

## Fenton Degradation of 4,6-Dinitro-*o*-cresol with Fe<sup>2+</sup>-Substituted Ion-Exchange Resin

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The Fenton degradation of 4,6-dinitro-*o*-cresol (DNOC) was studied under different experimental conditions using Amberlyst 15 ion-exchange resin containing ferrous ion. DNOC was found to be effectively degraded under most conditions, and it was observed that, with the addition of HCl, the desorption of ferrous ion from the resin into the solution played a major role in this degradation. The total iron concentration in the reaction solution was found to increase with the addition of HCl, and a pseudo-first-order kinetic model was applied to the desorption of ferrous ion from the resin on the basis of the assumption of a first-order ion-exchange process. The degradation rate of DNOC also increased as a function of HCl. A kinetic model was developed to simulate the degradation of DNOC under different operating conditions, assuming the first-order desorption of ferrous ion. Different cations were compared with H<sup>+</sup>, and H<sup>+</sup> was found to be the most efficient at facilitating the degradation reaction at low concentrations, whereas Ca<sup>2+</sup> was found to be most efficient at high concentrations. pH was measured during the reaction, and its effect on degradation was explored. It was found that a lower pH could lead to faster degradation of the target compound. Degradation of DNOC under different delivery rates of H<sub>2</sub>O<sub>2</sub> was studied, and optimal conditions were determined. The results also showed that the delivery rate of H<sub>2</sub>O<sub>2</sub> did not affect the ion-exchange process of the resin.

**KEYWORDS:** Ion-exchange resin; DNOC; Fenton degradation

### INTRODUCTION

Pollution of water and soil in the environment by toxic organic pollutants such as pesticides has become a widespread concern for water quality and as a source of serious hazards for humans and other living species. Advanced oxidation processes (AOPs) have been investigated as successful methods to remediate environmental pollutants in water (1–3). Among these methods, Fenton treatment has been extensively applied to degrade environmental pollutants (4–7), especially in wastewater and soil. Fenton and modified Fenton reactions use a metal catalyst to generate hydroxyl radicals from hydrogen peroxide (8, 9), with various methods being used to deliver the catalyst into the reaction system. Anodic Fenton treatment (AFT) was developed to provide a constant delivery of ferrous ion from a sacrificial iron electrode by electrolysis (10) while hydrogen peroxide was simultaneously pumped into the system. A kinetic model was developed to describe the AFT degradation process and to optimize experimental conditions (11). AFT was reported to effectively remove many pesticides in a short time period (12–15), and one of its several advantages is to provide the ferrous catalyst continuously.

Other sources of metal catalyst carriers such as resin, zeolite, and silica gel have been used to immobilize ferrous and other metal ions in Fenton and UV/Fenton reactions

(16–19). However, in these studies the reactions were heterogeneous, and only the effect of the catalyst bound to the carrier was studied. Fenton reactions associated with the catalyst released from the ion-exchange material were not explicitly explored. However, under given conditions, ion-exchange material can gradually release ions during the ion-exchange process, and studies have shown that the ion-exchange process can be described as a pseudo-first-order reaction and can be controlled by the concentration of ions (20, 21). Therefore, ion-exchange materials can be used as a novel source for continuous release of a metal catalyst.

It is of interest to investigate the kinetics of the Fenton reaction using ferrous iron released from an ion-exchange material. Resin was chosen as the carrier for ferrous ion because it has a large cation-exchange capacity and the ion-exchange process can be quantitatively described. Furthermore, resins have a smaller surface area than zeolite and silica gel (22–24); therefore, they can reduce the oxidation of ferrous ion on the surface of the resin and retard the adsorption of the target compound to the resin. Amberlyst 15, a sulfonated styrene–divinylbenzene copolymer cation-exchange resin, was selected in this study because of its excellent physical and chemical stability (22).

The purpose of this study was to investigate the use of a ferrous substituted resin to release metal catalyst continuously in an applied Fenton treatment and optimize the treatment conditions. 4,6-Dinitro-*o*-cresol (DNOC) was selected as the

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target compound. It has been widely used as a selective herbicide for more than 50 years (25). Although the use of DNOC was canceled by the U.S. EPA in 1987 because of its long-term health effects on humans (25), it is still found in the environment because of its slow degradation rate (26, 27). The degradation of DNOC using Fenton and modified Fenton processes was performed in early studies (28, 29), and the degradation rates using their methods were compared with our study. The specific objectives of this work were (i) to apply a kinetic model to the desorption of ferrous ion from the resin; (ii) to develop a kinetic model for Fenton degradation of DNOC using the ferrous desorption model; and (iii) to investigate the effect of pH, delivery rate of H<sub>2</sub>O<sub>2</sub>, and the type and concentrations of cations in solution. The proposed Fenton reaction can be potentially used for wastewater treatment and remediation when the controlled release of reaction reagent is required.

