

References

- Agency for Toxic Substances and Disease Registry (ASTDR). 1990. Toxicology profile for nitrobenzene. U.S. Department of Health and Human Service, Public Health Service.
- Bell, L.S., Devlin J.F., Gillham R.W. and Binning P.J. 2003. A sequential zerovalent iron and aerobic biodegradation treatment system for nitrobenzene. Journal of Contaminant Hydrology 66 : 201-217.
- Benjamin, M.M. 2002. Water Chemistry. McGraw-Hill Company. New York 2002.
- Bhatkhande, D.S., Pangarkar, V.G. and Beenackers A. 2003. Photocatalytic degradation of nitrobenzene using titanium dioxide and concentrated solar radiation. Water Research 37 : 1223-1230.
- Casero, I., Sicilia, D., Rubio, S. and Perez-Bendito, D. 1997. Chemical degradation of aromatic amines by Fenton's reagent. Water Research 31 : 1985-1995.
- Chou, S. and Huang, C.1999a. Effect of Fe^{2+} on the catalytic oxidation in the fluidized-bed reactor. Chemosphere 39 : 1997-2006.
- Chou, S. and Huang, C.1999b. Decomposition of H_2O_2 in a catalytic fluidized-bed reactor. Applied Catalysis A 185 : 237-245.
- Chou, S. and Huang, C.1999C. Application of support iron oxyhydroxide catalyst in oxidation of benzoic acid by hydrogen peroxide. Chemosphere 38 : 2719-2731.

- Chou, S., Huang, G.H., Liao, C.C., Hsu, S.F., Huang, Y.H. 2003. Fenton family-Advance oxidation technologies for wastewater treatment. Asian-Pacific Regional Conference on Practical Environmental Technologies :17-24.
- Chou, S., Liao, C.C., Perng, S.H. and Chang, S.H. 2004. Factor influencing the preparation of supported iron oxide in fluidized-bed crystallization. Chemosphere 54 : 859-866.
- Contreras S., Rodriguez M., Chamarro C. and Esplugas S. 2001. UV- and UV/Fe(III)-enhanced ozonation of nitrobenzene in aqueous solution. Journal of Photochemistry and Photobiology A: Chemistry 142 : 79-83.
- Haag, W.R. and Yao, C.D. 1992. Rate constants for chromate and other inorganic anions by Organo-zeolite. Environmental Science Technology 28 : 452-458.
- Himebaugh, W.S. 1994. Advance oxidation of munitions in water. Fer III and WM II Conference and Exhibition : 54-78.
- Hoigen, J. 1998. Chemistry of aqueous ozone and advanced oxidation processes. The Handbook of Environmental Chemistry : 83-141.
- Huang, C.P., Dong, C. and Tang, Z. 1993. Advanced chemical oxidation:Its present role and potential future in hazardous waste treatment. Water Management 13 : 361-377.
- Kiwi, J., Pulgarin, C. and Peringer, P. 1994. Effect of Fenton and phot-Fenton reactions on the degradation and biodegradability of 2 and 4-nitrophenol in water treatment. Applied Catalysis B Environment 3 : 335-350.
- Kong, S.H., Watts, R.J. And Choi, J.H. 1998. Treatment of petroleum-contaminated soils using iron mineral catalyzed Science. Chemosphere 37 : 1473-1482.

- Kwon, B.G., Lee, D.S., Kang, N. and Yoon, J. 1999. Characteristics of p-chlorophenol oxidation by Fenton's reagent. Water Research 33 : 2110–2118.
- Kosmulski, M. and Saneluta, C. 2004. Point of zero charge/isoelectric point of exotic oxide. Journal of Colloid and Interface Science 280 : 544-545.
- Khunikakorn, L. 2006. Oxidation of aniline and nitrobenzene by fluidized-bed Fenton process. Master's thesis. Degree of Master of Science Program in Environmental Management (Inter-Department). Chulalongkorn University.
- Liao, C.H., LU, M.C. and Su, S.H. 2001. Role of cupric ions in the H₂O₂/UV oxidation of humic acids. Chemosphere 44 : 913-919.
- Lin, S.S. and Gurol, M.D. 1996. Heterogeneous catalytic oxidation of organic compounds by hydrogen peroxide. Water Science Technology 34 : 57-64.
- Lu, M.C., Chen, J.N. and Chang, C.P. 1997. Effect of inorganic ions on the oxidation of dichlorvos insecticide with Fenton's reagent. Chemosphere 35 : 2285–2293.
- Lu, M.C., Chen, J.N. and Chang, C.P. 1999. Oxidation of dichlorvos with hydrogen peroxide using ferrous ion as catalyst. Journal of Hazardous Materials 65 : 277–288.
- Lu, M.C. 2000. Oxidation of chlorophenols with hydrogen peroxide in the presence of goethite. Chemosphere 40 : 125-130.
- Lu, M.C., Chen, J.N. and Huang H.H. 2002. Role of goethite dissolution in the oxidation of 2- chlorophenol with hydrogen peroxide. Chemosphere 46 : 131-136.

