



Phenol removal using zero-valent iron powder in the presence of dissolved oxygen: Roles of decomposition by the Fenton reaction and adsorption/precipitation

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ABSTRACT

The mechanism for removal of phenol by zero-valent iron (ZVI) was quantitatively evaluated in the presence of dissolved oxygen by varying the pH from 2 to 8.1 (natural). The measurement of OH radical concentration suggests that the removal of phenol by ZVI was occurred due to the decomposition by the Fenton reaction besides the adsorption/precipitation to the iron surface. From the measurements of dissolved organic carbon (DOC) in the filtrate with the 0.45 μm syringe filter and the solution obtained from acidification of suspended precipitates, the roles of decomposition by the Fenton reaction and adsorption/precipitation were separately evaluated. At solution pH 3, 91% of phenol removal was achieved and 24% of TOC (total organic carbon) decreased. The contribution of the Fenton reaction was found to be 77% of overall TOC reduction. When the pH values were 4 and 5, the overall TOC removal was found to be mainly due to the adsorption/precipitation. At pH 2 and 8.1, the reduction of TOC was very small. The pH and dissolved oxygen significantly affected the dissolution of iron and the production of OH radicals and changed the roles of phenol removal by the Fenton reaction and adsorption/precipitation.

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1. Introduction

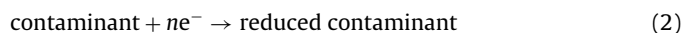
Zero-valent iron (ZVI) has drawn great attention as an inexpensive and environmentally friendly strong reducing agent [1,2]. Addition of ZVI to oxygen-containing water results in oxidation of organic compounds [3–5]. Therefore, extensive efforts have been directed to assess the potential application of ZVI for decomposition of organic pollutants in wastewater with the presence of dissolved oxygen (DO). However, little insight into the mechanism for removal of pollutants in water or wastewater by ZVI has been provided in the presence of DO. To date, views are mixed regarding the actual mechanism for the removal of dissolved organic compounds by ZVI [5,6].

Generally the degradation of organic contaminants has been considered to be mainly taken place due to reductive transformation and adsorption/precipitation [1]. According to the core-shell model, the shell consists of iron oxides/hydroxides formed by the oxidation of ZVI and the oxide film provides sites for chemical

reaction [1,2]. ZVI is reactive in water and can serve effectively as an electron donor:



Organic pollutants accept the electrons and undergo reductive decomposition:



First, the contaminant is diffused through the solution to the iron particle surface and adsorbed to a favorable reaction site. Then, electrons are transferred from the ZVI to the contaminant, producing intermediate products. The intermediate products are sequentially transformed on the ZVI surface. Finally, some of the products diffuse from the ZVI surface to the solution. At elevated pH, the ferrous and hydroxyl ions form iron oxides such as hydroxide and precipitate. The precipitation of ferrous hydroxide on the surface of ZVI could hinder the transport of the contaminant and block the reactive sites on ZVI, and hence decrease the overall decomposition rate [6]. It should be emphasized that the actual mechanisms of organic pollutant removal by the ZVI have not yet been completely elucidated, although significant progress has been made.

The Fenton or photo-Fenton process, which is a well-known example of advanced oxidation processes (AOPs) and strongly attributed to the oxidation power of OH radical formed during the decomposition of H₂O₂ catalyzed by ferrous ion, is being

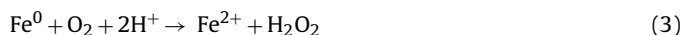
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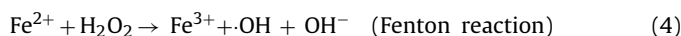
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increasingly used in the treatment of contaminated water [7–9]. Several studies have investigated the use of ZVI as a Fenton reagent, a mixture of H_2O_2 and Fe^{2+} , for pollutant degradation in water [10–13]. Certainly the use of ZVI as a source of Fe^{2+} is fairly effective. However, it still suffers from the major drawback that the addition of H_2O_2 is required.

Whereas the reduction of organic pollutants on the ZVI surface occurs, ZVI may generate strong oxidants and initiate the oxidative degradation of pollutants under appropriate solution conditions [1,5,16]. ZVI plays an important role as a source for the production of Fe^{2+} ions in the Fenton process. Some studies suggest the generation of H_2O_2 by the oxidation of Fe^0 in acidic and oxygen dissolved aqueous solution besides the formation of the Fe^{2+} [3,6,12,14–16]. Under acidic and oxic conditions the oxidative degradation of organic pollutants by OH radicals takes place in the ZVI process without addition of H_2O_2 . The first step in the oxidation of ZVI involves the oxidation of Fe^0 by O_2 .



As a result of Fe^0 oxidation, Fe^{2+} and H_2O_2 are formed. Under the acidic and oxic conditions, Reaction (3) supplies both Fe^{2+} and H_2O_2 which are necessary for the Fenton reaction generating OH radicals. While Reaction (1) is dominant in the generation of Fe^{2+} under anoxic condition, Reaction (3) controls the generation of Fe^{2+} ions in the presence of DO [12]. In the Fe^0 /air/water system, H_2O_2 is postulated to be continuously produced by the utilization of DO taking place either on the iron surface or in solution [17]. H_2O_2 could react with species such as $\text{Fe}(\text{II})$:



These reactions may occur on or adjacent to the Fe^0 surface. Fe^{2+} adsorbed on the ZVI surface or concentrated in the area immediately adjacent to the surface reacts with H_2O_2 and generates OH radicals. Hydroxyl radicals generated can react with target organic contaminants and lead to the mineralization of some organic compounds by converting to CO_2 , H_2O and inorganic ions. Organic compounds with a higher tendency to adsorb to the Fe^0 surface may be oxidized more quickly than those with a low affinity for Fe^0 surface [15]. If the above mechanism of ZVI actually occurs, an addition of a large amount of H_2O_2 is not required. The amount of OH radicals produced by the Fenton reaction is strongly affected by the pH and the optimum pH value for the Fenton reaction is around 3 [17,18]. The presence of DO to the ZVI-mediated oxidation process is also important. These reactions could occur on the Fe^0 surface or could involve transfer of electrons through an iron layer, depending on the reaction rates and affinity of the species for surfaces. Although the 4-electron transfer process is usually the dominant mechanism of O_2 -mediated corrosion, the 2-electron-transfer process can result in production of significant amounts of O_2^{2-} or H_2O_2 , especially after an oxide coating has been formed on the surface [19]. Although the concentration of powerful oxidizing OH radicals controls the rate of oxidation in AOPs, there are few studies concerned with the concentration measurements of OH radical formed during the ZVI oxidative degradation process.

The research objective is to gain insight into how the chemical reaction or the Fenton reaction and adsorption/precipitation affect the phenol removal by ZVI. We have investigated the influence of pH on the mechanism of phenol degradation by ZVI under oxic condition. Phenol, which is one of the common contaminants in industrial wastewater, was chosen as a model for other phenols and toxic aromatic compounds. Although Bremner et al. [10] and Sanchez et al. [20] investigated the degradation of phenol using ZVI, they did not examine the mechanisms of phenol degradation in the ZVI process. To prove the occurrence of the Fenton reaction, we have also conducted separate experiments for the production of OH radical using the scavenger probe technique [21,22]. To the best

of our knowledge, the generation of OH radical in the ZVI process has not yet been proven.

2. Experimental

2.1. Materials

The ZVI was obtained from Powder Tech Co. (Japan) with the average diameter of $75 \mu\text{m}$ and 97.9% purity was used without pretreatment. The BET specific surface area of the ZVI powder used in this study was $0.14 \text{ m}^2 \text{ g}^{-1}$. Reagent grade sulfuric acid, sodium hydroxide, potassium dihydrogen phosphate, acetonitrile, coumarin and phenol were all purchased from Kanto Chemical Co. (Japan). All reagents were used as received.

2.2. Degradation of phenol

Degradation of phenol in water was examined using a 1 L beaker. All experiments were carried out in a batch mode and at room temperature ($25 \pm 2 \text{ }^\circ\text{C}$). The pH was initially adjusted to the specified pH by addition of H_2SO_4 or NaOH and regulated by the pH controller.

All liquid samples withdrawn using a micro-syringe were filtered by $0.45 \mu\text{m}$ disposable syringe filters. The HPLC with UV detector (UV-2075Plus, JASCO Co., Japan) using a $5 \mu\text{m}$ particle size Inertsil ODS-3 V column ($4.6 \text{ mm} \times 250 \text{ mm}$) (GL Sciences Co., Japan) was utilized to determine the phenol concentration as well as the concentrations of the intermediates, i.e. hydroquinone and catechol [10,20,23]. The solvent used was the mixture of acetonitrile and potassium dihydrogen phosphate solution at the ratio of 65/35 (v/v). The concentration of total organic carbon (TOC) or dissolved organic carbon (DOC) in the solution was measured by a TOC analyzer (TOC-V_E, Shimadzu, Co., Japan) [8,9,23].

The concentrations of total Fe ion and Fe^{2+} ion in the sample solution were measured by the 1,10-phenanthroline method [24,25]. The concentration of solid state iron could be evaluated by subtracting the dissolved total Fe ion concentration from the initial ZVI concentration.

Air was injected at the flow rate of 0.5 L min^{-1} through a sintered glass ball sparger installed near the reactor base. The dissolved oxygen concentration was measured by a DO meter (SG6, Mettler Toledo International, Japan). The evaporation of phenol by aeration was experimentally found to be insignificant. A motor-driven six flat-blade disk turbine impeller installed near the reactor bottom was turned on at 400 rpm to ensure uniform distribution of ZVI powder through the reactor.

We measured the concentration of H_2O_2 using the glucose oxidase method [17,26,27] but could not detect. However, it does not imply that H_2O_2 was not generated during the removal of phenol by the ZVI under the oxic condition. Since H_2O_2 generated by Reaction (3) was not excessive and all H_2O_2 formed was almost instantaneously consumed to form OH radical by Reaction (4), the H_2O_2 concentration could not be detected. The measurement of OH radical concentration clearly suggested the formation of H_2O_2 by the oxidation of ZVI which was required in the Fenton reaction generating OH radicals.