## EXPERIMENTAL PROCEDURES

**Chemicals.** The ion-exchange resin, Amberlyst 15, was purchased from Sigma-Aldrich. Sodium chloride, calcium chloride, sodium acetate, acetic acid, hydroxylamine hydrochloride, 1,10-phenanthroline, methanol (HPLC grade), water (HPLC grade), and acetonitrile (HPLC grade) were purchased from Fisher Scientific (Fair Lawn, NY). Ferrous sulfate 7-hydrate and hydrogen peroxide (30%) were purchased from Mallinckrodt (Paris, KY). Iron standard solution (10 mg/L) was purchased from HACH (Loveland, CO). DNOC was purchased from Chem Service (West Chester, PA). DI water was obtained from an MP-1 Mega-Pure system (Corning, NY) with electrical resistance of > 18.1 MΩ/cm.

**Preparation of Ferrous-Substituted Resin.** Eight grams of Amberlyst 15 resin was first treated by 100 mL of 5% (w/w) NaOH solution and then 100 mL of 5% (w/w) HCl solution. The treated resin was rinsed with deoxygenated water and exchanged with 1 M FeSO<sub>4</sub> solution for 24 h under N<sub>2</sub> protection. The exchanged resin was then rinsed with deoxygenated water until no Fe<sup>2+</sup> was detected in solution and was vacuum-dried for 24 h. To determine the amount of ferrous ion exchanged on the resin, 1 g of prepared resin was extracted four times by 100 mL of 5 M NaCl solution over a 24 h period for each extraction. The extracted ferrous ion was determined to be 163 mg/g resin as measured by 1,10-phenanthroline according to the Standard Method for the Examination of Water and Wastewater (30) and analyzed by a Lambda 35 UV-vis spectrometer (PerkinElmer Instruments, Waltham, MA) at 510 nm. The quantification limit for ferrous ion detection, as a surrogate for total iron after reduction of ferric ion, is 0.01 μg/mL. Because the concentration of active sites on the Amberlyst 15 is ≥ 4.7 mequiv/g (from manufacturer's data), this result implies that the active sites on the resin were saturated with ferrous ions.

**Degradation of DNOC.** Fenton experiments were carried out in a 250 mL round-bottom flask. Typically, 100 mL of 11.4 μg/mL DNOC solution with 1 g of dry ferrous-substituted resin was added to the flask. H<sub>2</sub>O<sub>2</sub> solution was pumped into the system at the rate of 0.5 mL/min using a Stepdos peristaltic pump (Chemglass Inc., Vineland, NJ). The pH was measured using an IQ150 pH-meter (IQ Scientific Instruments, Carlsbad, CA). An aliquot of 0.7 mL of solution was taken out at specific time intervals, and 0.1 mL of methanol was added to quench the hydroxyl radical. The sample was then centrifuged for 10 min, and the supernatant was analyzed by HPLC. After the HPLC analysis, 0.5 mL of the sample was taken out, and the total amount of iron was measured using the phenanthroline method (30). Each experiment was repeated twice.

When the effect of HCl on the Fenton degradation of DNOC was investigated, 0.189 M H<sub>2</sub>O<sub>2</sub> was pumped into the system at a

constant delivery rate of 0.5 mL/min and different amounts of 1 M HCl from 0 to 0.3 mL were added to the solution at the start of the reaction. For the reactions facilitated by different cations, various amounts of 1 M HCl, NaCl, or CaCl<sub>2</sub> were added to the system at the start of the reaction. To investigate the Fenton degradation rate of DNOC under different H<sub>2</sub>O<sub>2</sub> delivery rates, H<sub>2</sub>O<sub>2</sub> solutions of different concentrations were prepared and pumped into the system at a rate of 0.5 mL/min, and 0.2 mL of 1 M HCl was added at the start of the reaction.

To simulate the experimental data with mathematical functions, a model was developed based on previous studies (11, 20) as described under Results and Discussion.

