CHAPTER 4
RESULTS AND DISCUSSION

4.1 Surface Water Samples

4.1.1 Characteristics of Surface Water Samples

Surface water samples were collected 3 times per week between June and July 2002. A total of 27 samples were collected and separately used for 27 different Fenton's experimental conditions shown in Table 4.1. Prior to the experiments, the samples were analyzed for initial pH, DOC, and AOC and the results are also shown in Table 4.1. Initial pH of the samples was between 7.3 and 7.8 whereas initial DOC ranged from 7.21 to 8.12 mg/L. AOC_{total} was between 115 and 150 µg C/L with more than 70% of which were contributed by AOC_{P17} in all samples. AOC_0/DOC_0 was quite low indicating that less than 2% of the organics could be used to support the growth of microorganisms.

Table 4.1 Initial pH (pH_0), DOC (DOC_0), AOC (AOC_0), and AOC_0/DOC_0 of surface water samples.

Conditions			pH_0	DOC_0 (mg/L)	AOC_0 (µg C/L)			AOC_0 DOC_0 x 100
H_2O_2:DOC	Fe^{2+}:H_2O_2	pH			P17	NOX	Total	
0.5:1	0.05:1	2	7.32	7.52	91	33	124	1.64
		3	7.30	7.55	104	30	134	1.77
		4	7.38	7.54	101	35	136	1.80
0.5:1	0.1:1	2	7.52	7.34	91	30	121	1.65
		3	7.52	7.35	93	31	124	1.69
		4	7.54	7.42	98	30	128	1.73
0.5:1	0.5:1	2	7.41	7.82	109	34	143	1.83
		3	7.44	7.77	112	33	145	1.87
		4	7.41	7.85	102	33	135	1.72
2:1	0.05:1	2	7.80	7.25	80	35	115	1.59
		3	7.77	7.21	86	32	118	1.64
		4	7.75	7.27	84	31	115	1.58
2:1	0.1:1	2	7.34	7.67	92	39	131	1.71
		3	7.37	7.61	93	34	127	1.67
		4	7.39	7.64	87	33	120	1.57
2:1	0.5:1	2	7.67	7.44	110	32	142	1.91
		3	7.73	7.50	103	35	138	1.84
		4	7.72	7.52	93	38	131	1.74

(Cont.)

Conditions			pH_0	DOC_0 (mg/L)	AOC_0 (μg C/L)			$\frac{AOC_0}{DOC_0}$ x 100
H_2O_2:DOC	Fe^{2+}:H_2O_2	pH			P17	NOX	Total	
10:1	0.05:1	2	7.46	7.43	113	35	148	1.99
		3	7.50	7.50	98	34	132	1.76
		4	7.50	7.51	109	35	144	1.91
10:1	0.1:1	2	7.76	8.12	114	36	150	1.85
		3	7.71	8.03	98	35	133	1.66
		4	7.74	8.07	108	37	145	1.80
10:1	0.5:1	2	7.52	7.87	114	34	148	1.88
		3	7.51	7.92	103	36	139	1.76
		4	7.46	7.94	105	38	143	1.80

4.1.2 DOC Changes during Fenton's Reaction

Figure 4.1 presents average normalized DOC (DOC_t/DOC_0) of surface water samples versus reaction time at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH. It was observed that DOC remarkably decreased during the early stage of reaction time. After which, it leveled off and remained quite constant until the end of experiments. DOC reduction ranged approximately from 5 to 15% or 0.35 to 1.2 mg/L. At all tested Fe^{2+}doses, the increases in H_2O_2 concentration resulted in dramatic reduction of DOC. Different Fe^{2+} doses did not significantly influence DOC elimination. However, Fenton's reaction with higher Fe^{2+} doses tended to have higher rates of DOC reduction. The effect of pH on DOC reduction was more significant at higher H_2O_2 doses. DOC reduction at pH 3 and pH 4 was more than that at pH 2. Even so, at some Fe^{2+}:H_2O_2:DOC ratios, pH 3 provided higher DOC reduction than pH 4.

Since AOC increase and DOC reduction simultaneously took place and AOC is part of DOC, this indicates that Fenton's reaction reacted with DOC to yield a simpler form, that was AOC, and in the mean time some portions of which were completely oxidized to CO_2.

4.1.3 Effects of H_2O_2 Dose on AOC Production in Surface Water Samples

Figure 4.2 shows average AOC production versus reaction time at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios and pH. After the onset of Fenton's reaction, AOC production for all conditions notably increased and leveled off at the reaction time of 6 or 10 minutes. Raising H_2O_2 dose notably resulted in the increase of AOC production at all three pH. For instance. At the 10-minute reaction time, Fenton's reaction under the H_2O_2 dose of 0.5:1, the Fe^{2+} dose of 0.05:1, and pH 3 yielded AOC production of 281 μg C/L. When H_2O_2 dose was changed to 2:1 and 10:1 with the same Fe^{2+} dose and pH, AOC production became 1,273 μg C/L (328 % higher than the H_2O_2 dose of 0.5:1) and 1,783 μg C/L (408 % higher than the H_2O_2 dose of 0.5:1), respectively. The rise in AOC concentration may be attributed to an increase of hydroxyl radicals (OH·) since H_2O_2 is the key component in OH· production. It should be noted that these AOC increases occurred simultaneously with DOC reduction and therefore some AOC produced might be mineralized to CO_2.

Figures 4.3 and 4.4 show increases of AOC_{P17} and AOC_{NOX} production versus reaction time at different conditions. Similar to AOC_{total} production, both AOC_{P17} and AOC_{NOX} production rapidly evolved with time during the first few minutes of early reaction time and remained quite constant after that. Higher H_2O_2 concentration provided increases in AOC production for both types. At the H_2O_2 dose of 0.5:1, the AOC_{NOX} production was around 3 times higher than AOC_{P17}. In contrast, at the two higher H_2O_2 doses, the AOC_{P17} production was between 2.5 and 3.5 times higher than the AOC_{NOX} production. This result indicates that such high H_2O_2 concentrations greatly favored the formation of organic by-products that can be used more efficiently by P17 strain such as amino acids, carboxylic acids, alcohols, and carbohydrates (excluding polysaccharides) rather than such compounds as formic, glyoxylic, and oxalic acids, which are major substrates for NOX strain. The low production of AOC_{NOX} may also be due to the fact that high doses of H_2O_2 gave rise to some organic by-products, which were inhibitory to the growth of NOX strain.

4.1.4 Effects of Fe^{2+} Dose on AOC Production in Surface Water Samples

As presented in Figure 4.2, the effect of changing Fe^{2+} dose was significant in the first 10-minute reaction time. At all conditions, more than 50% of AOC formation took place in the first minute; whereas, after 6 minutes, less than 10% of AOC was formed. At the highest Fe^{2+} dose shown in Figure 4.1 c), AOC production instantaneously occurred and was constant after the first minute of the reaction time. For a lower Fe^{2+} dose, AOC production developed slower (Figure 4.1 a and b). To demonstrate this effect, data at the 1-minute reaction time under the H_2O_2:DOC of 10:1 and pH 3 are used as an example. At the Fe^{2+} dose of 0.05:1, AOC production was 1,179 μg C/L but when the Fe^{2+}doses were at 0.1:1 and 0.5:1, AOC production became 1,425 μg C/L (20% higher the Fe^{2+}dose of 0.05:1) and 1,711 μg C/L (45% higher the Fe^{2+}dose of 0.05:1), respectively.

For each type of AOC production illustrated in Figures 4.3 and 4.4, the effects of Fe^{2+} on both were quite similar; higher doses resulted in faster rate of AOC production. It is clear that solely changing Fe^{2+} concentration did not have a remarkable influence (< 6%) on the final production of AOC_{total}, AOC_{P17}, and AOC_{NOX}. This could be probably due to the role of Fe^{2+} in Fenton's reaction, that is, primarily accelerating the rate of OH· production.

4.1.5 Effects of pH on AOC Production in Surface Water Samples

As presented in Figures 4.2, 4.3, and 4.4, besides H_2O_2 dose, initial pH was another factor responsible for the magnitude of AOC production. For all conditions, pH 3 was the most effective in increasing AOC production, whereas pH 4 and pH 2 were the second and the least, respectively. For AOC_{total} and $AOCP_{17}$, differences in AOC production among the three pH were insignificant when the H_2O_2 dose was low. On the contrary, when the H_2O_2 dose was high, the differences became significant. This suggests that the increases of AOC_{total} and AOC_{P17} were mainly due to applied H_2O_2 concentration while the pH had a complementary role on the phenomenon. For AOC_{NOX}, the role of pH in enhancing AOC production was as important as that of H_2O_2. Sometimes a lower H_2O_2 dose at one pH offered higher AOC production than a higher H_2O_2 dose at another pH. For instance, the production at the H_2O_2 dose of 2:1 and pH 3 was higher than that at the H_2O_2 dose of 10:1 and pH 2.

Figure 4.5 shows the increases of pH during the Fenton's reaction. Once Fenton's reaction began, pH briefly evolved before stabilization at all conditions. For each initial pH, the pH profiles were not significantly different. More H_2O_2 input resulted in a higher pH level. After 10 minutes of reaction, pH was quite constant and the H_2O_2 doses of 0.5:1, 2:1, and 10:1 offered the pH increases of 0.35 ± 0.05, 0.50 ± 0.10, 0.87 ± 0.07, respectively. This increase was likely due to the reaction between $OH\cdot$ and H^+ that yielded H_2O.

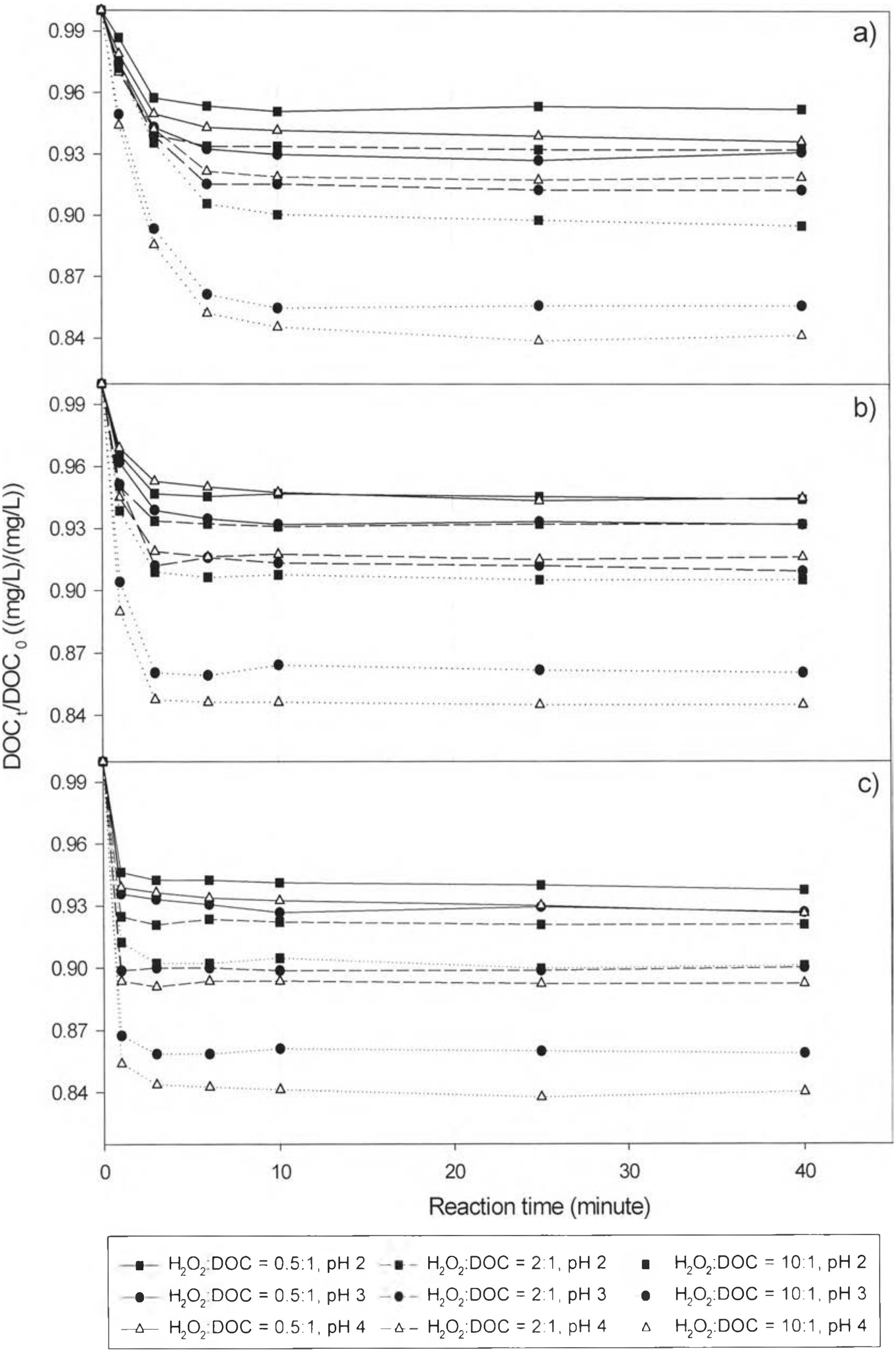

Figure 4.1 Average normalized DOC in surface water samples versus reaction time for different H_2O_2:DOC ratios and pH at a) Fe^{2+}:H_2O_2 of 0.05:1, b) Fe^{2+}:H_2O_2 of 0.1:1, and c) Fe^{2+}:H_2O_2 of 0.5:1.

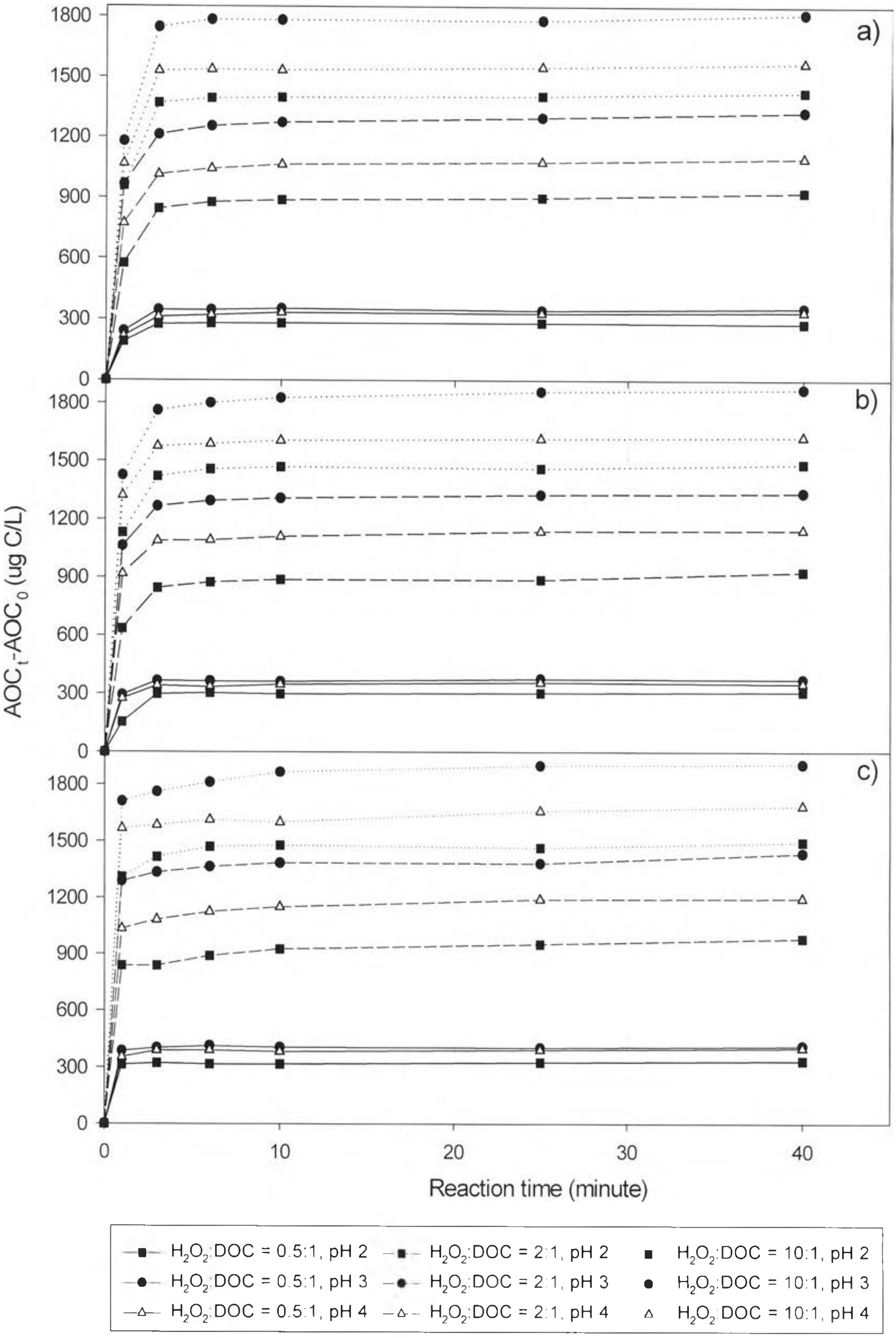

Figure 4.2 Average AOC_{total} increases in surface water samples versus reaction time for different H_2O_2:DOC ratios and pH at a) Fe^{2+}:H_2O_2 of 0.05:1, b) Fe^{2+}:H_2O_2 of 0.1:1, and c) Fe^{2+}:H_2O_2 of 0.5:1.