To characterize the phenol removal by chemical reaction and physical separation processes we used two defined fractions, namely “decomposition” and “adsorption/precipitation”. The TOC reduction attributed to phenol decomposition by the Fenton reaction is defined as “decomposition” and that attributed to adsorption on the Fe^0 surface and precipitation with iron corrosion products is defined as “adsorption/precipitation”. The amount of phenol removal by physical separation processes or adsorption/precipitation was defined through $0.45 \mu\text{m}$ syringe filter. The

TOC concentration in the liquid samples filtered using 0.45 μm syringe filters (TOC in the liquid phase) represents the total amount of dissolved organic compounds, i.e. phenol and its intermediates dissolved in the liquid phase. The TOC reduction in the liquid phase was attributed to both decomposition and adsorption/precipitation. After 24 h reaction time, the precipitated and non-dissolved ZVI were filtrated and dried at 30 °C for 3 h. This low temperature was chosen to avoid the evaporation of phenol. Acidification with 9.4 mM H_2SO_4 was performed to dissolve any suspended precipitates. The TOC concentration in the acidic solution (TOC originally adsorbed and/or precipitated on the solid phase) represents the amount of phenol and its intermediates captured by ZVI and Fe ions. From these two TOC concentrations in the liquid phase and on the solid phase obtained after 24 h reaction time, we calculated the amount of phenol and its intermediates decomposed by the Fenton reaction and that dissolved into the solution during ZVI oxidative degradation, respectively. The reduction of the TOC in the liquid phase after 24 h from the initial TOC indicates the overall TOC removal. By subtracting the TOC of phenol and its intermediates removed by the adsorption/precipitation (TOC adsorbed and/or precipitated on the solid phase) from the overall removal based on the TOC concentration in the filtrate of the liquid sample withdrawn from the reactor after 24 h reaction time, the amount of phenol mineralized by the Fenton reaction could be estimated. Since the removal of TOC due to the Fenton reaction estimated by the above calculation did not include the TOC reduction caused by the decomposition of phenol to the intermediates adsorbed and/or precipitated on the ZVI surface, it underestimated the contribution of the decomposition by the Fenton reaction on the overall TOC removal and might represent the minimum contribution of the Fenton reaction.

Experiments were also performed to assess the generation of OH radicals under the conditions identical to those used in the phenol removal experiments. A coumarin fluorescence probing technique was used to measure the cumulative amount of OH radical generated by ZVI [21,22].

3. Results and discussion

3.1. Effect of solution pH

The overall removal efficiency may be affected by pH-dependent changes in the mechanisms of the ZVI oxidative degradation. At lower pH, Fe^0 oxidizes to Fe^{2+} in aqueous acidic conditions due to the dissolution. Fe^{2+} present in the solution decomposes H_2O_2 formed by Reaction (3) to generate OH radicals [3,5,12]. Therefore, at lower pH the Fenton reaction generating OH radicals may occur near the ZVI powder surface and dominate the overall removal of phenol. The precipitation of a passive film on the iron surface at higher pH imposes mass transport limitations and inhibits the Fenton degradation of phenol. The adsorption of phenol and its intermediate on the undissolved Fe^0 surface and/or their precipitation with iron corrosion products may be mainly responsible for the reduction of dissolved TOC at higher pH.

The effects of the pH on the removal of phenol by ZVI particles are depicted in Fig. 1. The initial phenol concentration in the solution was 25 mg L^{-1} and the initial total iron concentration or iron dosage was 1000 mg L^{-1} . Incidentally, this iron dosage is rather smaller as compared with 50 g L^{-1} and 10–50 g L^{-1} for azo dye degradation used by Chang [4] and Wang et al. [5], respectively. The concentration profiles of phenol, TOC in the solution, DO, solid state iron and Fe^{2+} are plotted against the sampling time.

At pH 2 the removal of phenol proceeded rather quickly within the first 110 min and then slowed down (Fig. 1a). During the first 110 min the phenol concentration decreased from 25 to 20 mg L^{-1} .

The slower rate of degradation at lower pH is also due to the excess H^+ ions present in the solution acting as OH radical scavenger [28].



While the fresh surfaces were kept, the adsorption ability and reactivity of the ZVI might be high. At the initial stage, phenol molecules could easily transport and be oxidized by OH radicals formed near Fe^0 surface and/or adsorb to Fe^0 surface. As a result the phenol concentration rather quickly decreased. As the reaction proceeded, the surface adsorptive and reactive sites of Fe^0 were gradually occupied by corrosion products and as a result the removal rate decreased greatly. It is seen in Fig. 1a that there was practically no reduction of dissolved TOC in the solution. Little decrease in TOC of 0.7 mg L^{-1} was obtained after 24 h. It indicates the formation of the intermediates having poor degradability. In fact, as described below, catechol concentration was 13.5 mg L^{-1} even after 24 h at pH 2. As seen in Fig. 1a, furthermore, the Fe^{2+} ion concentration quickly increased to almost 1000 mg L^{-1} due to elution of Fe^{2+} by Reactions (1) and (3). We observed that at pH 2 all of added ZVI particles dissolved after first 110 min and none of ZVI particles were suspended in the solution. After first 110 min, therefore, Reaction (3) did not take place due to the lack of Fe^0 . Since H_2O_2 was not formed by Reaction (3) and OH radical was not generated after 110 min, as described above the rate of phenol degradation significantly slowed down. The DO concentration did not significantly change during the removal of phenol. The oxygen supply by aeration was much larger than its consumption by Reaction (3). As mentioned previously, we could not detect the H_2O_2 concentration in this study. However, it never implies that H_2O_2 was not formed. It is probable that the consumption rate of H_2O_2 by the Fenton reaction was much faster as compared with the generation rate of H_2O_2 by Reaction (3). As a result H_2O_2 concentration was minimal during ZVI oxidative degradation.