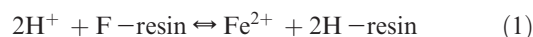
**Measurement of DNOC Concentration.** The concentration of DNOC was measured by an Agilent 1100 HPLC with a DAD detector (Agilent Technologies, Inc., Santa Clara, CA). The mobile phase was composed of 80% acetonitrile and 20% water (pH was adjusted to 3 by phosphoric acid). A C-18 5 μm 250 mm × 4.6 mm (i.d.) Restek reverse phase column was used. Flow rate, injection volume, and column temperature were set to 1.0 mL/min, 20 μL, and 25 °C, respectively. The UV wavelength for the DAD was set at 269 nm. Calibration of the instrument was performed using a series of DNOC solutions, and the calibration curve indicated that peak area in HPLC was directly proportional to the concentration of DNOC. Because the data for DNOC were all percent concentrations, the data of relative peak areas were used in this study.

**Experimental Data Analysis.** The model fitting and statistical analyses were performed using Sigmaplot 9.01 (Systat Software Inc., Richmond, CA).

## RESULTS AND DISCUSSION

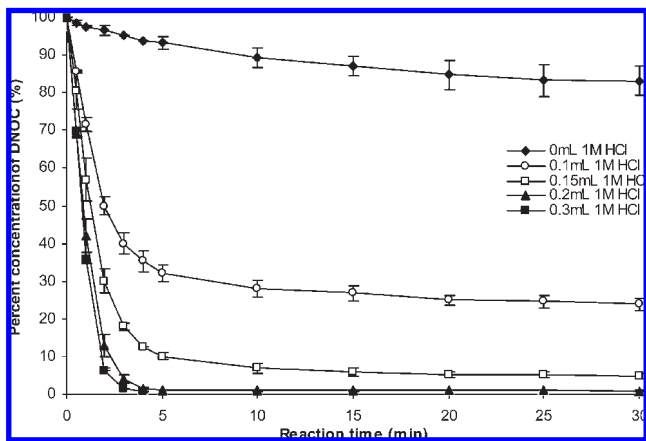
**Effect of HCl Concentration on Ion-Exchange Kinetics.** The degradation of DNOC on ferrous-substituted resin with a constant delivery rate of H<sub>2</sub>O<sub>2</sub> and the addition of 1 M HCl at the beginning of the reaction is shown in **Figure 1**. As a control experiment, the degradation of DNOC without the addition of HCl was very slow. The degradation rate increased with the amount of HCl added, indicating that a higher H<sup>+</sup> concentration could improve the reaction rate. A previous study (11) showed that the degradation of target compound in the Fenton reaction is affected by the delivery rate of the ferrous ion with a constant supply of H<sub>2</sub>O<sub>2</sub>. The effect of the added HCl on the delivery rate of the ferrous ion and thus on the Fenton reaction rate is important to understand and was modeled as described below.

The total concentration of iron in the DNOC degradation reaction mixtures under the conditions of **Figure 1** was measured, and the results are shown in **Figure 2**. Because Fe<sup>2+</sup> was continuously oxidized by H<sub>2</sub>O<sub>2</sub>, the concentration of total iron was used to represent the total Fe<sup>2+</sup> released from the resin. The results show that the total iron concentration in the solution increased with time, but eventually approached equilibrium after 10 min, and the higher concentration of H<sup>+</sup> led to higher iron concentration in the reaction solution. The kinetics of desorption of Fe<sup>2+</sup> from the ferrous-substituted resin can be considered as the reverse process of adsorption of H<sup>+</sup> to the resin.



The ion-exchange process can be described by the Lagergren first-order model (20, 21). Total ferrous ion in solution can be calculated as

$$[\text{Fe}_{\text{total}}^{2+}] = q_{\text{em}}(1 - e^{-k_2 t}) \quad (2)$$



**Figure 1.** Degradation of DNOC (11.4  $\mu\text{g/mL}$ ) in resin-Fe system with various amounts of HCl added. The delivery rate of 0.189 M  $\text{H}_2\text{O}_2$  was kept constant at 0.5 mL/min.

where  $[\text{Fe}_{\text{total}}^{2+}]$  is the total concentration of  $\text{Fe}^{2+}$ ,  $t$  is time,  $q_{\text{em}}$  is the equilibrium concentration of  $\text{Fe}^{2+}$  in solution, and  $k_2$  is the rate constant of the first-order ion-exchange reaction.