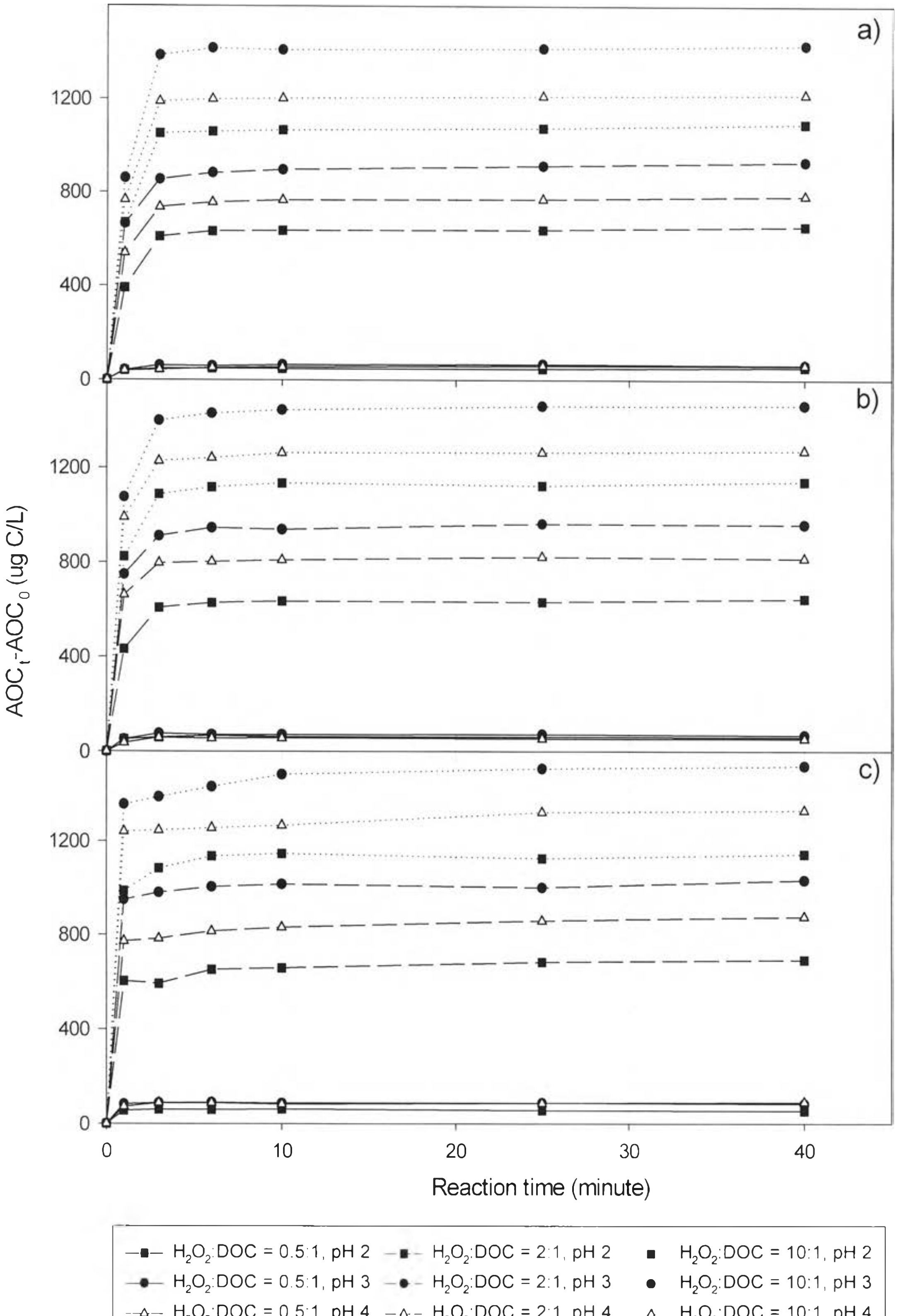

Figure 4.3 Average AOC_{P17} increases in surface water samples versus reaction time for different H_2O_2:DOC ratios and pH at a) Fe^{2+}:H_2O_2 of 0.05:1, b) Fe^{2+}:H_2O_2 of 0.1:1, and c) Fe^{2+}:H_2O_2 of 0.5:1.

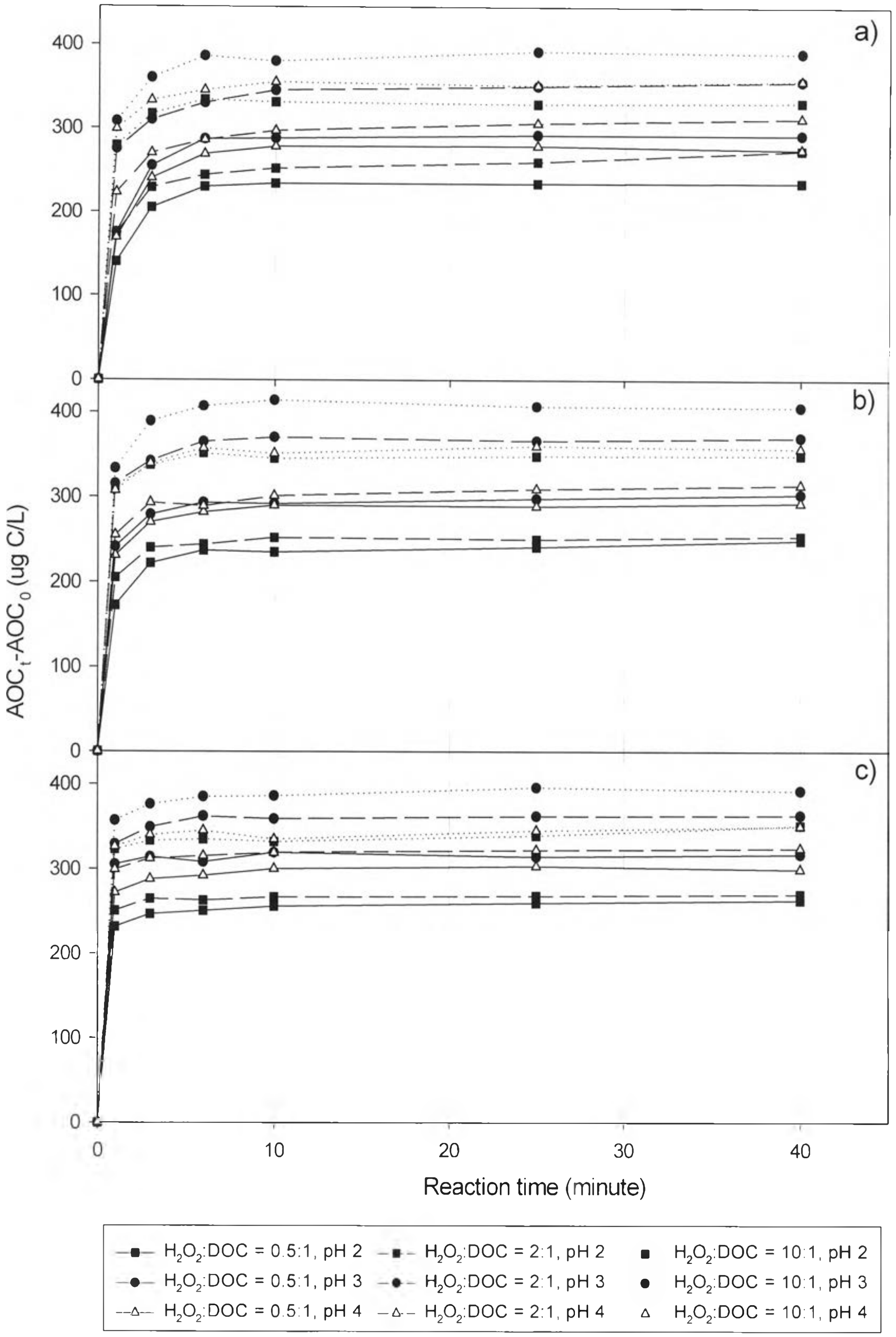

Figure 4.4 Average AOC_{NOX} increases in surface water samples versus reaction time for different H_2O_2:DOC ratios and pH at a) $Fe^{2+}:H_2O_2$ of 0.05:1, b) $Fe^{2+}:H_2O_2$ of 0.1:1, and c) $Fe^{2+}:H_2O_2$ of 0.5:1.

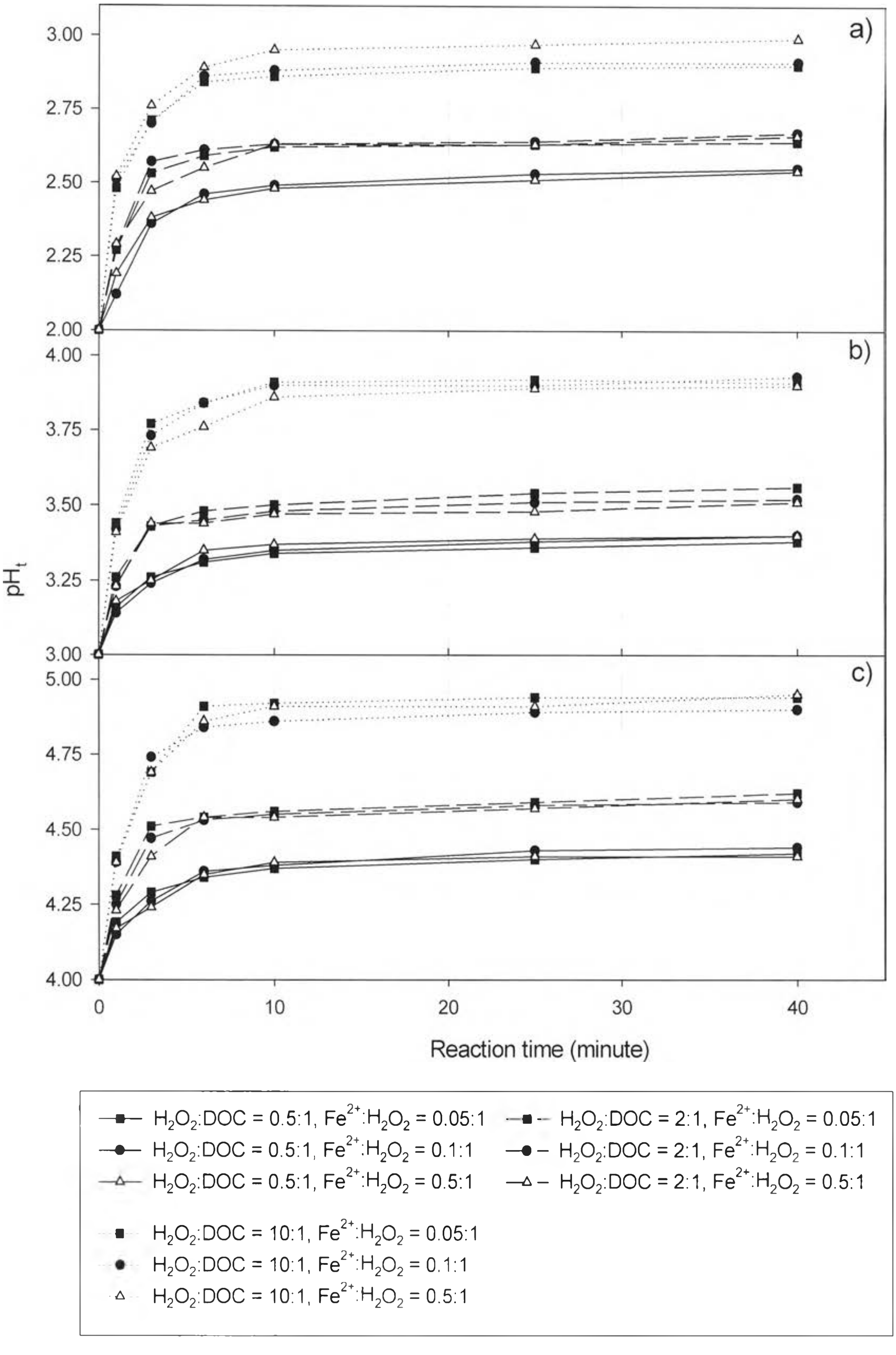

Figure 4.5 Average pH increases in surface water samples versus reaction time at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios: a) initial pH 2, b) initial pH 3, and c) initial pH 4.

4.1.6 Effects of Reaction Time and Kinetics of AOC Production in Surface Water Samples

Table 4.2 presents ratios of AOC productions between the 10-minute and 40-minute reaction time at different experimental conditions. For all conditions tested, more than 94% of AOC_{total} increases occurred during the first 10 minutes of reaction. While, during this reaction time, AOC increases for P17 strain and NOX strain were more than 90%. Therefore, 10 minutes is a minimum time requirement to ensure maximum or near maximum enhancement of AOC concentration by Fenton's reagent.

Table 4.2 Ratios of AOC production of surface water samples at the 10-minute and 40-minute reaction time for different H_2O_2 and Fe^{2+} doses, and pH

Conditions			$(AOC_{10}-AOC_0)/(AOC_{40}-AOC_0)$		
H_2O_2:DOC	Fe^{2+}:H_2O_2	pH	P17	NOX	Total
0.5:1	0.05:1	2	0.9068	1.0400	1.0108
		3	1.0323	0.9863	0.9915
		4	0.9052	1.0109	0.9852
0.5:1	0.1:1	2	1.0517	0.9438	0.9641
		3	1.0099	0.9574	0.9730
		4	1.0769	0.9732	0.9886
0.5:1	0.5:1	2	1.0509	0.9176	0.9548
		3	1.0361	0.9755	0.9902
		4	0.9111	0.9677	0.9550
2:1	0.05:1	2	0.9725	0.9197	0.9580
		3	0.9624	0.9691	0.9593
		4	0.9771	0.9519	0.9699
2:1	0.1:1	2	0.9845	0.9005	0.9558
		3	0.9781	0.9814	0.9798
		4	0.9914	0.9149	0.9694
2:1	0.5:1	2	0.9495	0.9303	0.9439
		3	0.9835	0.9202	0.9658
		4	0.9486	1.0031	0.9631
10:1	0.05:1	2	0.9744	1.0000	0.9804
		3	0.9853	1.0000	0.9840
		4	0.9861	0.9944	0.9771
10:1	0.1:1	2	0.9939	0.9766	0.9899
		3	0.9864	0.9361	0.9744
		4	0.9921	0.9744	0.9883
10:1	0.5:1	2	1.0035	0.9459	0.9893
		3	0.9775	0.9847	0.9786
		4	0.9533	0.9384	0.9496

First and second order kinetic models were employed to describe the rate of AOC increases in the first 10 minutes. The selection of these two models is based on two reasons. First, these models are generally used for determining the reaction rates occurring in the field of water and wastewater engineering. Second, several literatures reported the use of these models for identifying the rate of Fenton's degradation (Benitez et al., 2000; Beltran et al. 1998; and Hagg and Yao, 1992). Kinetic constant (k) of both models were determined graphically and reported with the coefficient of determination (r^2) in order to justify the adequacy of data fitting to the models. In this study, any k values, which have r^2 below 0.90, are considered weak fitting.

