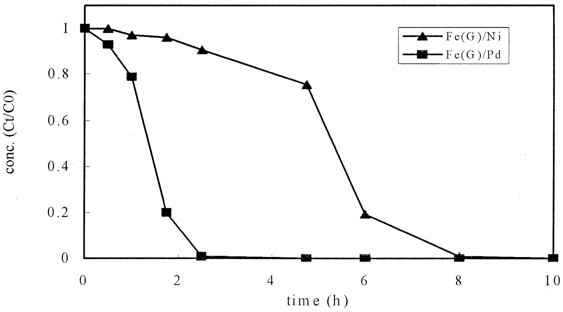

Fig. 4. TCE degradation by using granular Fe^0 combination with Pd^0 and Ni^0. Conditions: batch tests were performed in serum vials (15 ml by volume) in contact with 3 mg TCE l^{-1} at 25°C, 130 rpm. Curve Fe(G)/Pd used 3 g of Fe^0 and 50 mg of Pd^0. Curve Fe(G)/Ni used 3 g of Fe^0 and 3 g of Ni^0.

approximates a logarithmic rapid attenuation model. It can be assumed that the reaction rate at the initial stage was predominantly controlled by the transport mechanism (Burris et al., 1995; Scherer et al., 1997).

The addition of Pd^0 or Ni^0 does indeed have a significant promotional effect on the degradation of TCE by Fe^0. In particular, the addition of Pd^0 or Ni^0 has a reviving effect on iron that has lost the surface activities thereof.

4.2. The promotional effects of Pd^0 and Ni^0 on degradation of TCE by Zn^0

This research also tried to combine Zn^0 with a second metal of Ni^0 or Pd^0 in the degradation reaction of TCE in order to understand the promotional effect of Ni^0 or Pd^0 on the degradation of TCE by Zn^0. The research results indicated that the addition of Ni^0 or Pd^0 rapidly increased the degradation reaction rate of TCE by Zn^0. When Ni^0 was added, the half-life of the reaction system could be reduced to about 3% of that of the reaction system where Zn^0 was used singly. The half-life by the Hanawa powdered Zn^0 was 26.8 h, which fell to 0.86 h after combining with Ni^0. The half-life by the Aldrich granular Zn^0 was 56.8 h, which fell to 1.69 h after combining with Ni^0. The effects were even more significant for the Acros granular Zn^0 that had a weaker reactivity. When the Acros Zn^0 was used singly, the non-decomposed TCE concentration remained larger than 80% after a reaction time of 237 h. The half-life fell to less than 1 h when Ni^0 was added. The reaction rate increased even further when Pd^0 was added. The half-life of a degradation reaction where the Aldrich granular Zn^0 was used in conjunction with Pd^0 was 0.46 h. Fig. 5 shows the degradation reaction curve of TCE when Zn^0 was used in conjunction with Ni^0, and Fig. 6 for Pd^0. Fig. 5 clearly indicated that the degradation reaction of TCE exhibited a stagnation phenomenon after the reaction at the initial stage of the reaction, then rapidly attenuated exponentially. It was inferred that the reaction rate was predominantly controlled by the transport mechanism during the initial stage of the reaction (Burris et al., 1995; Scherer et al., 1997).

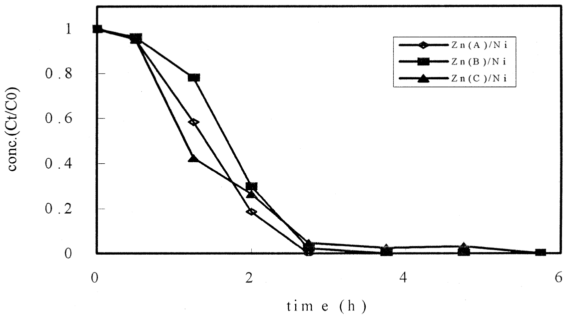

Fig. 5. TCE degradation by using different Zn^0 combination with Ni^0. Conditions: batch tests were performed by using 3 g of Zn^0 and 3 g of Ni^0 in serum vials (15 ml by volume) in contact with 3 mg TCE l^{-1} at 25°C, 130 rpm. Zn(A): Hanawa powdered Zn, Zn(B): Aldrich granular Zn, Zn(C): Acros granular Zn.