The model fitting shown in **Figure 2** matched well with the experimental data, indicating that it is appropriate to describe the ion-exchange process as a pseudo-first-order reaction.  $q_{\text{em}}$ , the equilibrium concentration of  $\text{Fe}^{2+}$ , and  $k_2$ , the rate constant of the ion-exchange reaction, were calculated by the model fitting and are listed in **Table 1** ( $\text{Fe}^{2+}$  measurement section). The values of  $k_2$  range from 0.703 to 1.13, whereas it would be expected to be constant in an ideal situation. Furthermore, the regression for  $\text{Fe}^{2+}$  desorption data is not optimal ( $R^2$  ranges from 0.778 to 0.941). This is mainly because total Fe was measured to represent the  $\text{Fe}^{2+}$  released from the resin. To measure total Fe,  $\text{Fe}^{3+}$  needs to be reduced to  $\text{Fe}^{2+}$  (30). This complicated process may cause inconsistent results. Furthermore, the pH change as a result of the Fenton reaction will also affect the desorption rate of  $\text{Fe}^{2+}$ .

The kinetics of the ion-exchange process can also be described as a second-order process (20, 21). The second-order model was tested on the desorption data (results not shown), but although it was a good fit for these data, it provided a very poor fit for the degradation model shown below and was not considered further.

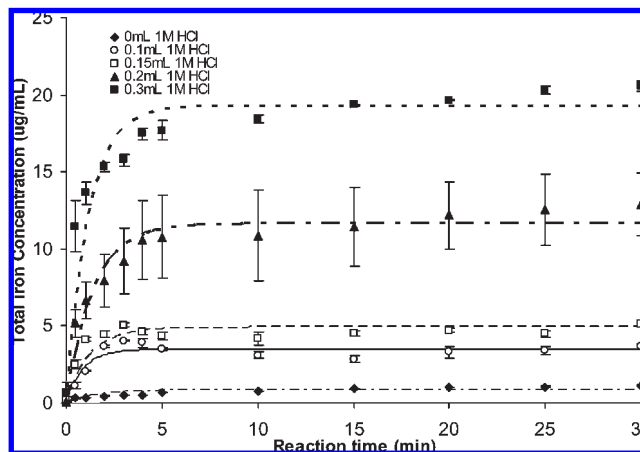
**Fenton Degradation Model for  $\text{Fe}^{2+}$ -Substituted Resin and  $\text{H}_2\text{O}_2$ .** On the basis of the desorption model, the addition of  $\text{Fe}^{2+}$  to the system in this study can be described as a first-order process (eq 2), and this assumption was used to develop a Fenton degradation model. In the Fenton system,  $\text{Fe}^{2+}$  is continually oxidized by  $\text{H}_2\text{O}_2$  (11). Therefore, available  $\text{Fe}^{2+}$  in the reaction solution for the Fenton reaction is proportional to the desorption rate of  $\text{Fe}^{2+}$  from the ferrous-substituted resin

$$[\text{Fe}^{2+}] = \frac{d[\text{Fe}_{\text{total}}^{2+}]}{dt} \pi = k_2 q_{\text{em}} \pi e^{-k_2 t} \quad (3)$$

where  $\pi$  is the average lifetime of  $\text{Fe}^{2+}$ . Because  $\text{H}_2\text{O}_2$  is supplied constantly, its concentration in the system can be simplified as

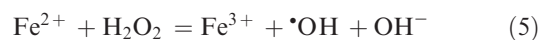
$$[\text{H}_2\text{O}_2] = \nu_0 t \quad (4)$$

where  $\nu_0$  is the delivery rate of  $\text{H}_2\text{O}_2$ . In the Fenton reaction, hydroxyl radicals are generated as shown in the following



**Figure 2.** Pseudo-first-order kinetics of  $\text{Fe}^{2+}$  desorption from  $\text{Fe}^{2+}$ -substituted resin with different amounts of HCl added. Total iron concentration was measured to represent  $\text{Fe}^{2+}$  released from resin. The lines are model fitting results.

equation:



As previously studied (11), the generation rate of hydroxyl radical in the Fenton reaction can be expressed as

$$\left(\frac{d[\cdot\text{OH}]}{dt}\right) = k_1 [\text{Fe}^{2+}] [\text{H}_2\text{O}_2] \quad (6)$$

where  $k_1$  is the rate constant for the generation rate of hydroxyl radical and  $[\text{H}_2\text{O}_2]$  is the concentration of hydrogen peroxide. Substituting eqs 3 and 4 into eq 6, we obtain

$$\left(\frac{d[\cdot\text{OH}]}{dt}\right) = k_1 k_2 q_{\text{em}} \pi e^{-k_2 t} \nu_0 t \quad (7)$$