As shown in Fig. 1b, when the pH was the optimum pH for the Fenton reaction of 3, the removal proceeded rapidly within the first 300 min and then slowed down. About 80% of phenol was removed within 300 min and then the removal rate decelerated. The dissolved TOC concentration decreased only 24% after 1400 min. Similar results can be found in the literature. Zazo et al. [29] obtained about 97% degradation of phenol of 100 mg L^{-1} with the initial H_2O_2 concentration of 500 mg L^{-1} and the Fe^{2+} dosage of 1 mg L^{-1} but only 12% reduction of TOC by Fenton's reagent after 240 min. Rather little TOC reduction might be due to the formation of the intermediates having poor degradability. The Fe^{2+} ion concentration reached almost 1000 mg L^{-1} and due to elution of Fe^{2+} by Reactions (1) and (3) after 300 min and all of ZVI dissolved as well as at pH 2. It is clear that the change in the phenol removal rate was strongly associated with the change in the concentration of ZVI controlling the generation of OH radicals. As described above the corrosion of ZVI under the acidic and oxic conditions is required to generate OH radicals (Reaction (3)). The DO concentration slightly decreased at the beginning of removal but increased to the saturated DO. At the initial stage of the oxidative degradation, DO was rather rapidly consumed to generate OH radicals by Reaction (3). This implies that the oxygen supply by the aeration was larger than the oxygen consumption except $t < 300$ min.

In the Fenton reaction system, the degradation of organic pollutants is generally limited by the amount of ferrous iron present in the solution. For the ZVI process, the concentrations of Fe^{2+} at pH 2 and 3 were large enough to proceed with the Fenton reaction. After all Fe^0 dissolved, however, Reaction (3) did not occur, as a result H_2O_2 which is necessary to generate OH radicals was not formed and only little decomposition of phenol took place. At pH 2 the elution of Fe^0 was rather rapid as compared with that at pH 3 and the generation of OH radical quickly terminated. Therefore,

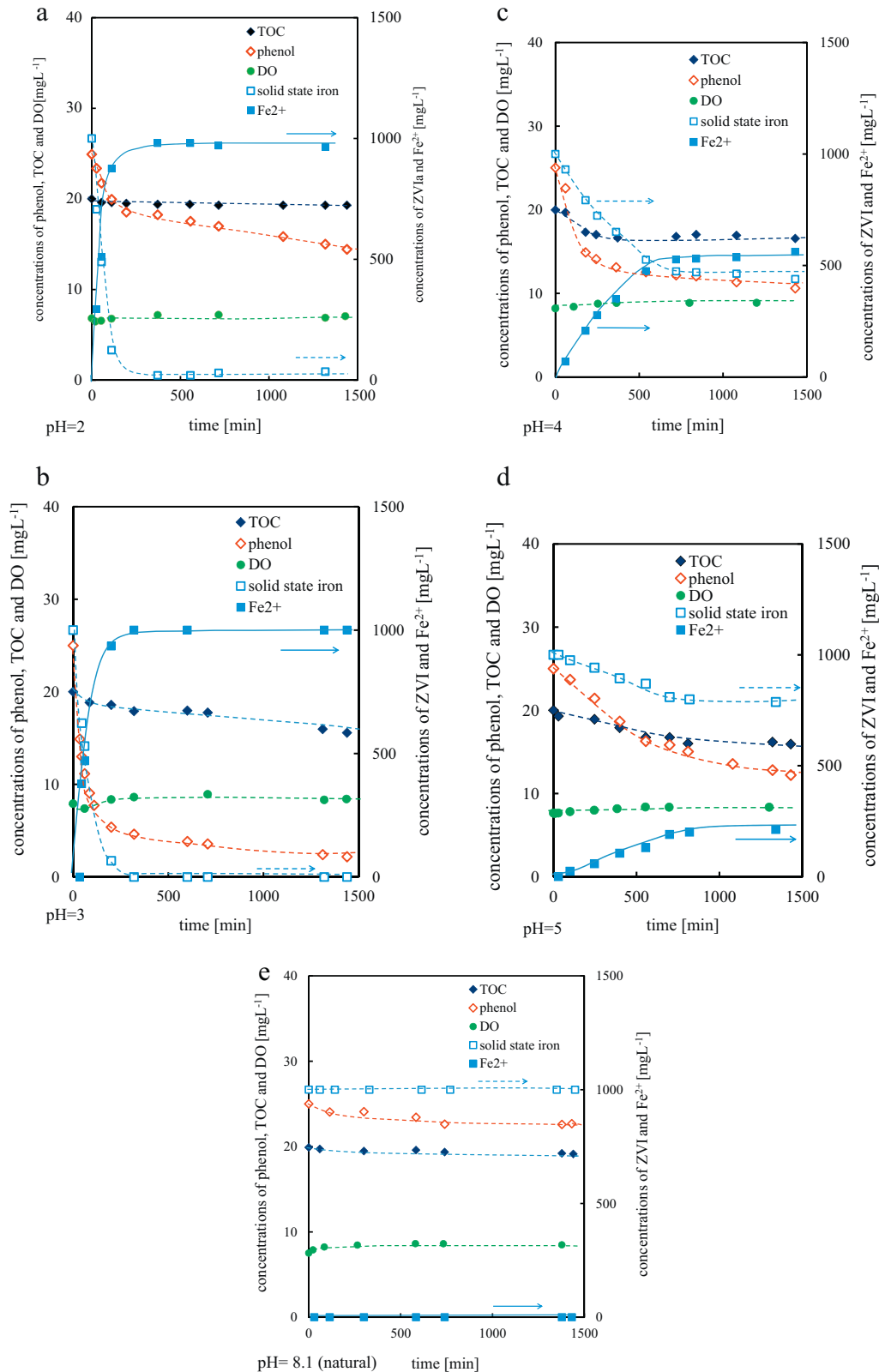


Fig. 1. Effects of pH on removal of phenol by ZVI (Note that the lines are average and smooth curves of experimental data and included to aid interpretation.): (a) pH=2, (b) pH=3, (c) pH=4, (d) pH=5, and (e) pH=8.1 (natural).

the removal of phenol at pH 2 was significantly slower than that at pH 3.