- Lu, M.C., Chang, Y.-F., Chen, I.M. and Huang, Y.Y. (2005). Effect of chloride ions on the oxidation of aniline by Fenton's reagent. Journal of Environmental Management 75 : 177-182.
- Lunar L., Sicilia D., Rubio S., Perez-Bendito D. and Nickel U. 2000. Degradation of photographic developers by Fenton's reagent: condition optimization and kinetics for metal oxidation. Water Research 34 : 1791-1802.
- Majumder, P.S. and Gupta, S.K. 2003. Hybrid reactor for priority pollutant nitrobenzene removal. Water Research 37 : 4331-4336.
- Masten, S. and Davies, S. 1994. The use of ozonation to degrade organic contaminants in wastewater. Environmental Science Technology 28 : 180A-185A.
- Mattel, A. E. 1952. Chemical of the Metal Chelate Compound. Prentice-Hall New York.
- Miller, C.M. and Valentine, R.L. 1995. Oxidation behavior of aqueous contaminants in the presence of hydrogen peroxide and filter media. Journal of Hazardous Materials 41 :105-116.
- Mu, Y., Yu, H.Q., Zheng, J.C., S.J. and Sheng, G.P. 2004. Reductive degradation of nitrobenzene in aqueous solution by zero-valent iron. Chemosphere 55 : 789-794.
- Munter, R. 2001. Advanced Oxidation Processes- current status and prospects. Process Estonian Academic Science Chemistry 50 : 59-80.
- National toxicology program (NTP). 2005. Substance Profiles. Report on Carcinogens for Nitrobenzene, Eleventh Edition. Available from: <http://ntp.niehs.nih.gov/ntp/roc/eleventh/profiles/s121zntb.pdf>.

- Neyens, E. and Baeyens, J. 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of hazardous materials B98 : 33-50.
- Noh, J.S. and Schwarz, J.A. 1988. Estimation of the point of zero charge of simple oxides by mass titration. Journal of Colloid and Interface Science 130 : 157-164.
- Pak, D. and Chang, W. 1999. Decolorizing Dye Wastewater with Low Temperature Catalytic Oxidation. Water science technology 40 : 115-121.
- Panizza M. and Cerisola G., 2001. Removal of organic pollutants from industrial wastewater by electrogenerated Fenton's reagent. Water Research, 35 : 3987-3992.
- Parson, S., editor. Advanced Oxidation Processes for Water and Wastewater Treatment. UK: TJ International(Ltd), 2004.
- Piccinini, P., Minero C., Vincenti, M. and Pelizzetti, E. 1997. Photocatalytic mineralization of nitrogen-containing benzene derivatives. Catalysis Today 39 : 187-195.
- Pignatello, J.J. 1992. Dark and photoassisted Fe^{3+} -catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environmental Science and Technology 26 : 944-951.
- Pollution abatement Technology Department Center for Environmental, Safety and Health Technology Development Industrial Technology Research Institute. 2003. Fenton family – advanced Oxidation Technologies for Wastewater Treatment. Environmental Technology Business Forum, Taiwan.

- Prengle, H.W., Symons, M.J. and Belhateche, D. 1987. H₂O₂/ visUV process for photo-oxidation of waterborne hazardous substances chlorinated hydrocarbons. Waste Management 16 : 327-333.
- Preocanin, T., Krehula, S. and Kallay, N. 2002. Enthalpy of surface reactions: temperature dependency of pH of acidic or basic concentrated hematite suspension. Applied surface Science 196 : 392-400.
- Reymond, J.P. and Kolenda, F. 1999. Estimation of the point of zero charge of simple and mixed oxides by mass titration. Powder Technology 103 : 30-36.
- Rodgers, D. J. and Bunce, N.J. 2001. Review Paper, Treatment methods for the remediation of nitroaromatic explosives. Water Research 35 : 2101-2111.
- Rodriguez, M., Kirchner, A., Contreras, S., Chamarro, E. and Esplugas, S. 2000. Influence of H₂O₂ and Fe (III) in photodegradation of nitrobenzene. Journal of Photochemistry and Photobiology A: Chemistry 133 : 123-127.
- Rodriguez, M.L., Timokhin, VI., Contreras, S., Chamarro, E. and esplugas, S. 2003. Rate equation for the degradation of nitrobenzene by 'Fenton-like' reagent. Advances in Environmental Research 7 : 583-595.
- Sakulkitimasak, P. 2004. Oxidation of nitrobenzene by fluidized-bed Fenton process. Master's thesis. Department of engineering environmental engineering faculty of engineering. King Mongkut's University of Technology Thonburi.
- Tai, C.Y. 1999. Crystal growth kinetics of two-step growth process in liquid fluidized-bed crystallizers. Journal of Crystal Growth 206 : 109-108.
- Teel, A.L., Warberg, C.R., Atkinson, C.A and Watts, R.J., 2001. Comparison mineral and soluble iron Fenton's catalysts for the treatment of thichloroethylene. Water Research 35 : 977-984.