According to previous work (11), the degradation of the target compound is a second-order reaction

$$-\frac{d[\text{DNOC}]}{dt} = k [\cdot\text{OH}] [\text{DNOC}] \quad (8)$$

where  $k$  is the rate constant of this reaction. Assuming that the instantaneous concentration of hydroxyl radical is proportional to its generation rate (11), we obtain

$$[\cdot\text{OH}] = \lambda \left(\frac{d[\cdot\text{OH}]}{dt}\right) \quad (9)$$

where  $\lambda$  is the average lifetime of the hydroxyl radical. Substituting eqs 7 and 9 into eq 8 we obtain

$$-\frac{d[\text{DNOC}]}{dt} = k \lambda (k_1 k_2 q_{\text{em}} \pi e^{-k_2 t} \nu_0 t) [\text{DNOC}] \quad (10)$$

and the integration format

$$\ln \frac{[\text{DNOC}]_t}{[\text{DNOC}]_0} = k \lambda k_1 q_{\text{em}} \pi \nu_0 \left( \frac{1}{k_2} - \frac{e^{-k_2 t}}{k_2} (tk_2 + 1) \right) \quad (11)$$

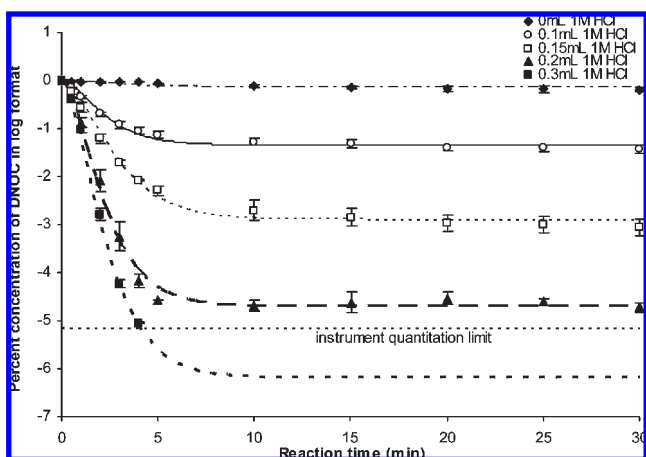
Equation 11 describes the Fenton degradation in this system with  $k \lambda k_1 q_{\text{em}} \pi \nu_0$  treated as one variable and  $k_2$  as the other variable.

**Fenton Degradation of DNOC with Different HCl Concentrations.** According to eq 11, the plot of  $\ln([\text{DNOC}]_t/[\text{DNOC}]_0)$  against time  $t$  can give the values of  $k_2$  and

**Table 1.** Regression Results of DNOC Degradation with Different Amounts of 1 M HCl Added<sup>a</sup>

		HCl added			
		0.100 mL	0.150 mL	0.200 mL	0.300 mL
Fe <sup>2+</sup> measurement	$q_{em}$ ( $\mu\text{g/mL}$ )	3.50	4.91	11.7	19.3
	$k_2$ (1/min)	1.13	0.798	0.703	0.853
	$R^2$	0.873	0.778	0.941	0.866
DNOC Fenton degradation measurement	$k\lambda k_1 q_{em} \pi \nu_0$	1.07	1.91	3.86	4.92
	$k_2$ (1/min)	0.797	0.659	0.824	0.795
	$R^2$	0.983	0.990	0.994	0.999
$k\lambda k_1 \pi \nu_0$		0.307	0.390	0.331	0.254

<sup>a</sup> The delivery rate of 0.189 M H<sub>2</sub>O<sub>2</sub> was kept constant at 0.5 mL/min.

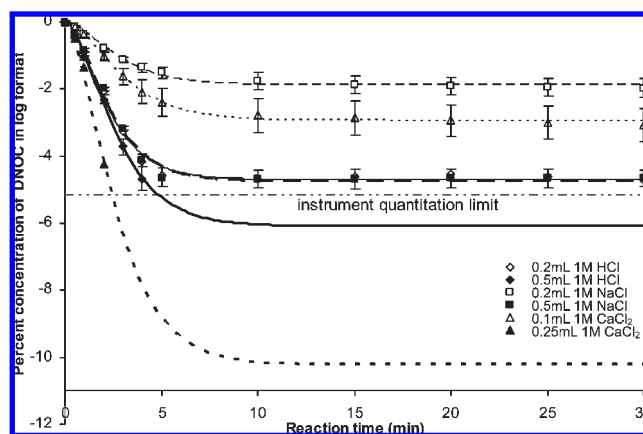


**Figure 3.** Degradation of DNOC (11.4  $\mu\text{g/mL}$ ) in resin-Fe system with various HCl concentrations in logarithm format. The delivery rate of 0.189 M H<sub>2</sub>O<sub>2</sub> was kept constant at 0.5 mL/min. The lines are model fitting results.