As depicted in Fig. 1c–e, when the pH was increased from 4 to 8.1 (natural), the degradation of phenol slowed down as well as

the results in the literature [19,30]. At higher pH, the process of hydrolysis of iron ions is dominant [6,19]. This leads to the deposition of precipitated iron hydroxides on Fe⁰ surface which blocks the further electron transfer process between Fe⁰ and phenol and

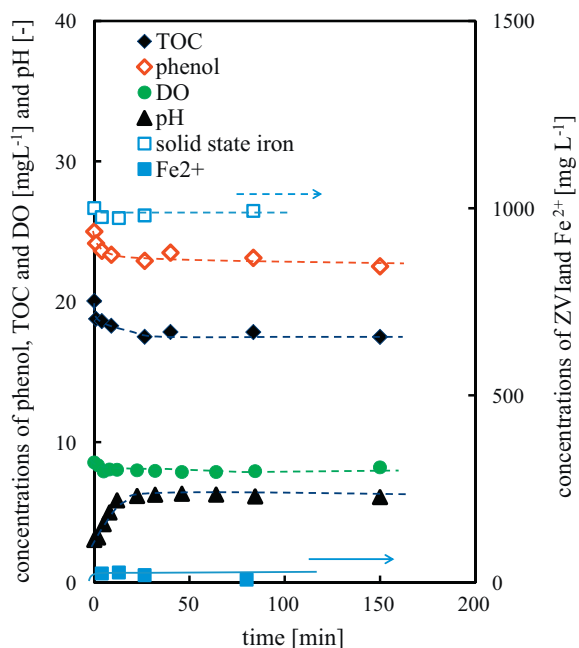


Fig. 2. Removal of phenol by ZVI without pH control (the initial pH is 3). (Note that the lines are average and smooth curves of experimental data and included to aid interpretation.)

as a result reduces the generation of OH radicals in the solution. As a result, the optimized condition for performing the Fenton reaction was found to be pH 3. It is seen in Fig. 1c that the reduction of phenol concentration terminated after 600 min at pH 4 and 48% reduction of the phenol concentration and 17% decrease in dissolved TOC were obtained. At pH 4 only partial elution of Fe^{2+} occurred and ZVI particles were suspended in the solution. The elution of Fe^0 terminated and the total dissolved iron concentration was about 56% of the added Fe^0 after around 600 min. The dissolved Fe^{2+} concentration rather slowly increased to around 550 mg L^{-1} and remained constant afterwards. Although the Fe(III) concentration was not presented in the figure, it was around 5 mg L^{-1} . It implies that a half of ZVI dosage remained in the solution as particles. The DO very slightly but continuously increased. The DO concentration practically remained constant. At the pH of 5, the removal of phenol rather slowly took place and about 50% decrease in phenol concentration was found after 1400 min (Fig. 1d). The concentrations of dissolved Fe ions were rather lower as compared with those at pH 4 and the Fe^{2+} concentration remained 213 mg L^{-1} after 800 min. As shown in Fig. 1e, experiments conducted at pH 8.1 (natural) indicated no significant changes in the concentrations of phenol, dissolved TOC, DO and Fe ions. Only slight decreases in phenol concentration and dissolved TOC were found. Phenol almost resisted removal at pH 8.1. It is clear from the figure that almost no measurable loss of Fe^0 was detected. In other words, practically no elution of Fe ions took place at pH 8.1. The concentration of Fe^{2+} remained approximately constant over the duration of the experiment and was less than 0.39 mg L^{-1} . Therefore, the Fenton reaction did not practically occur and the adsorption/precipitation of phenol on the Fe^0 particle surface might be responsible for the little removal of phenol. It appears that the release of dissolved iron was slower and less at higher pH values.

For comparison, we conducted the experiment in which no acid or alkali was added to maintain pH throughout the phenol removal process. The pH change was monitored during phenol removal. Fig. 2 presents the concentration profiles of phenol, dissolved TOC, DO and iron ions and pH profile without pH control. The initial pH was 3.0 which is the optimum pH for the Fenton reaction. The pH

rather quickly increased from 3.0 to around 6.2 within 20 min of oxidative degradation. After about 20 min the pH remained constant. Iron undergoes redox reaction with DO and water.



This reaction and the Fenton reaction form OH^- , which resulted in an increase in pH [30]. While the pH increased from 3.0 to 6.2, removals of phenol and TOC were around 10 and 13%, respectively. The elution of Fe ion occurred only for $t < 20$ min. After reaching of the pH of 6.2, almost no changes in the concentrations of phenol, dissolved TOC, DO and iron ions were taken place since OH radicals were not generated in the absence of the oxidation of Fe^0 (Reaction (3)).

3.2. OH radical generation

To understand the contribution of the Fenton degradation process taken place in the ZVI oxidative degradation process, the measurements of the generation and consumption rates of OH radicals in the reactor are necessary. Noradoun and Cheng [3] found that the ZVI/air/water reaction was effectively suppressed by the addition of 1-butanol being the OH radical scavenger and stated that this indicates the presence of reactive oxygen species including OH radical in the solution.