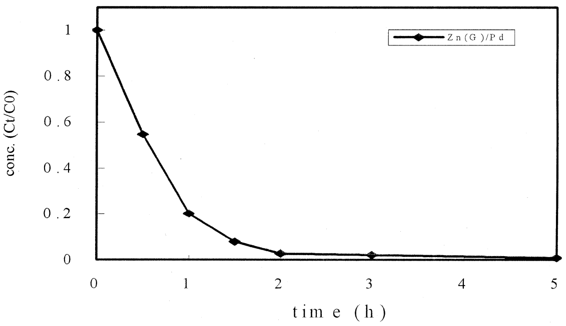

Fig. 6. TCE degradation by using Zn^0 combination with Pd^0. Conditions: batch tests were performed by using 3 g of Zn^0 and 50 mg of Pd^0 in serum vials (15 ml by volume) in contact with 3 mg TCE l^{-1} at 25°C, 130 rpm. Zn(G) was obtained from Aldrich granular Zn.

The bimetallics formed by Zn^0 or Fe^0 in conjunction with Ni^0 or Pd^0 did indeed have a tremendous promotional effect on the degradation reactions of TCE. Moreover, another characteristic of the bimetallics to the degradation reaction of TCE was that from our analysis result there was almost no formation of any chlorinated organic intermediate during the entire reaction process.

5. Conclusions

The results of this research indicated that factors such as the source characteristics, the purity, etc. of Fe^0, had a strong influence on the degradation rate of TCE. For Fe^0 of different sources, the reaction rates thereof could vary by up to three orders of magnitude. Furthermore, the storage of Fe^0 was another troublesome factor. Therefore, care must be taken in selecting zero-valent iron in the remediation technique.

In both electrochemical theory and the findings in the actual experiments, Zn^0 appeared far more suitable for the degradation of the chlorinated organic compounds than Fe^0 did. Zn^0 had a faster degradating rate to the chlorinated organic compounds. The half-life of TCE with Zn^0 was only one-tenth to that with Fe^0. The storage of Zn^0 was also easier than that of Fe^0. Even though a long period had elapsed since it was unsealed, a strong reactivity was still retained. Moreover, Zn^0 is an indispensable trace element required by the human body. The tolerable concentration thereof in the drinking water is rather high (5 mg/l). Therefore, the evaluation of the use of Zn^0 replacing Fe^0 in the techniques of remediation of groundwater contaminated by chlorinated organic compounds deserves further study.

The combinations of Zn^0 or Fe^0 with Ni^0 or Pd^0 did indeed have strong promotional effects on the degradation reactions of TCE. The half-life of Fe^0/Ni^0 could be reduced to 3.9–5 h; the half-life of Fe^0/Pd^0 could be reduced to 1.3 h, the half-life of Zn^0/Ni^0 could be reduced to 0.86 h, and the half-life of Zn^0/Pd^0 could be reduced to 0.46 h. The other characteristics of the bimetallics were that Fe^0 with inactive surfaces could be effectively revived and have an effective degradation on TCE. The application of the bimetallics technique enabled a substantially complete dechlorination reaction that was generally free of the formation of any chlorinated organic intermediates.

Although the combination use of Pd^0 gave an optimum result, Pd^0 is a precious metal and its use seems not feasible in economic terms. Ni^0 would be a more appropriate choice. The research results indicated that the combination of Zn^0 and Ni^0 had a promotional effect nearly the same as that of the combination of Zn^0 and Pd^0. It should be possible for the promotional effects thereof on the degradation rate of the chlorinated organic compounds to be raised further if further studies can be carried out on the combination ratios, the combination forms, and the control of reaction conditions. Furthermore, there is no specific regulation on the tolerable concentration of nickel in the standard of water qualities. The feasibility of this technique can be further evaluated by exploring other areas including the residual concentration of nickel in the aqueous solution after reaction, the influence of nickel on the human body, and the tolerable concentration of nickel in the drinking water.

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