For the first-order kinetic model, the kinetic constant (k_1) is the slope of the linear regression line of the data between Ln ((AOC_{40}-AOC_t)/(AOC_{40}-AOC_0)) and reaction time. For the second-order kinetic model, the slope of the linear regression of the plot between 1/(AOC_{40}-AOC_t) and reaction time is the kinetic constant (k_2). The use of AOC_{40} as the ultimate AOC is warranted because the data trend suggested that if there were increase of AOC products after 40 minutes, they should be negligible.

Fittings of AOC productions in the first order model at different conditions are illustrated in Figures 4.6 (AOC_{total}), 4.7 (AOC_{P17}), and 4.8 (AOC_{NOX}). For AOC_{total}, 21 out of 27 fits have $r^2 \geq 0.90$ and its k_1 values varied from 0.05 to 0.45 min^{-1}. For AOC_{P17} and AOC_{NOX}, there are 19 and 16 fits whose $r^2 \geq 0.90$. The k_1 values were between 0.04 and 0.55 min^{-1} for AOC_{P17}, and between 0.05 and 0.48 min^{-1} for AOC_{NOX}. The k_1 values for all type AOC increased when Fe^{2+} dose was changed from 0.05:1 to 0.1:1 but when the Fe^{2+} dose was raised to 0.5:1, the k_1 values decreased to close to zero.

The increases in k_1 values along with the increases in Fe^{2+} doses from 0.05:1 to 0.1:1 are attributed to the role of Fe^{2+} in increasing the rate of AOC production. At the Fe^{2+} dose of 0.5:1, the instantaneous increases of AOC close to the completion could be accounted for unusually and unreliably low k values. Therefore, the kinetics at the Fe^{2+} dose of 0.5:1 could not be determined. Determination of the kinetic of such instantaneous reaction is very difficult or almost possible since several samples have to be taken from the reactors between 0 and 1 minute. For the change of either H_2O_2 dose or pH, their effects on k_1 value were insignificant.

For the second order model, the results are shown in Figures 4.9 (AOCtotal), 4.10 (AOC_{P17}), and 4.11 (AOC_{NOX}). A number of reliable k_2 values ($r^2 \geq 0.90$) were low in comparing with those for the first order model; 12 for AOC_{total}, 11 for AOC_{P17}, and 9 for AOC_{NOX}. At all types of AOC, the effect of Fe^{2+} doses on AOC production is similar to that of the first order model. However, most of the k_2 values were quite low ($<$ 0.056 L/mg.min) and showed insignificant differences. As such, it could be concluded that the first order model is more suitable to describe the increase in AOC production induced by Fenton's reaction.

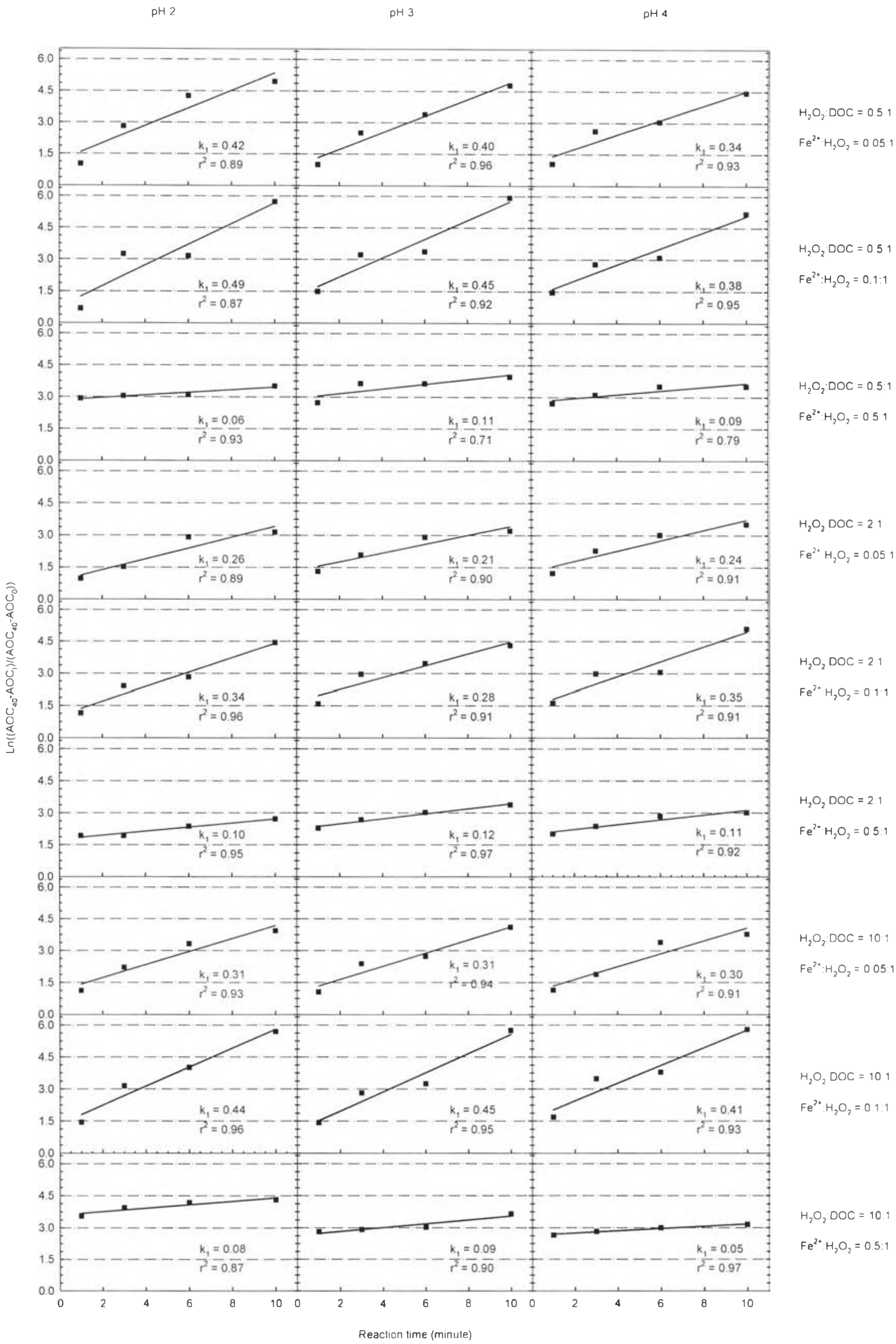

Figure 4.6 Fitting of AOC$_{total}$ production in surface water samples with the first order kinetics at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH

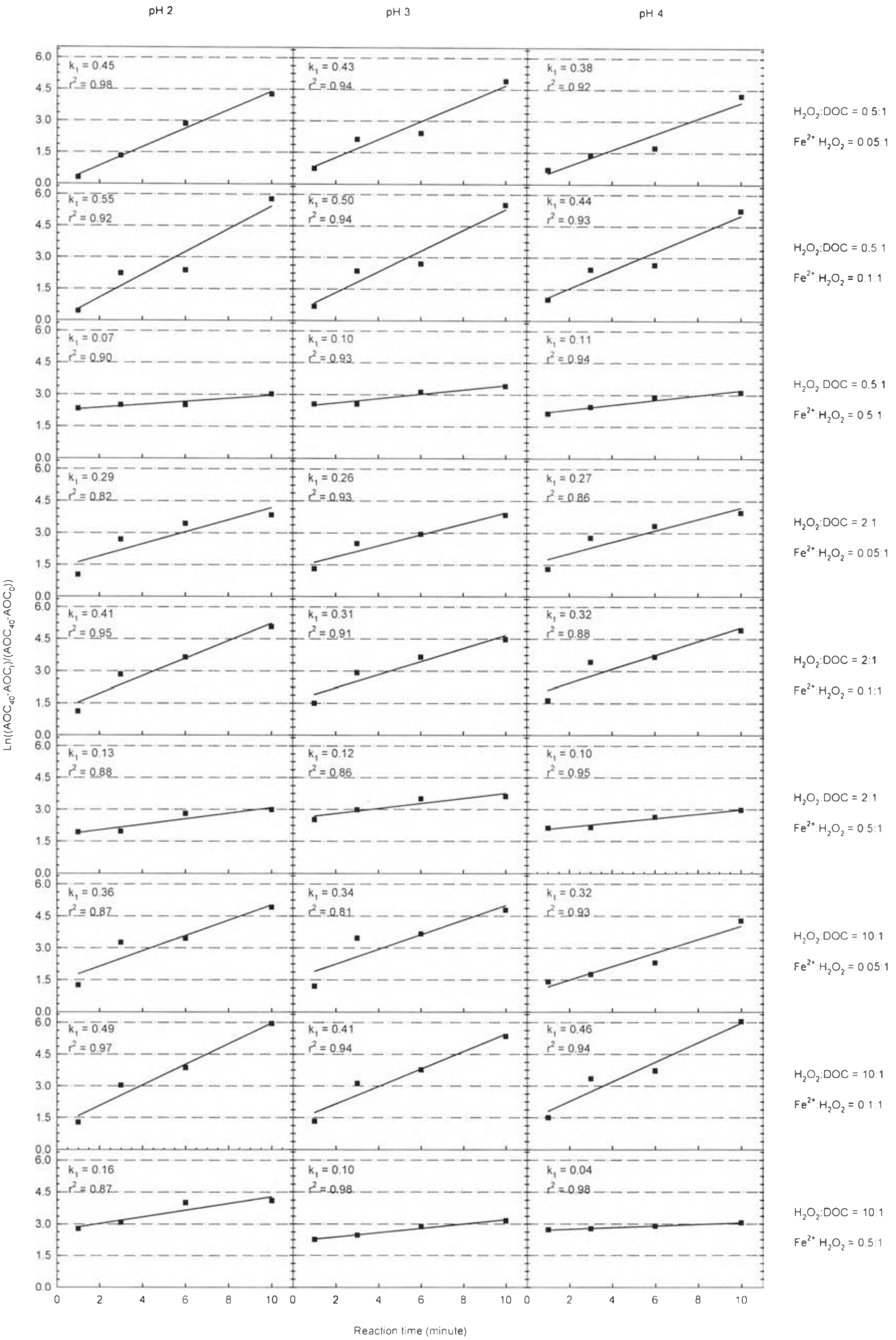

Figure 4.7 Fitting of AOC$_{P17}$ production in surface water samples with the first order kinetics at different H$_2$O$_2$:DOC and Fe^{2+}:H$_2$O$_2$ ratios, and pH

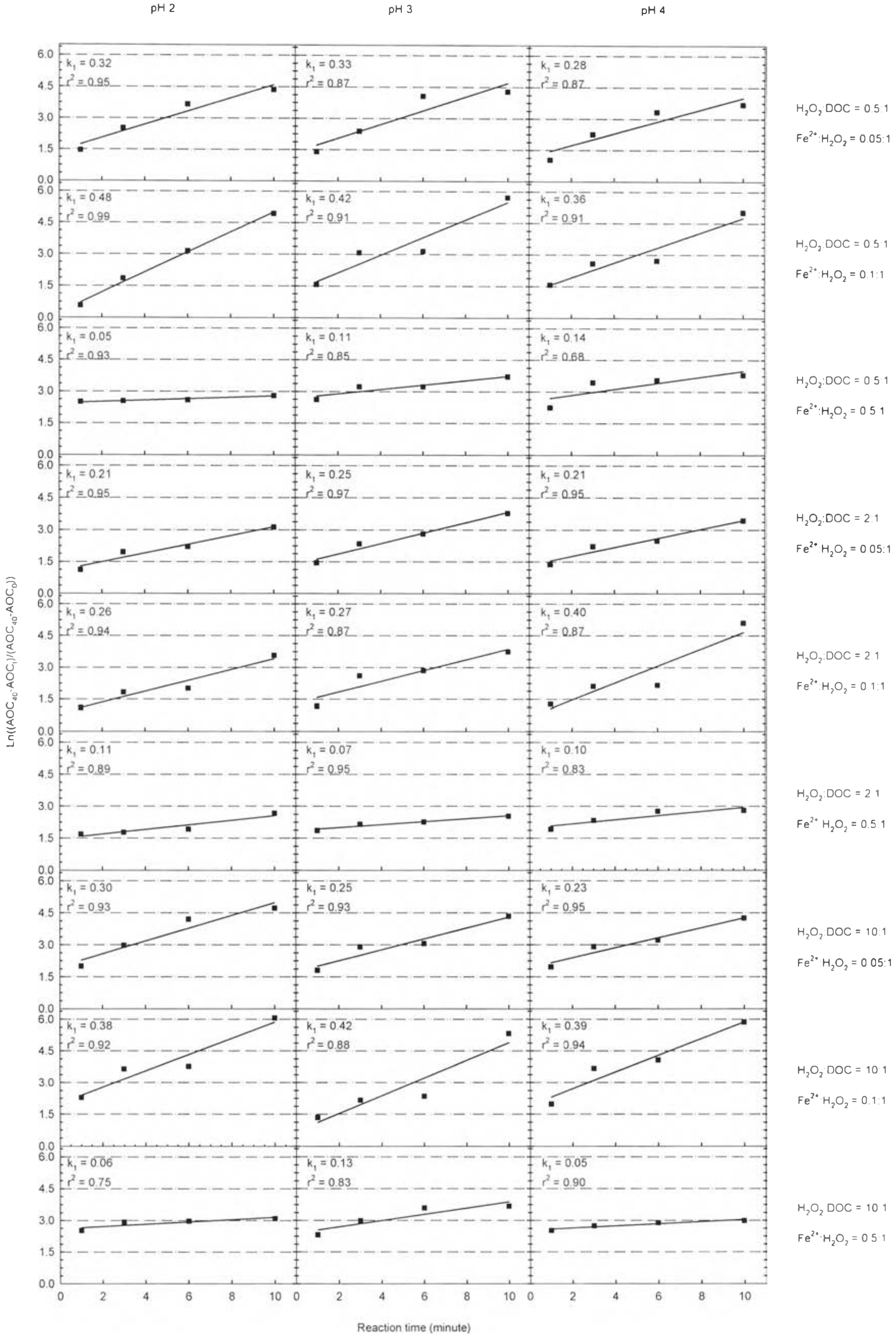

Figure 4.8 Fitting of AOC_{NOX} production in surface water samples with the first order kinetics at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH

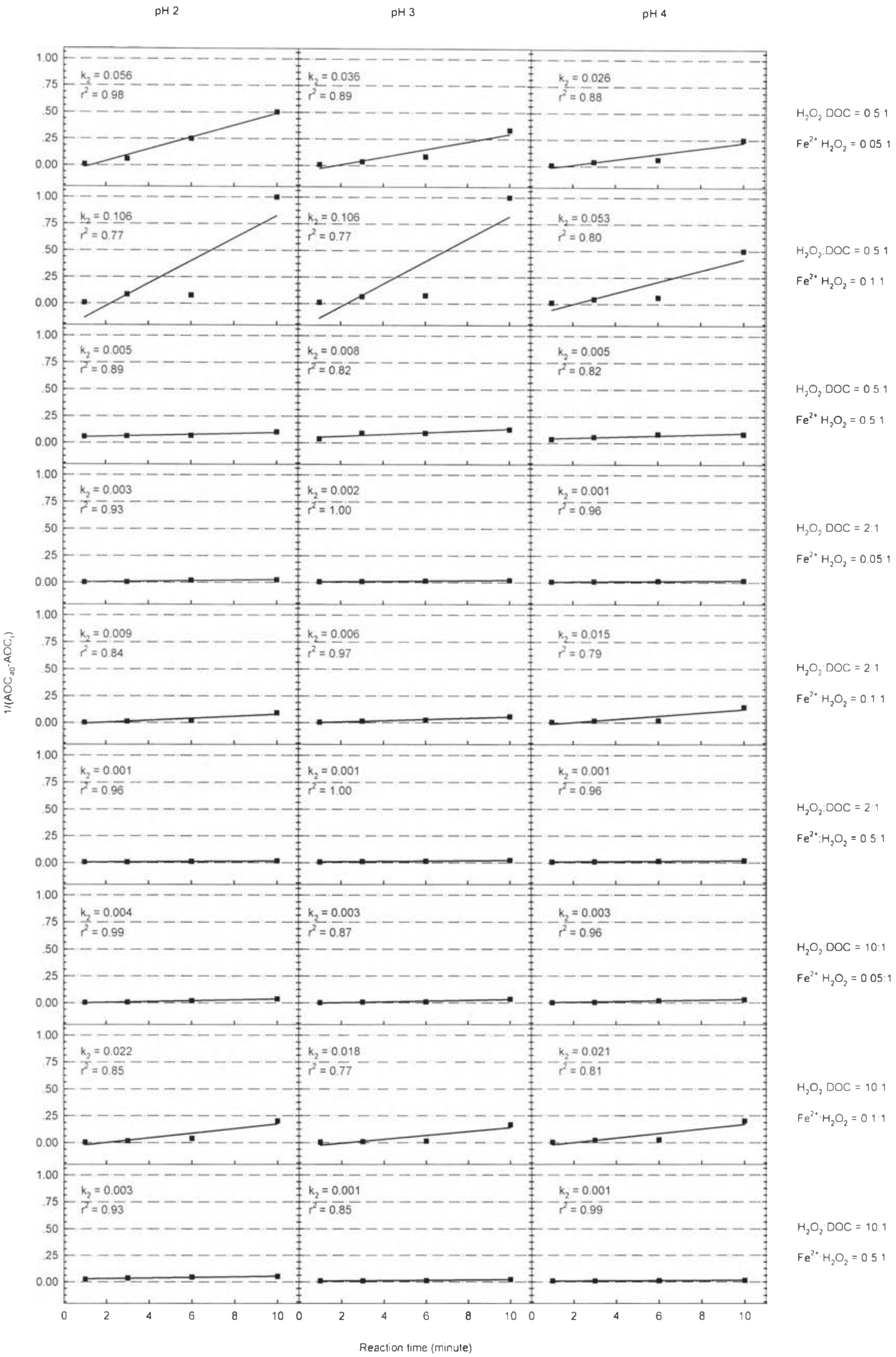

Figure 4.9 Fitting of AOC$_{total}$ production in surface water samples with the second order kinetics at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH

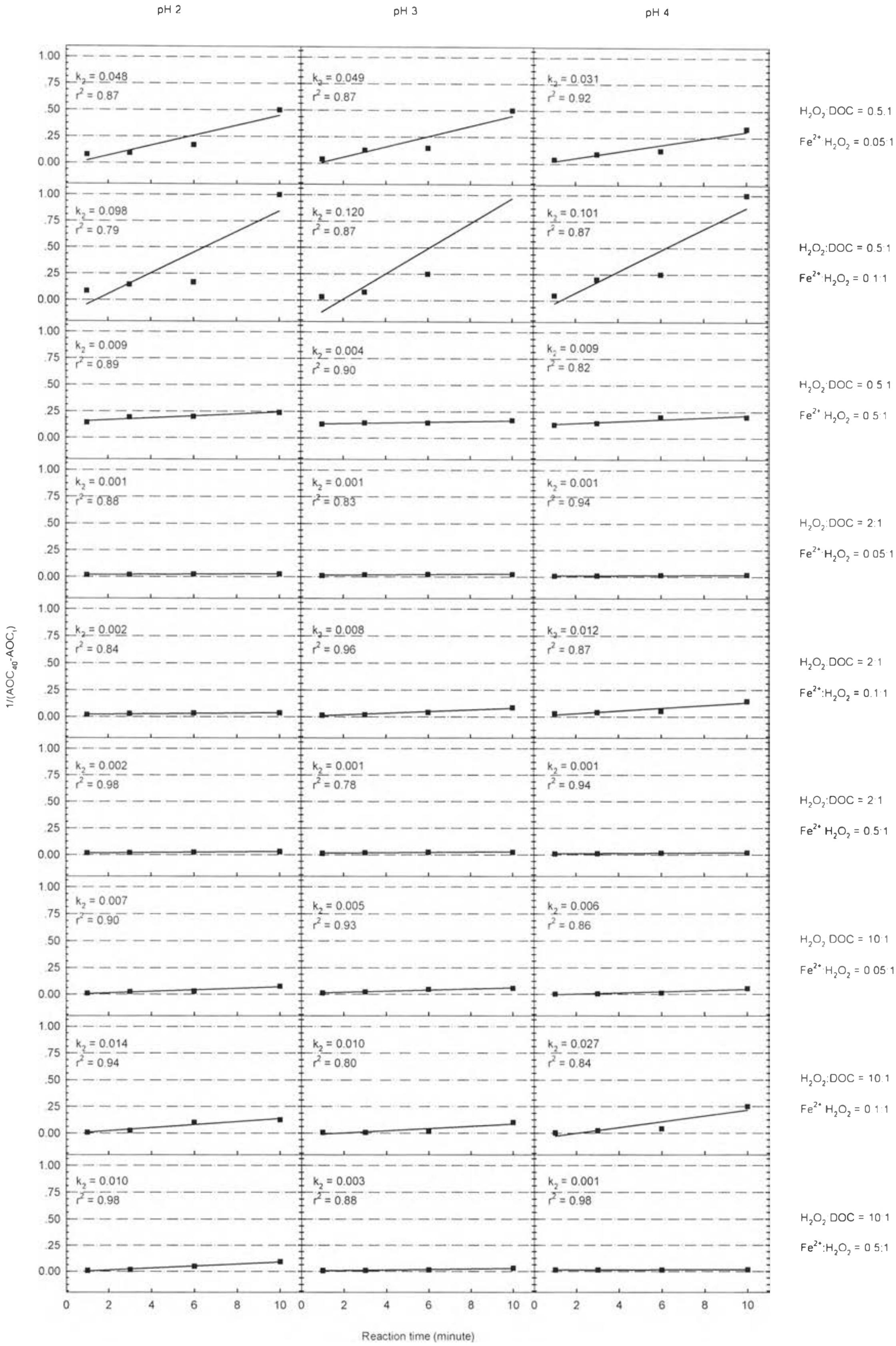

Figure 4.10 Fitting of AOC$_{P17}$ production in surface water samples with the second order kinetics at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH

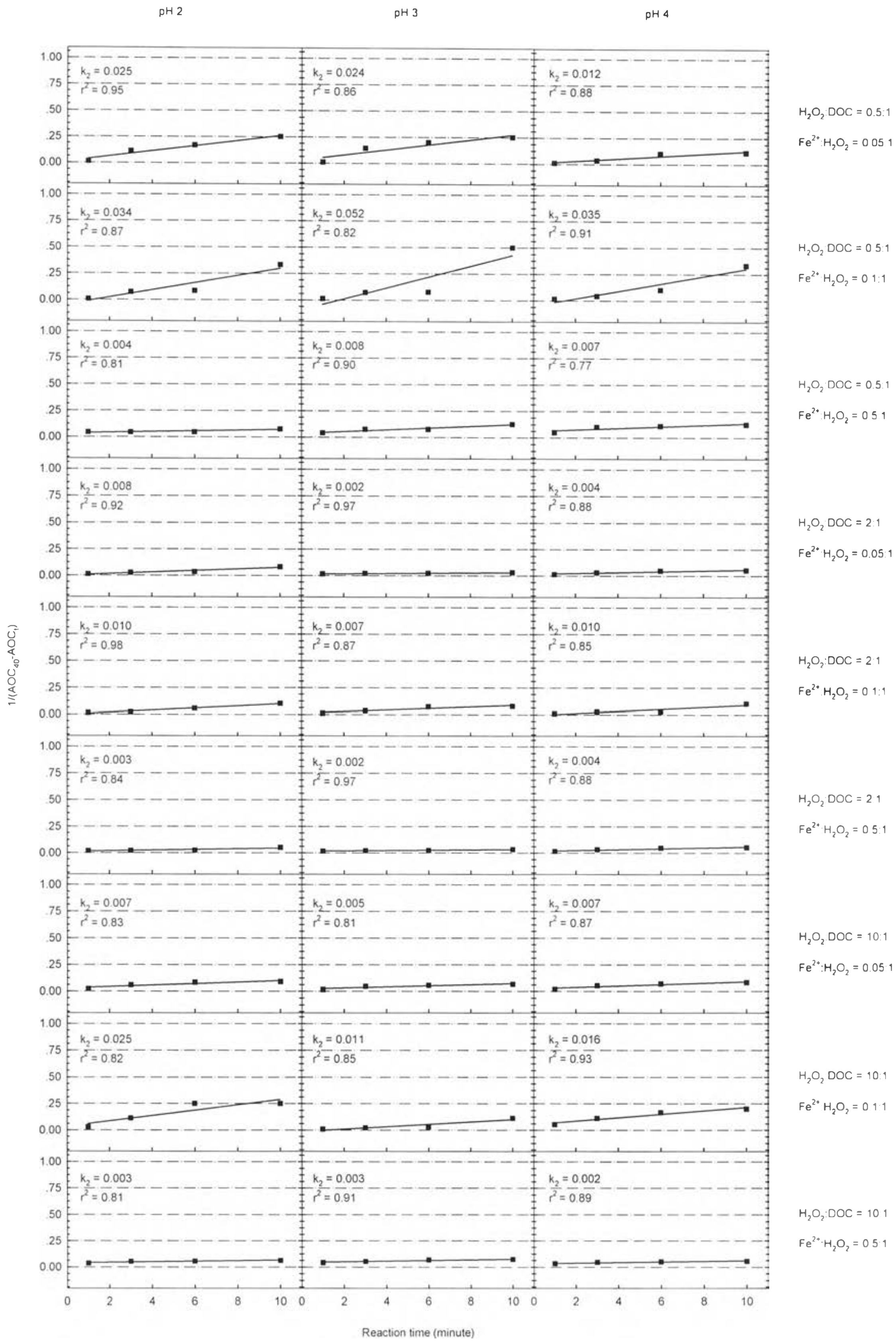

Figure 4.11 Fitting of AOC_{NOX} production in surface water samples with the second order kinetics at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH

4.2 Synthetic Water Samples

4.2.1 Initial Characteristics of Synthetic Water Samples

After the synthetic water samples were prepared by diluting the 2,4-DCP standard solution, they were analyzed for DOC and AOC concentrations. As presented in Table 4.3, the initial pH of synthetic water samples was between 5.7 and 6.0. Initial DOC concentrations varied from 4.10 to 4.30 mg/L, whereas all initial AOC concentrations were zero. The absence of AOC in all samples indicates that 2,4-DCP was biorecalcitrant to the P17 and NOX strains used in the analysis. This is presumably due to the characteristics of 2,4-DCP, which are toxic to some microorganisms, and its aromatic structure that makes it more difficult to be biodegraded.

Table 4.3 Initial pH (pH_0), DOC (DOC_0), and AOC (AOC_0) of synthetic water samples

Conditions			pH_0	DOC_0 (mg/L)	AOC_0 (μg C/L)		
H_2O_2:DOC	Fe^{2+}:H_2O_2	pH			P17	NOX	Total
0.5:1	0.05:1	2	5.72	4.12	0	0	0
		3	5.74	4.20	0	0	0
		4	5.77	4.12	0	0	0
0.5:1	0.1:1	2	5.78	4.23	0	0	0
		3	5.80	4.12	0	0	0
		4	5.83	4.27	0	0	0
0.5:1	0.5:1	2	5.95	4.22	0	0	0
		3	5.97	4.17	0	0	0
		4	6.00	4.28	0	0	0
2:1	0.05:1	2	5.88	4.18	0	0	0
		3	5.92	4.12	0	0	0
		4	5.90	4.20	0	0	0
2:1	0.1:1	2	5.93	4.11	0	0	0
		3	5.95	4.18	0	0	0
		4	5.94	4.26	0	0	0
2:1	0.5:1	2	5.78	4.28	0	0	0
		3	5.74	4.24	0	0	0
		4	5.80	4.21	0	0	0
10:1	0.05:1	2	5.70	4.10	0	0	0
		3	5.73	4.26	0	0	0
		4	5.72	4.21	0	0	0
10:1	0.1:1	2	5.83	4.23	0	0	0
		3	5.88	4.21	0	0	0
		4	5.89	4.18	0	0	0
10:1	0.5:1	2	5.92	4.3	0	0	0
		3	5.94	4.27	0	0	0
		4	5.95	4.24	0	0	0

4.2.2 DOC Changes during Fenton's Reaction

Figure 4.12 presents average normalized DOC versus reaction time at different H_2O_2:DOC and Fe^{2+}:H_2O_2, and pH. For all Fe^{2+}:H_2O_2 ratios, the DOC reduction was mainly dependent on H_2O_2 dose. More reduction was observed when higher H_2O_2 doses were provided. pH 3 and pH 4 were optimal for the DOC reduction. The changes in Fe^{2+} dose did not significantly affect the amount of final DOC reduction but resulted in faster completion of Fenton's degradation. At the Fe^{2+} dose of 0.05:1, DOC reduction was complete in 25 minutes. When Fe^{2+} dose was at 0.1:1 and 0.5:1, Fenton's degradation was complete at approximately 10 and 6 minutes, respectively. The maximum DOC reduction of 21% was observed at the Fe^{2+} dose of 0.5:1, H_2O_2 dose of 10:1, and pH 4.

4.2.3 Effects of H_2O_2 Dose on AOC Production in Synthetic Water Samples

Figure 4.13 shows average AOC production with time for different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH. At all conditions tested, AOC was produced immediately after initiating Fenton's reaction and reached a constant level before 10 minutes. The AOC production indicates the reduction of 2,4-DCP. Its chlorinated aromatic structure could be destroyed to yield by-products that were available for the growth of P17 and NOX stains. The effect of H_2O_2 dose was similar to that observed with the surface water samples; increasing H_2O_2 doses resulted in higher AOC production. Under pH 3, H_2O_2 dose of 10:1 and Fe^{2+} dose of 0.5:1, the highest AOC_{total} production of 1,335 μg C/L was obtained at the reaction time of 40 minutes.

Figures 4.14 and 4.15 illustrate the productions of AOC_{P17} and AOC_{NOX} versus reaction time under different conditions. AOC production profiles of P17 and NOX stains were similar except that their magnitudes were different. Nearly same amounts of AOC_{P17} and AOC_{NOX} were produced at the H_2O_2 dose of 0.5:1. However, higher H_2O_2 doses resulted in more AOC_{P17} production; 1.1 to 1.5 times of AOC_{NOX}. This result was similar to that of surface water samples; however, the effect for synthetic samples was less significant. This lower fraction of AOC_{P17} may be because fewer substrates were available in the by-products.

4.2.4 Effects of Fe^{2+} Dose on AOC Production in Synthetic Water Samples

The effect of Fe^{2+} dose on AOC production is illustrated in Figures 4.13 (AOC_{total}), 4.14 (AOC_{P17}), and 4.15 (AOC_{NOX}). Among the three types of AOC, the effect of Fe^{2+} was insignificantly different. Higher doses did not intensify the AOC production; they accelerated to the AOC production. The effects were very pronounced in the first 10 minutes at the Fe^{2+} doses of 0.05:1 and 0.1:1. At the Fe^{2+} dose of 0.5:1, the AOC increases were very rapid and remained stable after the first minute. In comparison with the DOC reduction (Figure 4.12), AOC production was much more instantaneous. This is probably because the mineralization underwent several oxidation stages to yield CO_2 and H_2O, whereas complete oxidation to CO_2 is not required for the AOC formation.