The measurements of cumulative amount of OH radical production were conducted with the initial coumarin concentration of 10 mM and the ZVI dosage of 1000 mg. Fig. 3a illustrates effects of pH on the OH radical production. The detection of OH radicals in the solution suggests that the phenol removal was due to the Fenton degradation besides the adsorption/precipitation. The rate of OH radical generation was the maximum at pH 3. The cumulative OH radical production increased rapidly within the first 10 min and then somewhat slowed down. At pH 3, it reached to $11 \mu\text{M}$ after 40 min. At pH 2, the amount of OH radical produced increased to around $5 \mu\text{M}$, which was almost half of that at pH 3 after 30 min and then remained approximately constant. For $\text{pH} > 3$, the amount of OH radical generated decreased as the pH increased. The values of cumulative OH radical production at pH 4, 5 and 8.1 were 2.9, 0.84 and $0.32 \mu\text{M}$, respectively. It is obvious that the cumulative OH radical generations at pH 2, 4, 5 and 8.1 were considerably smaller as compared with that at pH 3 (optimal pH for the Fenton reaction). This dependency of pH on the OH radical generation rate indicates that the generation of OH radical in the ZVI process might be controlled by the dissolution of Fe^0 forming Fe^{2+} (Reaction (3)).

Huang and Zhang [31] examined the effect of DO on the nitrate degradation by ZVI. They found that the presence of DO resulted in a thick layer of iron oxides and then decreased the reactivity of Fe^0 . Effects of DO on the OH radical generation are depicted in Fig. 3b. When air was continuously supplied to the solution, the DO concentration was almost constant at the saturated DO concentration. Under this condition in which the DO supply was excessive, the OH radical generation continuously increased and reached to $11 \mu\text{M}$ after around 40 min. We obtained the interesting result when the aeration was stopped at the beginning of the experiment. The DO concentration quickly decreased from the saturated concentration to 0.32 mg L^{-1} at 20 min. Until around 5 min in which the concentration of DO used to form Fe^{2+} (Reaction (3)) was adequate, the OH radical generation without aeration was similar to that with aeration. Afterward the OH generation without aeration was significantly suppressed due to the shortage of DO. When nitrogen gas was sparged into the solution instead of air, the DO concentration was almost zero over the duration of the experiment. Under this condition of DO shortage, as seen in Fig. 3b, the generation of OH radical was little. The OH radical generation was significantly related to the DO concentration. It may be concluded, therefore, that in the ZVI/air/water system H_2O_2 was generated by Reaction

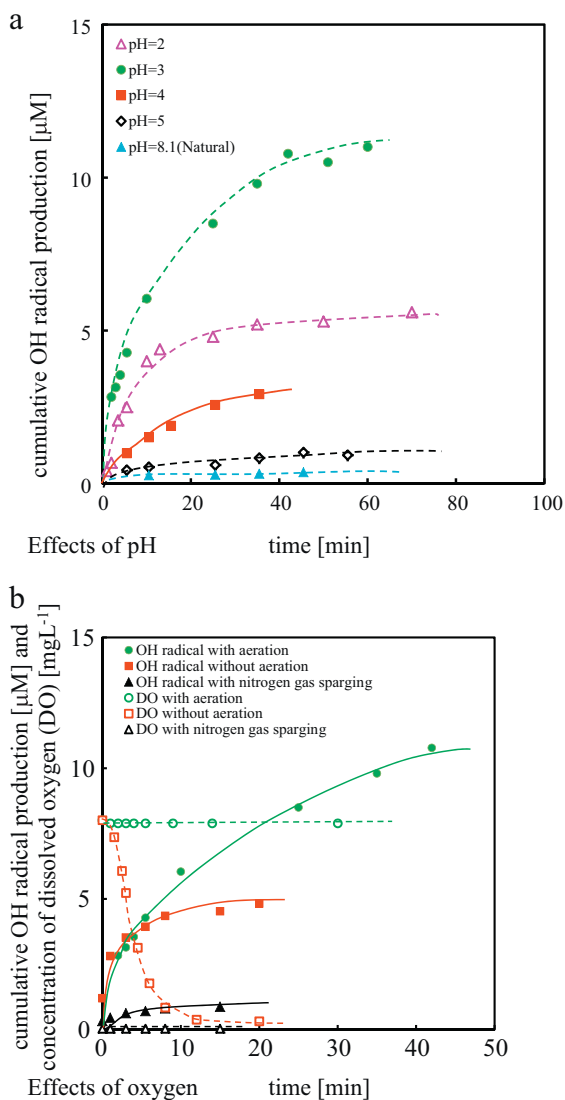


Fig. 3. OH radical generation by ZVI (Note that the lines are average and smooth curves of experimental data and included to aid interpretation.): (a) effects of pH and (b) effects of oxygen.

(3) in which oxygen is required and was used to form OH radical by Reaction (4).

3.3. Roles of Fenton degradation and adsorption/precipitation on phenol removal

Fig. 4 shows the effects of pH on phenol removal, TOC removal (TOC removals by the Fenton reaction and adsorption/precipitation) and cumulative OH radical generation. It is apparent that the optimal pH for the ZVI oxidative degradation process was 3 as well as that for the Fenton reaction. When the pH was 3, about 91% removal of phenol and 24.3% TOC reduction were found. The possible reason for rather low TOC reduction is that at pH 3 all ZVI dissolved and as a result the adsorption/precipitation on ZVI surface could not play an important role. Only adsorption/precipitation with iron oxides in the solution took place. Furthermore, some intermediates formed might have poor degradability. As described in Section 3.4, the intermediates were formed by the Fenton reaction. The phenol removal defined as the decrease in phenol concentration includes the intermediates and removal by the adsorption/precipitation besides mineralized phenol as shown

in Fig. 4. On the other hand, the TOC removal does not include the intermediates. Since the intermediates are included in the residual TOC, the TOC removal is rather smaller as compared with the phenol removal. It should be emphasized that around 77% of overall TOC reduction was due to the decomposition by the Fenton reaction.