$k\lambda k_1 q_{em} \pi \nu_0$ . The term  $k\lambda k_1 q_{em} \pi \nu_0$  can be used to evaluate the degradation rate of the target compound. A greater value of  $k\lambda k_1 q_{em} \pi \nu_0$  implies a greater degradation rate of DNOC.  $q_{em}$ , the equilibrium concentration of Fe<sup>2+</sup>, can be obtained from the first-order fitting of the Fe<sup>2+</sup> desorption data (Table 1). Knowing  $q_{em}$  and  $k\lambda k_1 q_{em} \pi \nu_0$ , the term  $k\lambda k_1 \pi \nu_0$  can be calculated.  $k$ ,  $k_1$ , and  $k_2$  are reaction rate constants; therefore, their values should be constant under different concentrations of H<sup>+</sup>; the delivery rate of H<sub>2</sub>O<sub>2</sub>,  $\nu_0$ , was also fixed in these experiments. It is of interest to examine the value of  $k\lambda k_1 \pi \nu_0$  under different H<sup>+</sup> concentrations because it can be used as a measurement of the lifetime of Fe<sup>2+</sup> and the hydroxyl radical ( $\lambda\pi$ ).

The experimental results shown in Figure 1 are replotted in logarithmic format in Figure 3. The dots are experimental data, and the lines are the fitting of the model. The model fits the experimental data well, especially in the first 5 min. The plots become flat after 10 min, implying that the reaction rates decrease dramatically after the initial steps. This result coincides with the Fe<sup>2+</sup> concentrations in solutions, indicating that the reaction rate is determined by the concentration of Fe<sup>2+</sup> released from the resin.

The fitting of the DNOC concentration gives the values of  $k\lambda k_1 q_{em} \pi \nu_0$  and  $k_2$ , which are listed in Table 1. With more HCl added to the system, the values of  $k\lambda k_1 q_{em} \pi \nu_0$  increase, implying a greater degradation rate of DNOC. The values of  $k_2$  remain relatively stable and range from 0.659 to 0.824 (DNOC Fenton degradation measurement section in Table 1), suggesting that the model describes the experiment



**Figure 4.** Degradation of DNOC (11.4  $\mu\text{g/mL}$ ) in resin-Fe system with various cation concentrations in logarithm format. The lines are model fitting results. The delivery rate of 0.189 M H<sub>2</sub>O<sub>2</sub> was kept constant at 0.5 mL/min.

well. Because lifetimes  $\lambda$  and  $\pi$  cannot be obtained separately, the term  $k\lambda k_1 \pi \nu_0$  was used to indicate the reaction of DNOC. The value of  $k\lambda k_1 \pi \nu_0$ , derived from  $k\lambda k_1 q_{em} \pi \nu_0$  and  $q_{em}$ , increases from 0.307 (1 mL of HCl) to 0.390 (0.15 mL of HCl) and then decreases to 0.254 (0.3 mL of HCl). This suggests that the lifetimes of Fe<sup>2+</sup> and/or the hydroxyl radical ( $\lambda\pi$ ) are relatively stable under constant delivery rate of H<sub>2</sub>O<sub>2</sub> and a varying delivery rate of Fe<sup>2+</sup> within a certain range, whereas the optimal values can be obtained when 0.15 mL of 1 M HCl is added.