4.2.5 Effects of pH on AOC Production in Synthetic Water Samples

Figures 4.13, 4.14, and 4.15 show the effects of pH 2, pH 3, and pH 4 on AOC production at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios. As presented in Figure 4.13, the magnitude of AOC_{total} produced at the three initial pH can be ranked as follows: pH 3 > pH 4 > pH 2. In Figure 4.14 (AOC_{P17}) and Figure 4.15 (AOC_{NOX}), the same order was also observed for all conditions. An exception was found at the Fe^{2+} dose of 0.5:1 and the H_2O_2 dose of 2:1 that pH 2 turned out to be the second next to pH 3. Comparing to the effect of H_2O_2 dose, this effect was still less significant. Figure 4.16 shows that most of pH increases occurred during the first 10 minutes. Among the three pH, the increases were quite similar. Adding more H_2O_2 concentration provided to an increase of pH. At the highest H_2O_2 dose, an increase of 0.80 ± 0.07 was observed while the increases of 0.55 ± 0.10 and 0.35 ± 0.05 occurred at the H_2O_2 doses of 0.2:1 and 0.5:1, respectively. Changing in Fe^{2+} concentration did not significantly affect to pH. At each H_2O_2 concentration, pH changes provided by the three Fe^{2+} doses were less than ± 0.10.

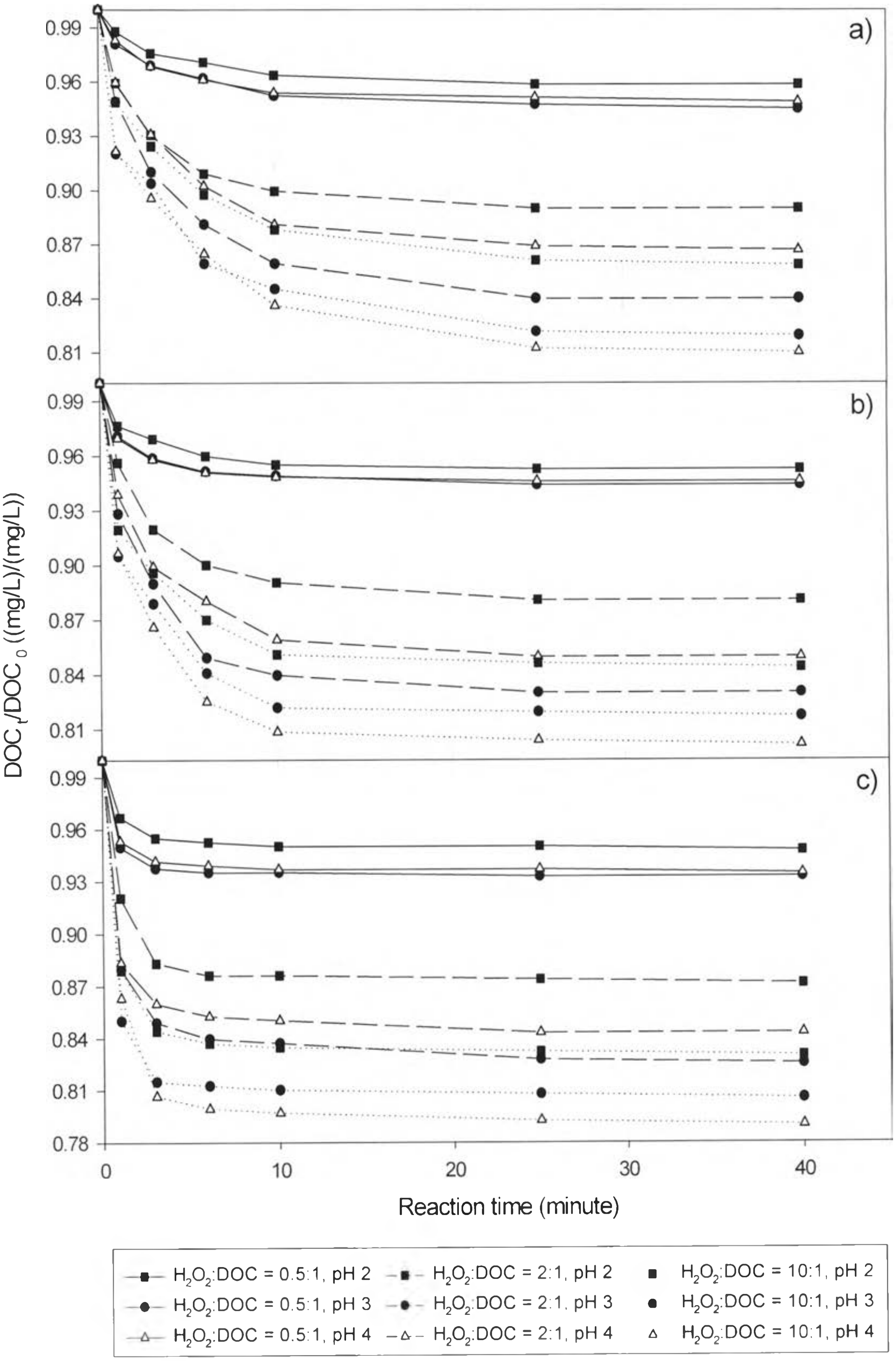

Figure 4.12 Average normalized DOC in synthetic water samples versus reaction time for different H_2O_2:DOC ratios and pH at a) Fe^{2+}:H_2O_2 of 0.05:1, b) Fe^{2+}:H_2O_2 of 0.1:1, and c) Fe^{2+}:H_2O_2 of 0.5:1.

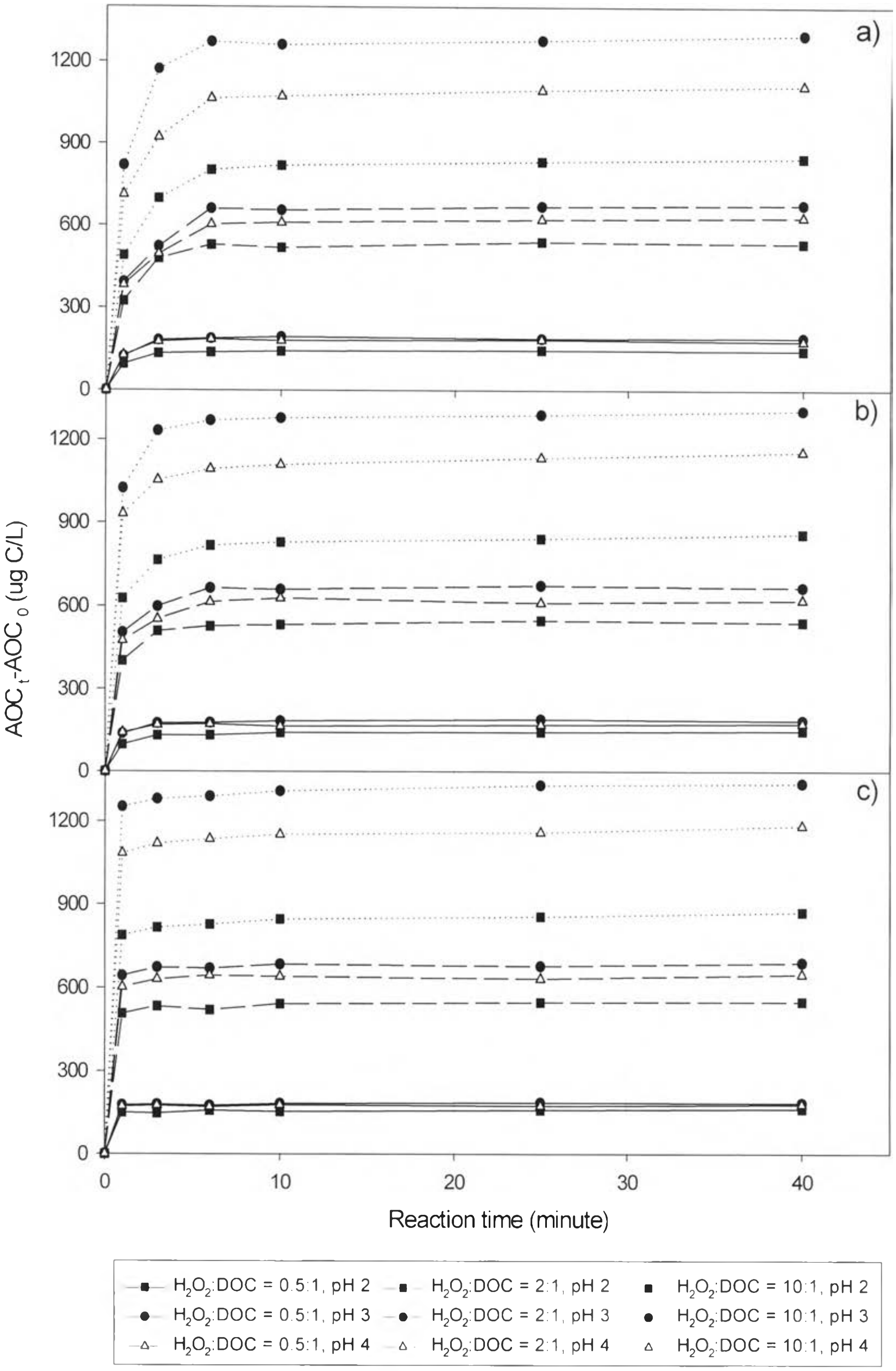

Figure 4.13 Average AOC$_{total}$ increases in synthetic water samples versus reaction time for different H_2O_2:DOC ratios and pH at a) Fe^{2+}:H_2O_2 of 0.05:1, b) Fe^{2+}:H_2O_2 of 0.1:1, and c) Fe^{2+}:H_2O_2 of 0.5:1

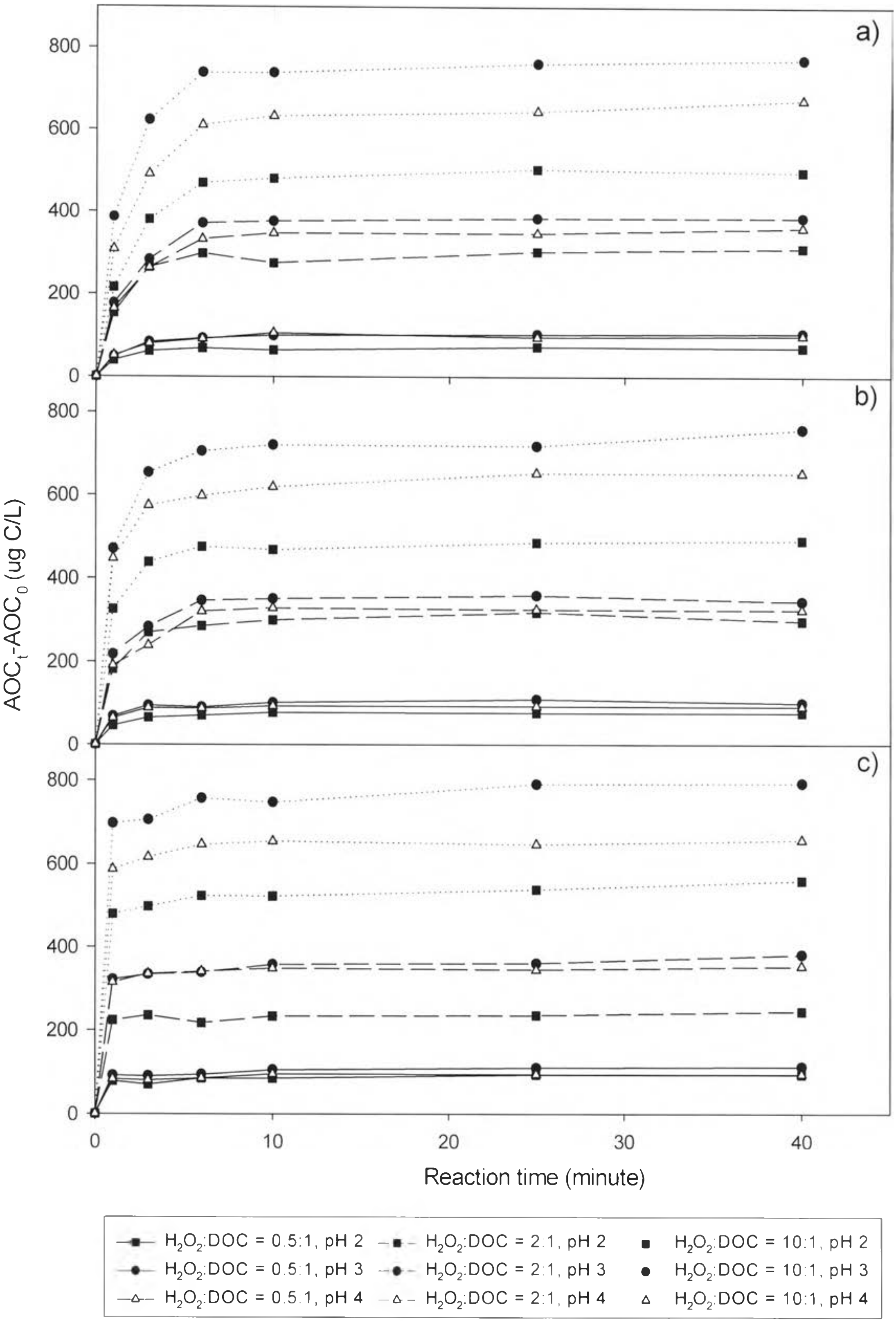

Figure 4.14 Average AOC$_{P17}$ increases in synthetic water samples versus reaction time for different H_2O_2:DOC ratios and pH at a) Fe^{2+}:H_2O_2 of 0.05:1, b) Fe^{2+}:H_2O_2 of 0.1:1, and c) Fe^{2+}:H_2O_2 of 0.5:1

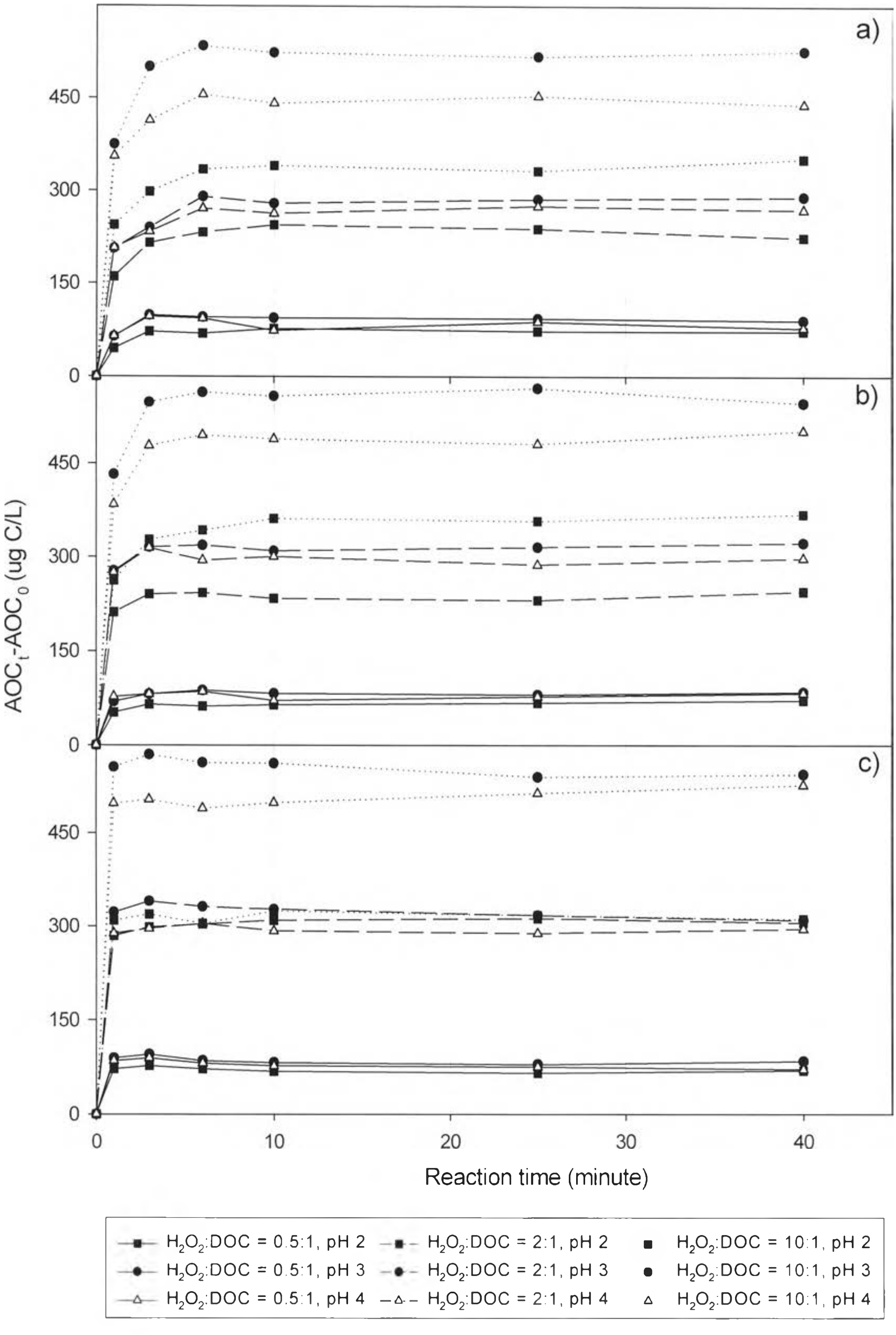

Figure 4.15 Average AOC$_{NOX}$ increases in synthetic water samples versus reaction time for different H_2O_2:DOC ratios and pH at a) Fe^{2+}:H_2O_2 of 0.05:1, b) Fe^{2+}:H_2O_2 of 0.1:1, and c) Fe^{2+}:H_2O_2 of 0.5:1