Using the technique described above, we estimated the amount of the TOC removal by the adsorption/precipitation. At the end of the experiment (after 24 h), phenol and its intermediates adsorbed on the ZVI surface and/or precipitated with iron corrosion products such as iron hydroxides and iron oxides were dissolved into the acidic solution and the TOC on the solid phase was measured. As a result we could roughly distinguish the roles of the Fenton degradation and adsorption/precipitation on overall TOC removal. It should be noted that the TOC change due to the Fenton reaction calculated represents the minimum contribution of the Fenton reaction. Since the adsorption/precipitation TOC on the solid phase or iron oxides includes the intermediates formed by the decomposition of phenol such as hydroquinone and catechol besides phenol, the Fenton reaction contributed not only to the TOC removal in the liquid phase but also to the TOC removal in the solid phase. The role of the oxidative degradation by the Fenton reaction in the ZVI system depended on the pH. As seen in Fig. 4 that the maximum contribution of the Fenton reaction in the ZVI degradation process was obtained at pH 3 as well as the Fenton or photo-Fenton reaction in which a mixture of H_2O_2 and Fe^{2+} was used.

Beyond the optimum pH 3 for the Fenton reaction, the phenol removal efficiency significantly decreased. The removals of phenol and overall TOC at pH 4 and 5 were 58 and 15.3% and 51 and 17.3%, respectively. Only 1.9% reduction of the TOC was found at pH 8.1 (natural). The ZVI surface could be covered by the corrosion products in alkaline conditions. For $\text{pH} > 3$, the contribution of the decomposition by the Fenton reaction to the TOC removal dramatically decreased and was almost negligible as well as that at pH 2. The contribution of the decomposition by the Fenton reaction on the overall TOC reduction was less than 0.3%. Under this pH range the removal of TOC was mainly due to the adsorption/precipitation.

For reference, the values of cumulative OH radical production are plotted. The change in the contribution of the decomposition by the Fenton reaction on the overall TOC reduction was found to be strongly linked to that in the cumulative OH radical generation. The decomposition of phenol by the Fenton reaction obviously depended on the cumulative OH radical generation. Although as shown in Fig. 3a the cumulative OH radical production at pH 2 were about a half of that at pH 3, the contribution of the Fenton degradation at pH 2 was only 0.1%. The excess acidity retarded the degradation rate as excess H^+ ions act as hydroxyl radical scavenger (Reaction (5)) [28,32].

3.4. Effects of solution pH on intermediates formed by the ZVI process

The intermediate organic compounds formed by the decomposition of phenol reduced the removal of phenol but not the removal of TOC. The main intermediates have been identified as catechol, hydroquinone, benzoquinone and maleic acid [23,29,33]. The hydroxylation of phenol leads to catechol and hydroquinone. Profiles of hydroquinone and catechol formed over the duration of the experiment are shown in Fig. 5. At pH 2, the hydroquinone concentration increased to 0.87 mgL^{-1} in 110 min and remained constant afterwards (Fig. 5a). This profile is related to the change in the rate of phenol removal. As shown in Fig. 1a, the phenol concentration decreased during the first 110 min reaction period and after that the removal of phenol slowed down. At the optimum pH 3 for the Fenton reaction, the hydroquinone concentration increased during the first 200 min, reached a maximum after around 200 min and then gradually decreased until the end of the experiment. This