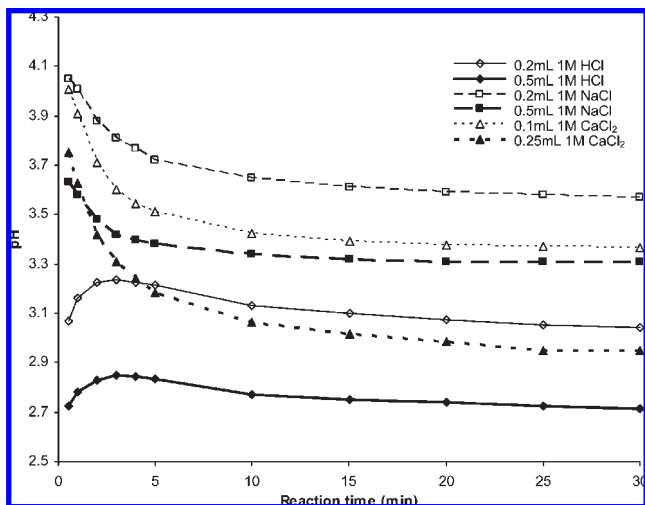
**Fenton Degradation of DNOC with Different Cations Added.** In addition to H<sup>+</sup>, other cations such as Na<sup>+</sup> and Ca<sup>2+</sup> were also used to exchange with the Fe<sup>2+</sup> in the resin. Different amounts of 1 M HCl, NaCl, and CaCl<sub>2</sub> were added to the system at the beginning of the reaction. The experimental results as well as the model simulation are shown in Figure 4. The model successfully simulated the experimental data. DNOC was completely degraded within 10 min of reaction when 0.5 mmol of cations was added (Figure 4). The performance of our method was much faster than sono-electro-Fenton and electro-Fenton processes, which took > 90 min to completely degrade DNOC (28). It was also faster than photo-Fenton and Fenton, which took > 30 min to completely degrade DNOC (29).

It is of interest to examine the pH during these reactions; the values are shown in Figure 5. The starting pH values before the addition of cations were 5–5.2 for all of the reactions (not shown in the figure). In the Fenton reaction facilitated by H<sup>+</sup>, the pH curve reaches a peak at 3 min and decreases slowly thereafter. The pH change can be described

**Table 2.** Regression Results of DNOC Degradation under Different Delivery Rates of H<sub>2</sub>O<sub>2</sub><sup>a</sup>

H <sub>2</sub> O <sub>2</sub> concn (M)	0.0118	0.0236	0.0473	0.0946	0.189	0.378	0.757
H <sub>2</sub> O <sub>2</sub> delivery rate (μmol/min)	5.91	11.8	23.6	47.3	94.6	189	378
q <sub>em</sub> (μg/mL)	8.21	7.90	8.46	11.9	9.20	6.78	8.22
av Fe <sup>2+</sup> delivery rate during first 5 min (μmol/min)	2.85	1.68	2.15	2.74	3.19	2.40	2.93
delivery ratio H <sub>2</sub> O <sub>2</sub> :Fe <sup>2+</sup>	2.07	7.03	11.0	17.2	29.6	78.7	129
kλk <sub>1</sub> q <sub>em</sub> πν <sub>0</sub>	0.662	1.16	1.80	2.45	3.86	3.52	3.73
kλk <sub>1</sub> πν <sub>0</sub>	0.0806	0.147	0.213	0.206	0.420	0.518	0.453

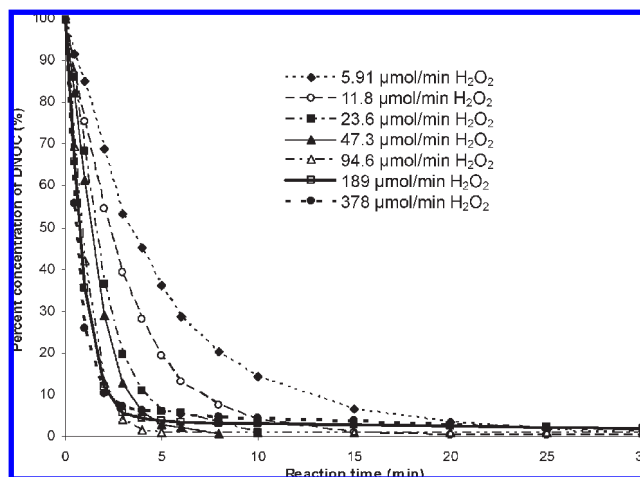
<sup>a</sup> HCl (1 M, 0.2 mL) was added at the start of all reactions.



**Figure 5.** Measured pH data in Fenton degradation of DNOC (11.4 μg/mL) with various amount of cations added. The delivery rate of 0.189 M H<sub>2</sub>O<sub>2</sub> was kept constant at 0.5 mL/min.

as the sum of three different processes, the adsorption of H<sup>+</sup> to the resin, the generation of H<sup>+</sup> during the Fenton degradation of DNOC, and the continuous addition of acidic H<sub>2</sub>O<sub>2</sub>. It is expected that the process of adsorption of H<sup>+</sup> to the resin mainly takes place in the first few minutes, and the rate is greatly reduced after that. Therefore, the generation of H<sup>+</sup> during the Fenton degradation and the continuous addition of acidic H<sub>2</sub>O<sub>2</sub> should be the dominant determinants of pH after 3 min, resulting in a slow decrease of pH, as seen in the figure. For the reactions facilitated by the other cations, Ca<sup>2+</sup> and Na<sup>+</sup>, the pH values should be mainly controlled by only two processes, namely, the generation of H<sup>+</sup> during Fenton degradation of DNOC and the continuous addition of acidic H<sub>2</sub>O<sub>2</sub>. If this is the case, the pH curves for these reactions should decrease throughout the entire reaction, and this is what is seen in **Figure 5**.