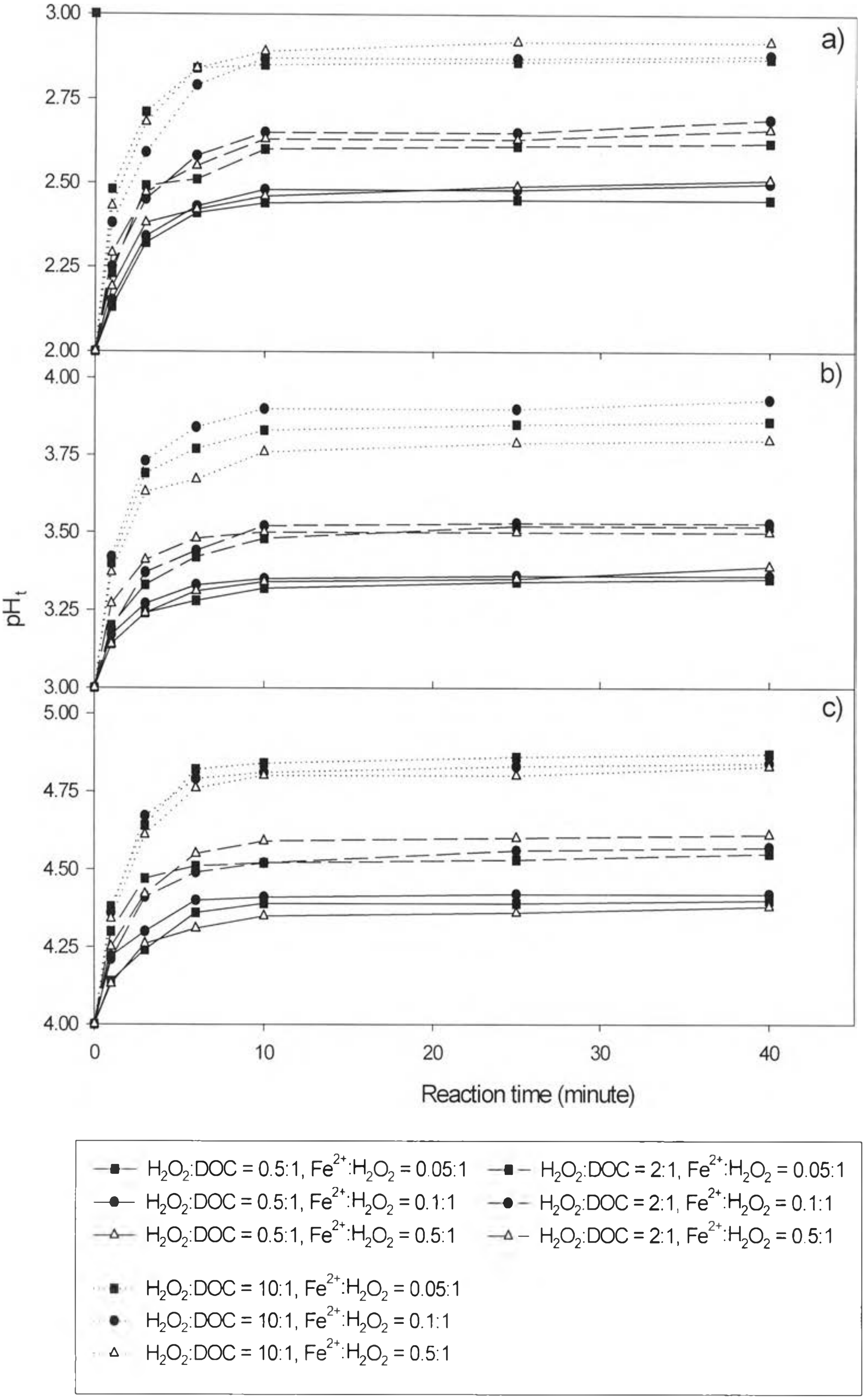

Figure 4.16 Average pH increases in synthetic water samples versus reaction time at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios: a) initial pH 2, b) initial pH 3, and c) initial pH 4.

4.2.6 Effects of Reaction Time and Kinetics of AOC Production in Synthetic Water Samples

The fraction of AOC produced at the 10-minute and 40-minute reaction time for all conditions tested is reported in Table 4.4. At the reaction time of 10 minutes, AOC production was almost complete; the completion > 94% for AOC_{total}, > 89% for AOC_{P17}, and > 87% for AOC_{NOX}. Therefore, 10 minutes can be used as a minimum time requirement to ensure near maximum AOC enhancement.

Table 4.4 Ratios of AOC production of synthetic water samples at the 10-minute and 40-minute reaction time for different H_2O_2 and Fe^{2+} doses, and pH

Conditions			$(AOC_{10}-AOC_0)/(AOC_{40}-AOC_0)$		
H_2O_2:DOC	Fe^{2+}:H_2O_2	pH	P17	NOX	Total
0.5:1	0.05:1	2	0.9143	1.0548	0.9860
		3	0.9900	1.0444	1.0157
		4	1.0606	0.9487	1.0113
0.5:1	0.1:1	2	1.0132	0.9014	0.9591
		3	1.0100	0.9762	0.9945
		4	1.0220	0.8759	0.9479
0.5:1	0.5:1	2	0.9140	0.9855	0.9444
		3	0.9375	1.0845	0.9945
		4	1.0106	0.9762	0.9943
2:1	0.05:1	2	0.8910	1.0893	0.9682
		3	0.9741	0.9621	0.9689
		4	0.9612	0.9777	0.9682
2:1	0.1:1	2	1.0101	0.9549	0.9851
		3	1.0204	0.9596	0.9909
		4	1.0155	1.0101	1.0129
2:1	0.5:1	2	0.9549	1.0131	0.9872
		3	0.9395	1.0583	0.9927
		4	0.9886	0.9898	0.9891
10:1	0.05:1	2	0.9658	0.9687	0.9669
		3	0.9560	0.9943	0.9714
		4	0.9391	1.0046	0.9649
10:1	0.1:1	2	0.9551	0.9810	0.9662
		3	0.9499	1.0201	0.9793
		4	0.9494	0.9741	0.9601
10:1	0.5:1	2	0.9338	1.0418	0.9724
		3	0.9432	1.0331	0.9797
		4	0.9970	0.9468	0.9746

The fittings of AOC_{total} production with the first and second order models are shown in Figure 4.17 and 4.20, respectively. For each type of AOC production, fittings are presented in Figures 4.18 (1^{st} order of AOC_{P17}), 4.19 (1^{st} order of AOC_{NOX}), 4.21 (2^{sd} order of AOC_{P17}), and 4.22 (2^{sd} order of AOC_{NOX}). For the first order kinetic, a sum of 57 fits had $r^2 \geq 0.90$; 23 fits for AOC_{total}, 16 fits for AOC_{P17}, and 18 fits for AOC_{NOX}. For the second order kinetic, there were only 31 fits whose $r^2 \geq 0.90$; 19 fits for AOC_{total}, and 11 fits for each AOC_{P17} and AOC_{NOX}. This justifies that the first order kinetic was more reliable than the second order kinetic. Moreover, most of second order kinetic constants (k_2) were very low (< 0.08 L/mg.min) and were not meaningful, especially at the H_2O_2:DOC ratios of 2:1 and 10:1.

For the first order model, among the three variables (H_2O_2 and Fe^{2+} doses, and pH), only the effect of Fe^{2+} doses on the changes of k_1 values was remarkable. The k_1 values ranged from 0.19 to 0.36 min^{-1} at a Fe^{2+} dose of 0.05:1; 0.26 to 0.34 min^{-1} for the AOC_{total} fits, 0.28 to 0.36 min^{-1} for the AOC_{P17} fits, and 0.19 to 0.32 min^{-1} for the AOC_{NOX} fits. When Fe^{2+} dose was increased to 0.1:1, these values rose to between 0.31 and 0.46 min^{-1}; 0.35 to 0.42 min^{-1} for the AOC_{total} fits, 0.41 to 0.46 min^{-1} for the AOC_{P17} fits, and 0.31 to 0.35 min^{-1} for the AOC_{NOX} fits. Similar to the kinetics of AOC production of the surface water samples, the Fe^{2+} dose of 0.5:1 provided lowest first order rate constants because most of AOC production took place very instantaneously that it was not possible to obtain the data points during the significant increase of AOC.

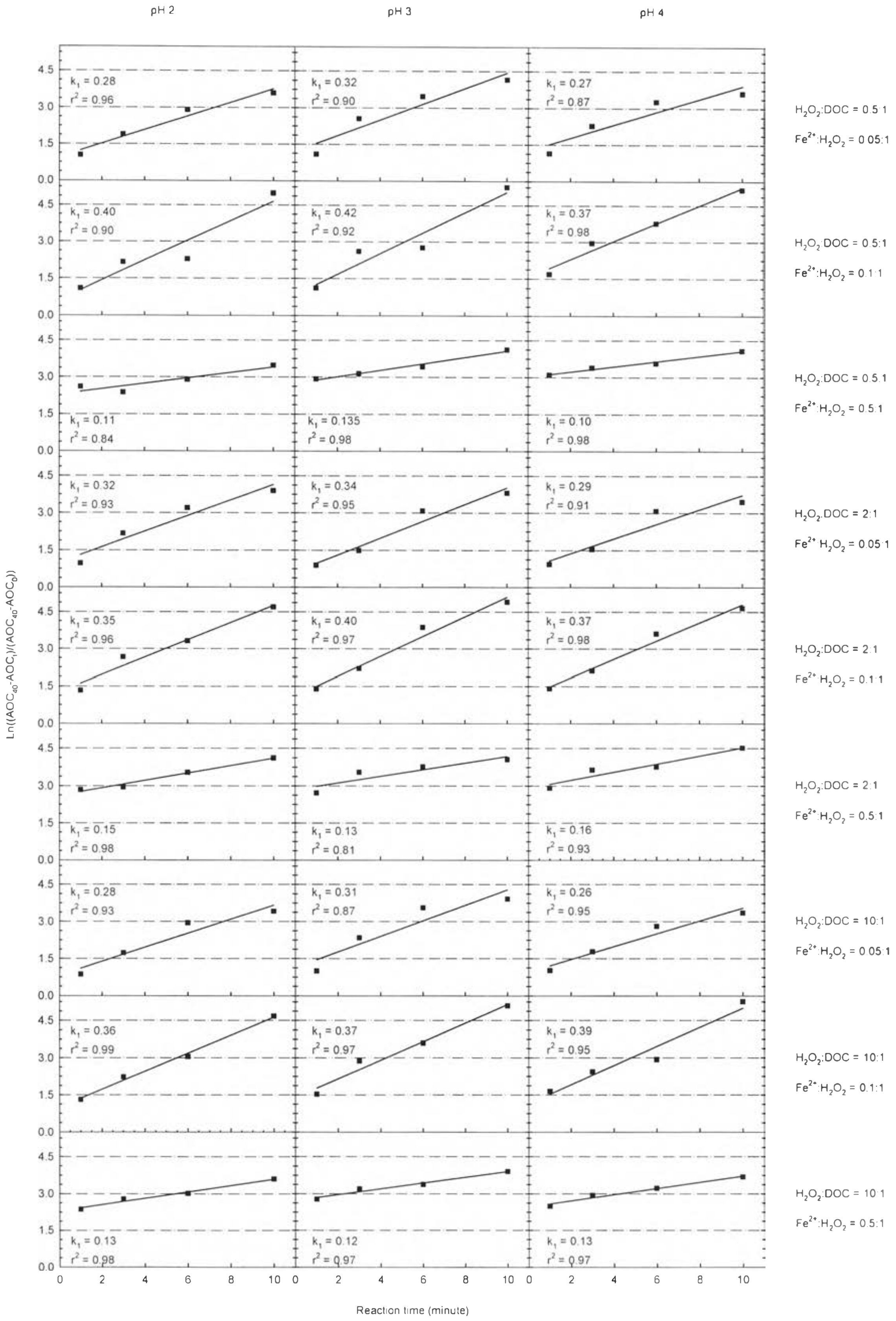

Figure 4.17 Fitting of AOC_{total} production in synthetic water samples with the first order kinetics at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH

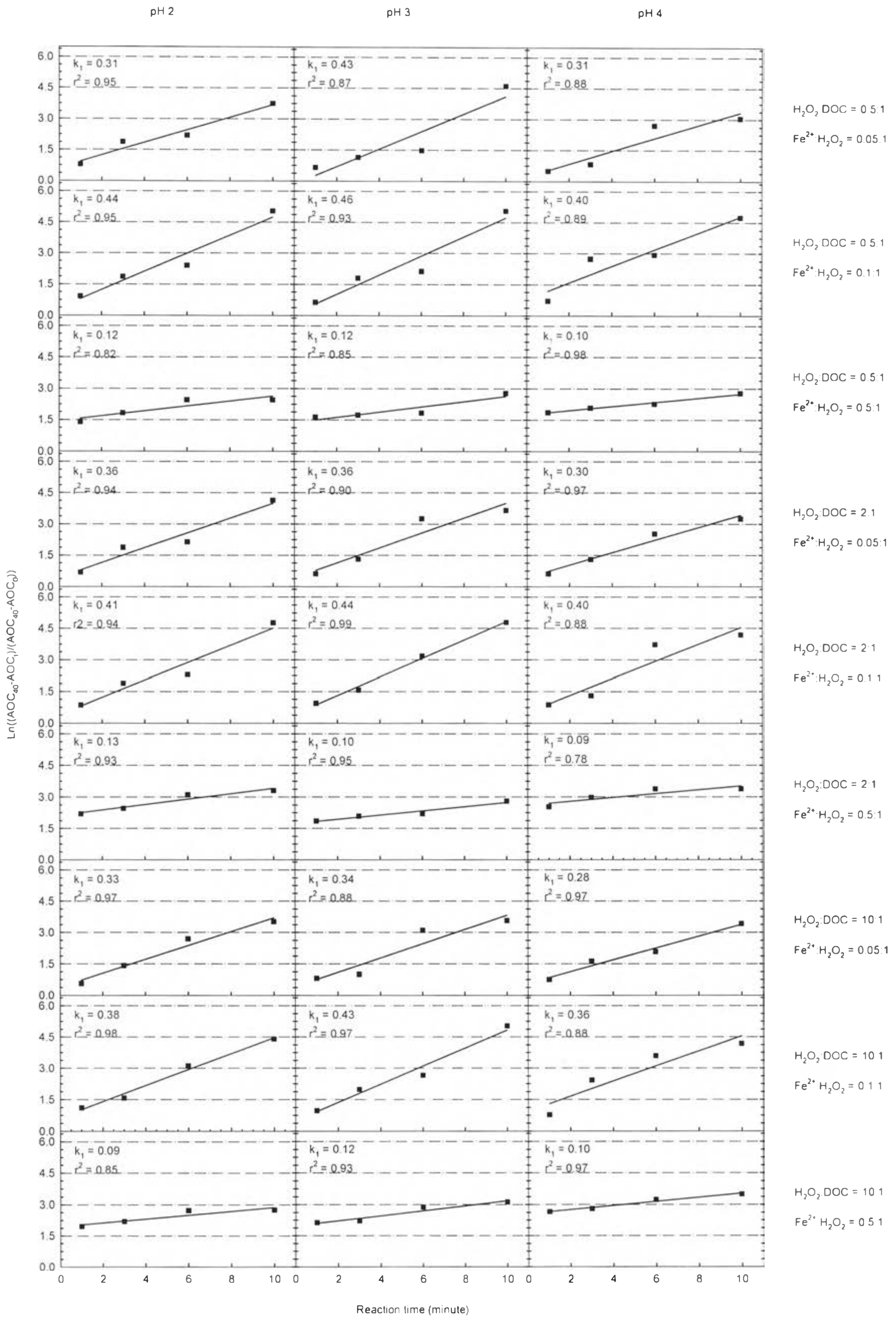

Figure 4.18 Fitting of AOC$_{P17}$ production in synthetic water samples with the first order kinetics at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH

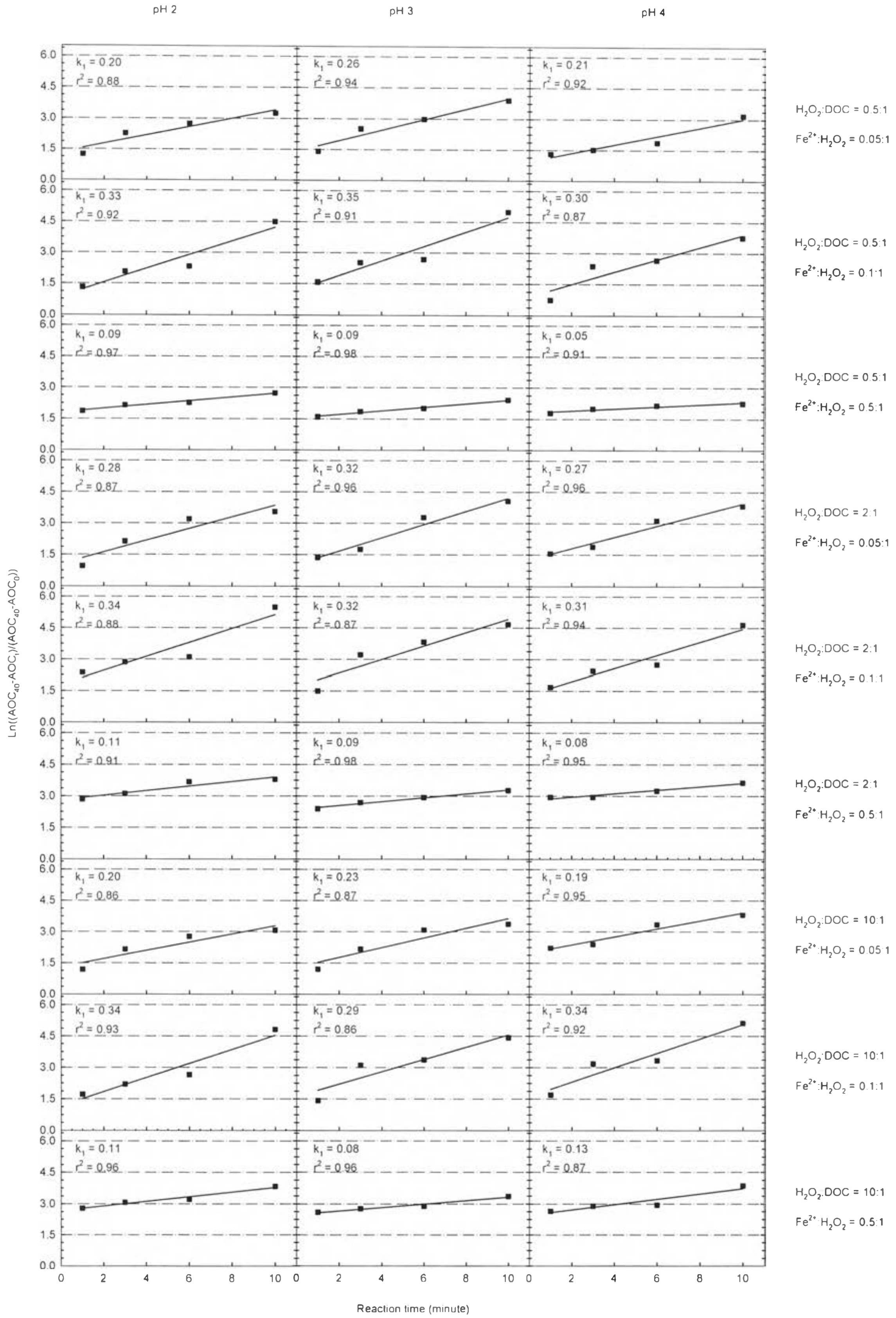

Figure 4.19 Fitting of AOC_{NOX} production in synthetic water samples with the first order kinetics at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH.

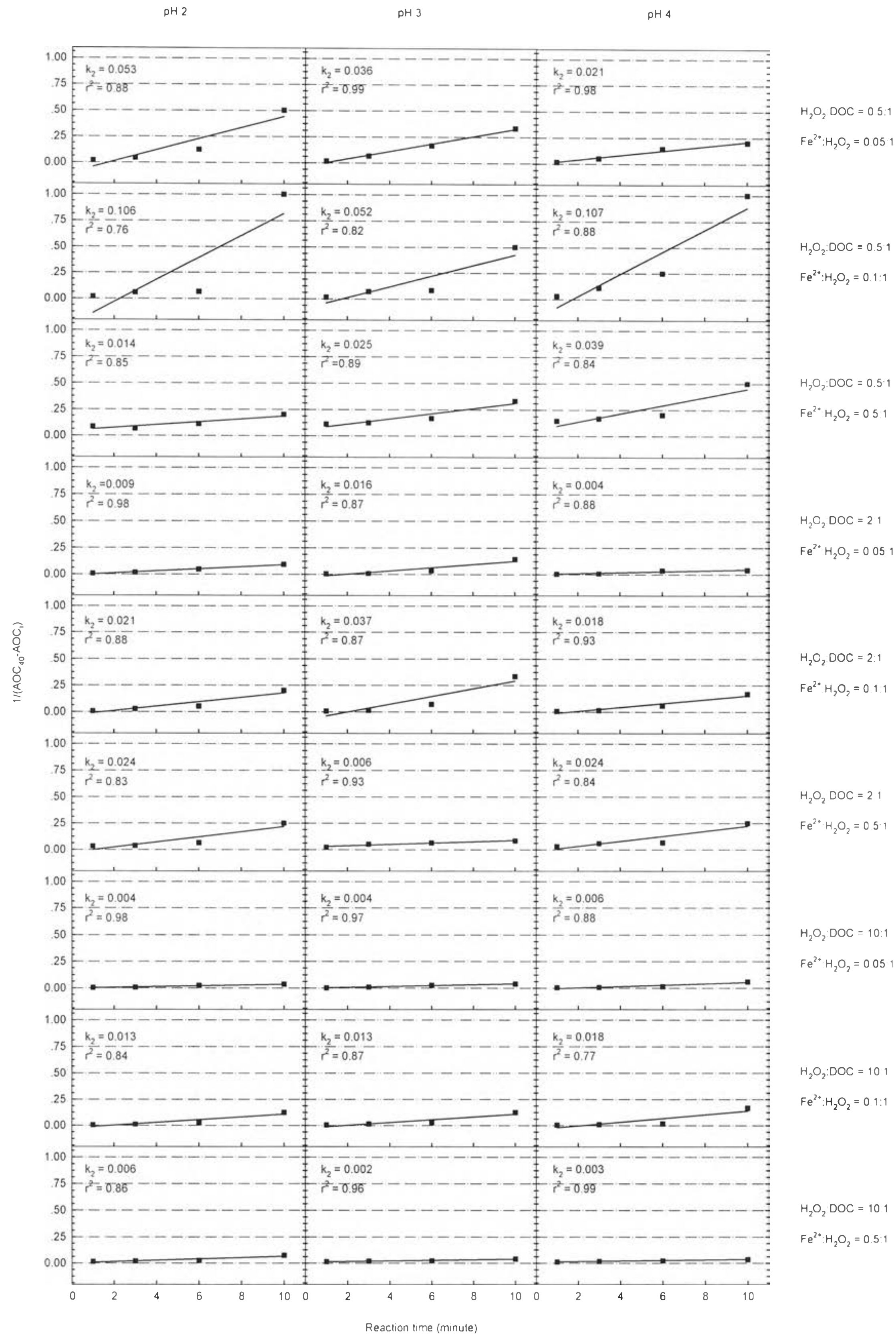

Figure 4.20 Fitting of AOC_{total} production in synthetic water samples with the second order kinetics at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH

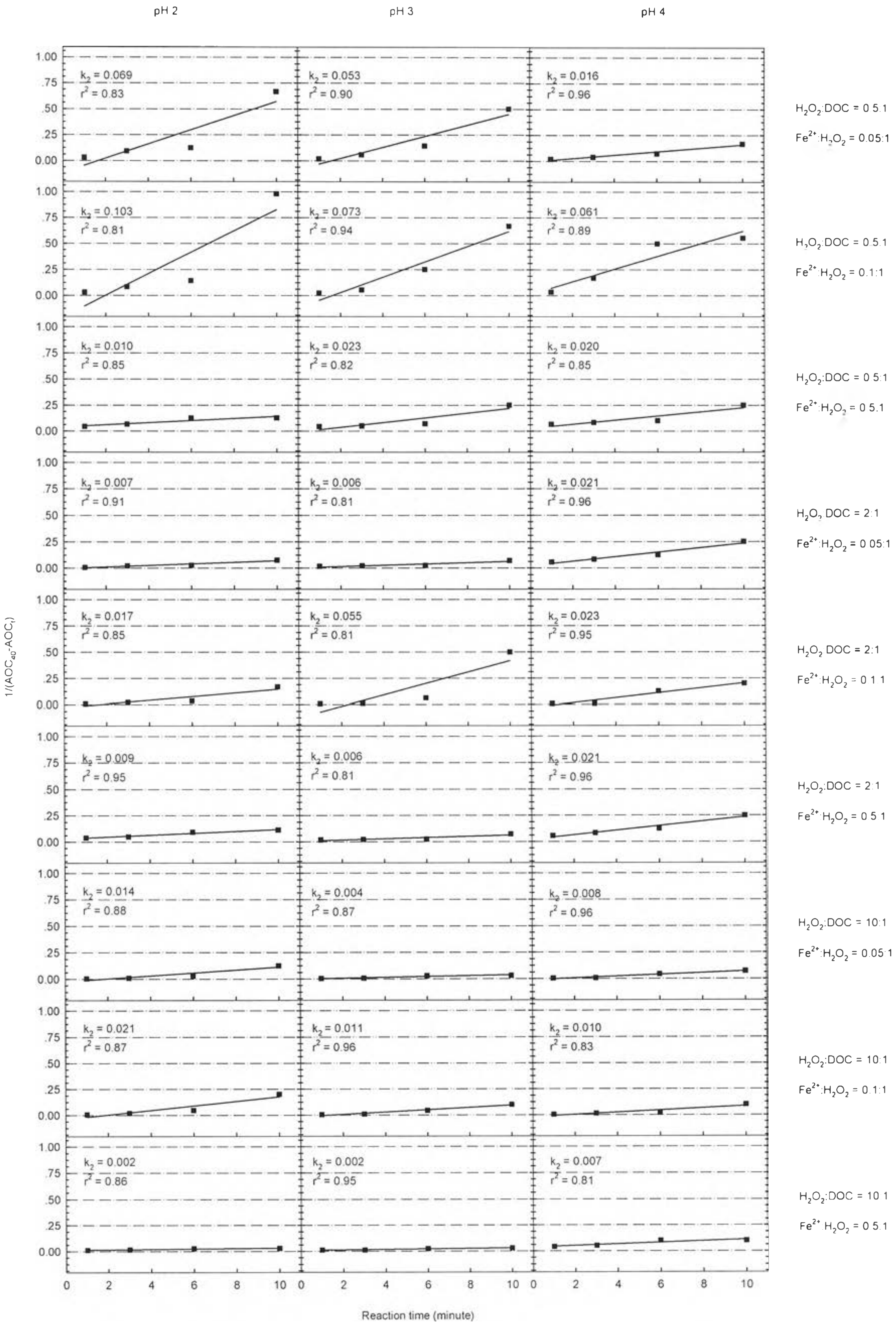

Figure 4.21 Fitting of AOC_{P17} production in synthetic water samples with the second order kinetics at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH

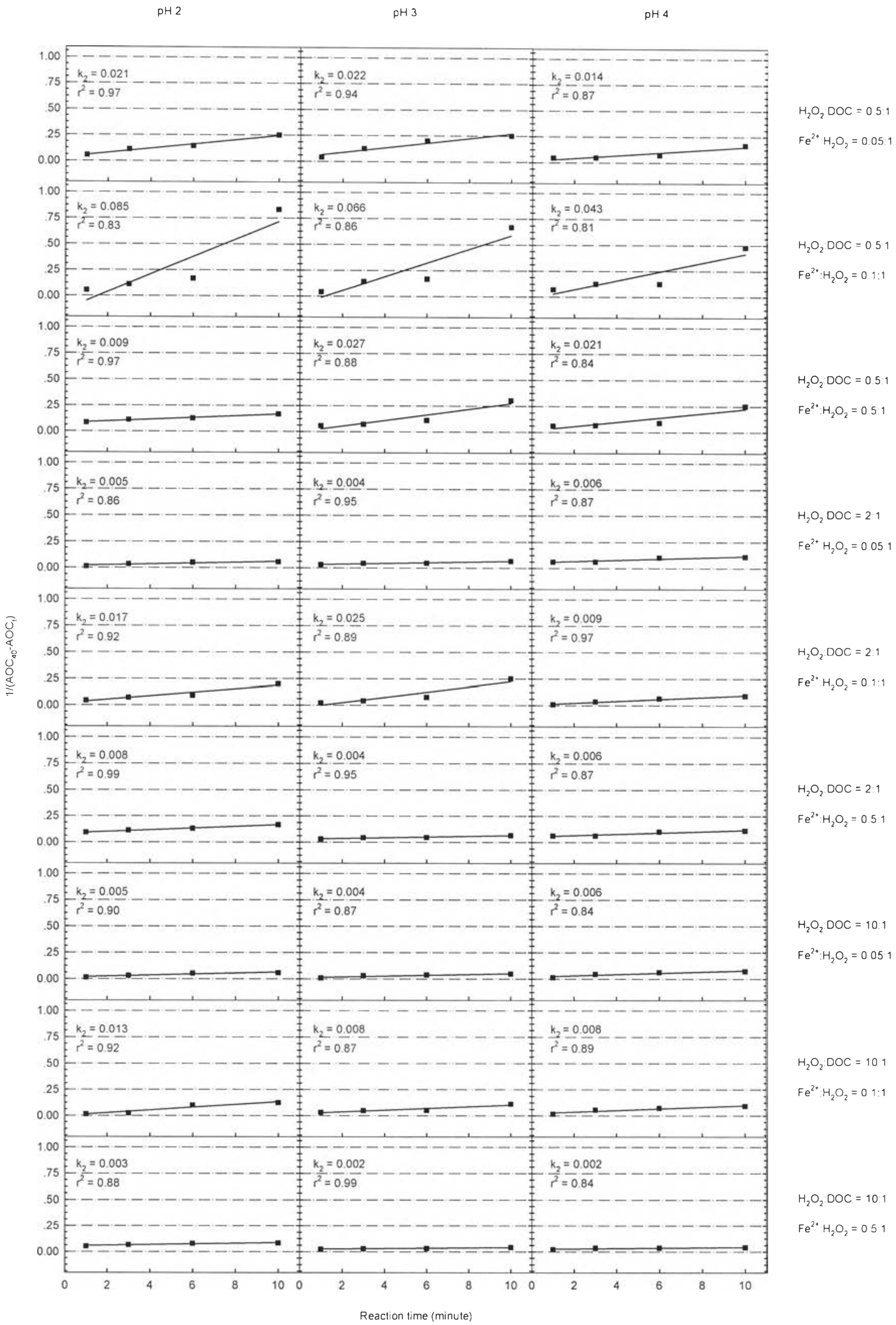

Figure 4.22 Fitting of AOC_{NOX} production in synthetic water samples with the second order kinetics at different H_2O_2:DOC and Fe^{2+}:H_2O_2 ratios, and pH

4.3 Comparison between Fenton's Effects on AOC in Surface and Synthetic Water Samples

Since 10 minutes is considered as an optimum reaction time, its AOC production and DOC change data are used to compared the effects of Fenton's reagent on the two types of water samples

4.3.1 DOC Changes

Table 4.5 shows the average remaining DOC fraction and percent completion (DOC reduction/DOC reduction at 40 minutes) at the reaction time of 10 minutes for both surface and synthetic water samples. Insignificantly more DOC reduction was found in surface water samples at the H_2O_2 dose of 0.5:1 while, at the other two higher H_2O_2 doses, DOC reduction of the synthetic water samples was slightly higher than that of the surface water samples. For both sample types, pH 3 and pH 4 offered more DOC reduction than pH 2. Higher Fe^{2+} doses resulted in faster DOC reduction in both types of water samples but the effect was more pronounced with the surface water samples. In the first 10 minutes, more than 95% of DOC reduction occurred for the surface water samples whereas only 86 to 98% of DOC reduction was observed for the synthetic water samples.