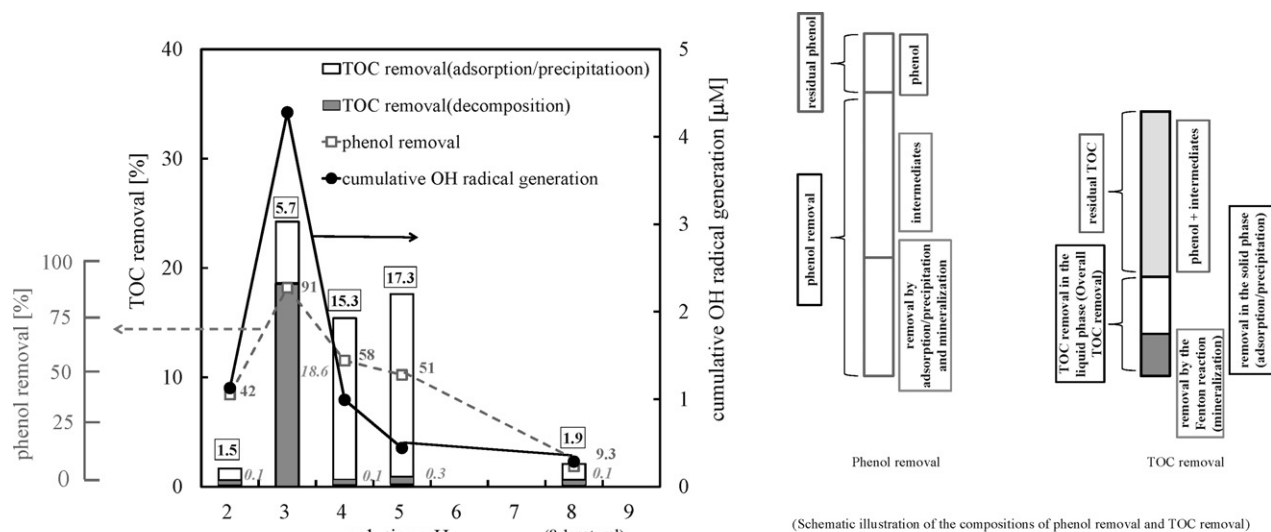


Fig. 4. Effects of pH on phenol removal and TOC removal after 24 h reaction of phenol. (The phenol loading and the ZVI dosage are 25 mg L^{-1} and 1000 mg L^{-1} , respectively. The number in the rectangle represents the TOC removal in the solid phase and the italic number represents the TOC removal by the Fenton reaction.)

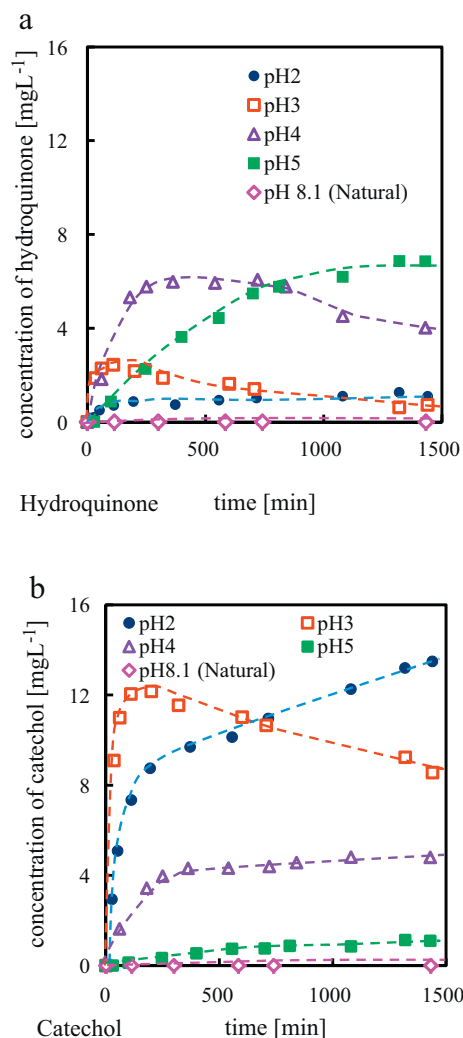


Fig. 5. Profiles of intermediates during the decomposition of phenol (The phenol loading and the ZVI dosage are 25 mg L^{-1} and 1000 mg L^{-1} , respectively.) (Note that the lines are average and smooth curves of experimental data and included to aid interpretation.): (a) hydroquinone and (b) catechol.

suggests that the hydroquinone was decomposed to smaller intermediates such as organic acids by the Fenton reaction. At pH 4 the concentration of hydroquinone increased during the initial reaction phase and the maximum concentration of 6.0 mg L^{-1} was found at about 360 min and after that the hydroquinone concentration decreased with time slowly. At pH = 5 the hydroquinone concentration continuously increased to 6.9 mg L^{-1} . Since the decomposition of hydroquinone was slow at pH 5, the maximum concentration was not observed. At pH 8.1 (natural), only a trace of hydroquinone was detected because no removal of phenol practically occurred.

It can be seen in Fig. 5b that at the optimum solution pH of 3 the catechol concentration increased quickly, reached the maximum of 12 mg L^{-1} after around 200 min and gradually decreased. Although the change in catechol concentration was similar to that in hydroquinone concentration, the observed catechol concentration was significantly higher than hydroquinone concentration. The profiles of hydroquinone and catechol at pH 3 in this study are similar to those previously reported [10,23,29]. At pH > 3, the concentration of catechol continuously increased throughout the reaction as well as that at pH 2. Increasing pH from 4 to 8.1 resulted in the decrease in catechol concentration. At pH 8.1 (natural), only small amount of catechol was detected as well as hydroquinone. This is reasonable because as seen in Fig. 1e no reduction of TOC practically occurred.

4. Conclusions

The measurement of cumulative amount of OH radical production confirmed the generation of OH radical in the ZVI/air/water systems. This is the first study that the quantitative detection of OH radicals provided evidence for the removal of phenol via the Fenton reaction besides adsorption/precipitation. The role of ZVI in these systems may be two-folds, a source of Fe^{2+} and a production of H_2O_2 (Reaction (3)) used to generate OH radicals (Reaction (4)).

Solution pH affected phenol removal to a different extent. The maximum removal efficiencies of phenol and TOC (91% and 24.3%) were obtained at pH 3. The present result suggests that at pH 3 the Fenton reaction is mainly responsible for removal of phenol. When the pH was 2, adsorption/precipitation controlled the reduction of TOC rather than the decomposition by the Fenton reaction. At pH values above 3, the contribution of the Fenton reaction on the removal of phenol was insignificant as compared with that of the adsorption/precipitation.

In the present study, roles of decomposition by the Fenton reaction and adsorption/precipitation have been quantitatively evaluated from the two measurements of the overall TOC removal and the TOC removal due to adsorption/precipitation. However, the mechanism of adsorption/precipitation of phenol and intermediates based on iron particle surface characteristics was not examined. Future study is ongoing to examine adsorption and precipitation separately. A kinetic model for removal of pollutants by ZVI taking place both by the Fenton reaction and by adsorption/precipitation is also one of our future subjects.

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