When a small amount of cation (0.2 mL of 1 M for H<sup>+</sup> and Na<sup>+</sup> and 0.1 mL of 1 M for Ca<sup>2+</sup>) was added, H<sup>+</sup> had the highest efficiency to facilitate the Fenton reaction (**Figure 4**). It is suggested that H<sup>+</sup> not only released the Fe<sup>2+</sup> from the resin but also reduced the pH to about 3 (**Figure 5**), which provided optimal acidic conditions for the Fenton reaction (II). Ca<sup>2+</sup> at 0.1 mL of 1 M accelerated the degradation of DNOC more efficiently than 0.2 mL of 1 M Na<sup>+</sup>, which has an equivalent charge to 0.1 mL of Ca<sup>2+</sup>. This result provided strong evidence that doubly charged Ca<sup>2+</sup> is a more efficient exchanger cation than singly charged Na<sup>+</sup>. In the case when a larger amount of cation (0.5 mL 1 M) was added, the H<sup>+</sup>-facilitated Fenton reaction was slower than the Ca<sup>2+</sup>-facilitated reaction. This is due to the fact that the pH of the Fenton reaction produced by H<sup>+</sup> is similar to that produced by Ca<sup>2+</sup> (**Figure 5**); hence, the advantage of low pH from H<sup>+</sup> no longer exists.



**Figure 6.** Degradation of DNOC (11.4 μg/mL) in resin-Fe system with various H<sub>2</sub>O<sub>2</sub> delivery rates. HCl (1 M, 0.2 mL) was added at the start of the reaction.

**Fenton Degradation of DNOC with Various H<sub>2</sub>O<sub>2</sub> Delivery Rates.** The Fenton degradation of DNOC was performed with the same amount of HCl added (0.2 mL of 1 M) at the beginning of each reaction and different H<sub>2</sub>O<sub>2</sub> delivery rates. Experimental results and model fitting are shown in **Figure 6**.

The iron concentrations were measured, and the calculated q<sub>em</sub> values are listed in **Table 2**. The equilibrium concentration of Fe<sup>2+</sup> is relatively stable under different delivery rates of H<sub>2</sub>O<sub>2</sub>. No obvious correlation between q<sub>em</sub> and delivery rate of H<sub>2</sub>O<sub>2</sub> was found, implying that H<sub>2</sub>O<sub>2</sub> does not affect the ion-exchange process of the resin.

Values of kλk<sub>1</sub>q<sub>em</sub>πν<sub>0</sub> from model fitting are listed in **Table 2**. The values of kλk<sub>1</sub>q<sub>em</sub>πν<sub>0</sub> indicate that increasing the H<sub>2</sub>O<sub>2</sub> delivery rate from 5.91 to 94.6 μmol/min significantly increased the degradation rate of DNOC. However, for the reactions with the highest H<sub>2</sub>O<sub>2</sub> delivery rate (189 and 378 μmol/min), the values of kλk<sub>1</sub>q<sub>em</sub>πν<sub>0</sub> are lower than that at 94.6 μmol/min. Furthermore, the reaction with the two highest H<sub>2</sub>O<sub>2</sub> delivery rates slowed after 3 min, leading to incomplete degradation of DNOC. The high delivery rate of H<sub>2</sub>O<sub>2</sub> may have reduced the lifetime of hydroxyl radical and Fe<sup>2+</sup>, thus causing the degradation rate of DNOC to be reduced compared to the lower delivery rate of H<sub>2</sub>O<sub>2</sub>.

To calculate the delivery molar ratio of H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup>, the average delivery rate of Fe<sup>2+</sup> at the end of 5 min was calculated because most of the reaction had taken place at that time. From the information obtained, it can be concluded that the delivery rate of H<sub>2</sub>O<sub>2</sub> at 94.6 μmol/min, when the delivery molar ratio of H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> equals 29.6, is the optimal condition for this reaction.

This is the first time that kinetic modeling of the Fenton degradation of a herbicide, using an ion-exchange resin as the source of iron, has been done. The developed model

increases the understanding of the ion-exchange mechanism of the resin and its effect on the Fenton reaction.

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