Table 4.5 Comparison between average DOC changes in surface and synthetic samples.

Conditions			Surface water samples		Synthetic water samples	
H_2O_2:DOC	Fe^{2+}:H_2O_2	pH	DOC_{10}/DOC_0	Percent Completion	DOC_{10}/DOC_0	Percent Completion
0.5:1	0.05:1	2	0.9508	100	0.9636	88
		3	0.9298	100	0.9524	87
		4	0.9416	95	0.9539	90
0.5:1	0.1:1	2	0.9469	95	0.9551	95
		3	0.9320	100	0.9490	91
		4	0.9474	95	0.9485	95
0.5:1	0.5:1	2	0.9412	96	0.9502	95
		3	0.9266	100	0.9353	96
		4	0.9325	95	0.9369	96

(Cont.)

Conditions			Surface water samples		Synthetic water samples	
H_2O_2:DOC	Fe^{2+}:H_2O_2	pH	DOC_{10}/DOC_0	Percent Completion	DOC_{10}/DOC_0	Percent Completion
2:1	0.05:1	2	0.9338	98	0.8995	91
		3	0.9154	97	0.8592	88
		4	0.9188	100	0.8810	89
2:1	0.1:1	2	0.9309	100	0.8905	92
		3	0.9133	96	0.8397	94
		4	0.9175	98	0.8592	94
2:1	0.5:1	2	0.9220	98	0.8762	96
		3	0.8987	100	0.8373	93
		4	0.8936	99	0.8504	95
10:1	0.05:1	2	0.9004	95	0.8780	86
		3	0.8547	100	0.8451	86
		4	0.8455	97	0.8361	86
10:1	0.1:1	2	0.9076	97	0.8511	95
		3	0.8643	97	0.8219	97
		4	0.8463	99	0.8086	96
10:1	0.5:1	2	0.9047	96	0.8349	97
		3	0.8611	98	0.8103	98
		4	0.8413	99	0.7972	96

4.3.2 Effects of H_2O_2 Dose on AOC Production

Table 4.6 presents average $(AOC_{10}-AOC_0)/DOC_0$ values for surface and synthetic water samples at different conditions. The use of $(AOC_{10}-AOC_0)/DOC_0$ value provides a fair comparison since initial DOC values of the two types of water samples were significantly different. The result shows that increasing H_2O_2 dose provided the enhancement of AOC production for both types of water samples. The differences in average normalized AOC_{tatal} production between the two types of samples were quite small at the H_2O_2 doses of 0.5:1 and 2:1. At the H_2O_2 dose of 10:1, normalized AOC_{total} production for the synthetic water samples was much higher than that for the surface water samples. In case of AOC_{P17}, the normalized production for the surface water samples was slightly higher than that for the synthetic water samples. On the contrary, Fenton's oxidation of the synthetic water samples provided significantly higher normalized AOC_{NOX} production than that of the surface water samples.

Table 4.6 Average $(AOC_{10}-AOC_0)/DOC_0$ of surface and synthetic water samples at different conditions.

Conditions			$((AOC_{10}-AOC_0)/DOC_0) \times 10^3$					
H_2O_2:DOC	$Fe^{2+}:H_2O_2$	pH	Surface water samples			Synthetic water samples		
			P17	NOX	Total	P17	NOX	Total
0.5:1	0.05:1	2	6	31	37	16	19	35
		3	8	38	46	24	22	46
		4	7	37	44	25	18	43
0.5:1	0.1:1	2	8	32	40	18	15	33
		3	9	40	49	25	20	44
		4	8	39	47	22	17	39
0.5:1	0.5:1	2	8	33	41	20	16	36
		3	11	41	52	25	18	43
		4	10	38	48	22	19	41
2:1	0.05:1	2	88	35	123	66	58	124
		3	124	48	172	91	68	159
		4	106	41	147	83	63	146
2:1	0.1:1	2	83	33	116	73	57	130
		3	123	49	172	84	74	158
		4	106	39	145	77	70	147
2:1	0.5:1	2	88	36	124	54	72	126
		3	135	49	184	84	77	161
		4	111	42	153	83	69	152
10:1	0.05:1	2	144	45	189	117	83	200
		3	188	50	238	173	123	296
		4	160	47	207	150	105	255
10:1	0.1:1	2	140	41	181	111	85	196
		3	180	52	232	171	133	304
		4	157	42	199	148	117	265
10:1	0.5:1	2	146	42	188	121	75	196
		3	187	49	236	175	131	306
		4	159	42	201	154	117	271

4.3.3 Effects of Fe^{2+} Dose on AOC Production

From Figure 4.2 to 4.4 and Figure 4.16 to 4.18, it is clear that Fe^{2+} concentration affected the rate of AOC production but did not significantly affect the ultimate amount of AOC production. For both surface and synthetic water samples, the rate of AOC production at the Fe^{2+} dose of 0.5:1 was very rapid. After one minute, the reactions were complete or very close to completion and due to the lack of data between 0 and 1 minute, they could not be modeled. AOC production rates were slower in samples with lower Fe^{2+} doses. However, the rates of AOC production between the two types of water samples were not dramatically different.

4.3.4 Effects of pH on AOC Production

As shown in Table 4.6, it is apparent that, next to H_2O_2, pH was the second factor that influenced on AOC production. In both types of water samples, pH 3 was the most favorable condition for enhancing AOC production while pH 2 provided the least AOC production. As presented in Figures 4.8 and 4.22, the effect of pH was similar for the two types of water samples. The increase of pH during the experiment was influenced by H_2O_2 dose. For Fe^{2+} dose, it was evident that it had no effect on pH during Fenton's reaction.

4.3.5 Kinetics of AOC Production

Tables 4.7, 4.8, and 4.9 summarize the first order kinetic constants (k_1) as well as coefficients of determination (r^2) of AOC_{total}, AOC_{P17}, and AOC_{NOX}, respectively, for surface and synthetic samples. It can be seen that the differences of k_1 values between the two types of water samples for each condition were not the same and no trend could be established. For both types of samples, changing Fe^{2+} dose from 0.05:1 to 0.1:1 resulted in the increase of k_1 values but when Fe^{2+} dose of 0.5:1 was applied, k_1 values were greatly reduced. The k_1 values were not affected by H_2O_2 and pH.

Table 4.7 First order kinetic constants of the AOC_{total} production and coefficients of correlation of the fitting for surface and synthetic water samples.

Conditions			Surface water samples		Synthetic water samples	
H_2O_2:DOC	Fe^{2+}:H_2O_2	pH	k_1 (min.$^{-1}$)	r^2	k_1 (min.$^{-1}$)	r^2
0.5:1	0.05:1	2	0.42	0.89	0.28	0.96
		3	0.40	0.96	0.32	0.90
		4	0.34	0.93	0.27	0.87
0.5:1	0.1:1	2	0.49	0.87	0.40	0.90
		3	0.45	0.92	0.42	0.92
		4	0.38	0.95	0.37	0.98
0.5:1	0.5:1	2	0.06	0.93	0.11	0.84
		3	0.11	0.71	0.14	0.98
		4	0.09	0.79	0.10	0.98

(Cont.)

Conditions			Surface water samples		Synthetic water samples	
H_2O_2:DOC	$Fe^{2+}:H_2O_2$	pH	k_I (min.$^{-1}$)	r^2	k_I (min.$^{-1}$)	r^2
2:1	0.05:1	2	0.26	0.89	0.32	0.93
		3	0.21	0.90	0.34	0.95
		4	0.24	0.91	0.29	0.91
2:1	0.1:1	2	0.34	0.96	0.35	0.96
		3	0.28	0.91	0.40	0.97
		4	0.35	0.91	0.37	0.98
2:1	0.5:1	2	0.10	0.95	0.15	0.98
		3	0.12	0.97	0.13	0.81
		4	0.11	0.92	0.16	0.93
10:1	0.05:1	2	0.31	0.93	0.28	0.93
		3	0.31	0.94	0.31	0.87
		4	0.30	0.91	0.26	0.95
10:1	0.1:1	2	0.44	0.96	0.36	0.99
		3	0.45	0.95	0.37	0.97
		4	0.41	0.93	0.39	0.95
10:1	0.5:1	2	0.08	0.87	0.13	0.98
		3	0.09	0.90	0.12	0.97
		4	0.05	0.97	0.13	0.97

Table 4.8 First order kinetic constants of the AOC$_{P17}$ production and coefficients of correlation of the fitting for surface and synthetic water samples.

Conditions			Surface water samples		Synthetic water samples	
H_2O_2:DOC	$Fe^{2+}:H_2O_2$	pH	k_I (min.$^{-1}$)	r^2	k_I (min.$^{-1}$)	r^2
0.5:1	0.05:1	2	0.45	0.98	0.31	0.95
		3	0.43	0.94	0.43	0.87
		4	0.38	0.92	0.31	0.88
0.5:1	0.1:1	2	0.55	0.92	0.44	0.95
		3	0.50	0.94	0.46	0.93
		4	0.44	0.93	0.40	0.89
0.5:1	0.5:1	2	0.07	0.90	0.12	0.82
		3	0.10	0.93	0.12	0.85
		4	0.11	0.94	0.10	0.98
2:1	0.05:1	2	0.29	0.82	0.36	0.94
		3	0.26	0.93	0.36	0.90
		4	0.27	0.86	0.30	0.97
2:1	0.1:1	2	0.41	0.95	0.41	0.94
		3	0.31	0.91	0.44	0.99
		4	0.32	0.88	0.40	0.88
2:1	0.5:1	2	0.13	0.88	0.13	0.93
		3	0.12	0.86	0.10	0.95
		4	0.10	0.95	0.09	0.78

(Cont.)

Conditions			Surface water samples		Synthetic water samples	
H_2O_2:DOC	Fe^{2+}:H_2O_2	pH	k_1 (min.$^{-1}$)	r^2	k_1 (min.$^{-1}$)	r^2
10:1	0.05:1	2	0.36	0.87	0.33	0.97
		3	0.34	0.81	0.34	0.88
		4	0.32	0.93	0.28	0.97
10:1	0.1:1	2	0.49	0.97	0.38	0.98
		3	0.41	0.94	0.43	0.97
		4	0.46	0.94	0.36	0.88
10:1	0.5:1	2	0.16	0.87	0.09	0.85
		3	0.10	0.98	0.12	0.93
		4	0.04	0.98	0.10	0.97

Table 4.9 First order kinetic constants of the AOC_{NOX} production and coefficients of correlation of the fitting for surface and synthetic water samples.

Conditions			Surface water samples		Synthetic water samples	
H_2O_2:DOC	Fe^{2+}:H_2O_2	pH	k_1 (min.$^{-1}$)	r^2	k_1 (min.$^{-1}$)	r^2
0.5:1	0.05:1	2	0.32	0.95	0.20	0.88
		3	0.33	0.87	0.26	0.94
		4	0.28	0.87	0.21	0.92
0.5:1	0.1:1	2	0.48	0.99	0.33	0.92
		3	0.42	0.91	0.35	0.91
		4	0.36	0.91	0.30	0.87
0.5:1	0.5:1	2	0.05	0.93	0.09	0.97
		3	0.11	0.85	0.09	0.98
		4	0.14	0.68	0.05	0.91
2:1	0.05:1	2	0.21	0.95	0.28	0.87
		3	0.25	0.97	0.32	0.96
		4	0.21	0.95	0.27	0.96
2:1	0.1:1	2	0.26	0.94	0.34	0.88
		3	0.27	0.87	0.32	0.87
		4	0.40	0.87	0.31	0.94
2:1	0.5:1	2	0.11	0.89	0.11	0.91
		3	0.07	0.95	0.09	0.98
		4	0.10	0.83	0.08	0.95
10:1	0.05:1	2	0.30	0.93	0.20	0.86
		3	0.25	0.93	0.23	0.87
		4	0.23	0.95	0.19	0.95
10:1	0.1:1	2	0.38	0.92	0.34	0.93
		3	0.42	0.88	0.29	0.86
		4	0.39	0.94	0.34	0.92
10:1	0.5:1	2	0.06	0.75	0.11	0.96
		3	0.13	0.83	0.08	0.96
		4	0.05	0.90	0.13	0.87

4.3.6 Optimal Conditions

Optimal conditions for AOC production are summarized in Table 4.10 based on a 10-minute reaction time. H_2O_2 dose was the most obvious factor contributing to AOC production in surface and synthetic water samples. It is clear that the H_2O_2 dose of 10:1 was the most effective for AOC production for both types of water samples. Second to H_2O_2 was pH: the extent of AOC production depended on a favorable pH. The highest AOC production was at pH 3.

Fe^{2+} concentration had a little effect on the magnitude of ultimate AOC production. The Fe^{2+} dose of 0.05:1 was optimal for the surface water samples while, for the synthetic water samples, the Fe^{2+} dose of 0.5:1 offered the highest production. The optimal H_2O_2 dose and pH for AOC_{P17} and AOC_{NOX} production for both types of water samples were the same as AOC_{total} production. For optimal Fe^{2+} dose, 0.1:1 was the most favorable dose for AOC_{NOX} production for both types of water samples. For AOC_{total} and AOC_{P17}, Fe^{2+} doses of 0.05:1 and 0.5:1 were optimal for surface and synthetic water samples, respectively.

Table 4.10 Optimal conditions for AOC production.

Type of production	Surface water samples (H_2O_2:DOC, Fe^{2+}:H_2O_2, pH)	Synthetic water samples (H_2O_2:DOC, Fe^{2+}:H_2O_2, pH)
AOC_{total}	10:1, 0.05:1, pH 3	10:1, 0.5:1, pH 3
AOC_{P17}	10:1, 0.05:1, pH 3	10:1, 0.5:1, pH 3
AOC_{NOX}	10:1, 0.1:1, pH 3	10:1, 0.1:1, pH 3