U.S. EPA. 1995. Nitrobenzene Fact Sheet : Support Document 98-95-3. Pollution Prevention and Toxics 7407.

U.S. Peroxide. Fenton's Reagent [online]. Available from:

<http://www.h2o2.com/applications/industrialwastewater/fentonsreagent.html>

[2005, November 15].

Appendices

Appendix A

Carriers Characterization

Table A.1 Carriers Characterization, pH_{pzc} of carriers.Table A.1a pH_{pzc} of Al_2O_3

Mass, g/l	pH	
	DI water	Nitrobenzene & ionic strength ^a
0.000	6.36	5.89
0.200	6.62	6.04
0.400	7.02	6.41
0.600	8.01	7.45
1.200	8.71	8.20
2.400	8.92	8.52
5.000	9.3	8.90
10.000	9.4	9.14
20.000	9.5	9.14
30.000	9.5	9.15
40.000	9.51	9.15
50.000	9.51	9.16

Note: 24 hours of reaction, 0.010 M of NB and 0.0250 M of Na_2SO_4

Table A.1b pH_{pzc} of SiO_2

Mass, g/l	pH	
	DI water	Nitrobenzene & ionic strength ^a
0.000	6.97	6.45
0.200	6.87	6.43
0.400	6.77	6.41
0.600	6.57	6.40
1.200	6.45	6.39
2.400	6.43	6.37
5.000	6.42	6.36
10.000	6.41	6.36
20.000	6.41	6.36
30.000	6.4	6.35
40.000	6.4	6.35
50.000	6.41	6.35

Note: 24 hours of reaction, 0.010 M of NB and 0.0250 M of Na_2SO_4

Appendix B

Control Experiment (adsorption)

Table B.1 Control Experiment in fluidized-bed reactor (adsorption).

Table B.1a Nitrobenzene remaining with Al_2O_3 .

Time, min	Nitrobenzene, C/Co					
	only	+ H_2O_2	+ Fe^{2+}	+ Al_2O_3	+ Al_2O_3 + H_2O_2	+ Al_2O_3 + Fe^{2+}
0	1.000	1.000	1.000	1.000	1.000	1.000
2	0.981	0.974	0.969	0.984	0.98	0.986
5	0.969	0.951	0.948	0.967	0.951	0.968
10	0.951	0.932	0.922	0.956	0.92	0.945
20	0.932	0.912	0.913	0.925	0.891	0.911
30	0.91	0.892	0.899	0.911	0.88	0.894
60	0.895	0.875	0.887	0.881	0.869	0.878

Note: 0.010 of Nitrobenzene, pH 2.8, Al_2O_3 100 g/l.

Table B.1b Nitrobenzene remaining with SiO_2 .

Time, min	Nitrobenzene, C/Co					
	only	+ H_2O_2	+ Fe^{2+}	+ SiO_2	+ SiO_2 + H_2O_2	+ SiO_2 + Fe^{2+}
0	1.000	1.000	1.000	1.000	1.000	1.000
2	0.981	0.974	0.969	0.988	0.981	0.987
5	0.969	0.951	0.948	0.978	0.969	0.964
10	0.951	0.932	0.922	0.965	0.942	0.935
20	0.932	0.912	0.913	0.934	0.909	0.908
30	0.91	0.892	0.899	0.901	0.891	0.891
60	0.895	0.875	0.887	0.887	0.874	0.88

Note: 0.010 of Nitrobenzene, pH 2.8, SiO_2 100 g/l.

Appendix C

Comparison of different carriers

Table C.1 Comparison of different carriers onto the degradation of nitrobenzene.

Table C.1a Nitrobenzene remaining with Al_2O_3 .

Time, min	Nitrobenzene , C/Co			
	free Cl^-	0.0015 M of Cl^-	0.02 M of Cl^-	0.2 M of Cl^-
0	1.000	1.000	1.000	1.000
2	0.804	0.773	0.823	0.861
5	0.423	0.411	0.601	0.728
10	0.31	0.301	0.321	0.519
20	0.119	0.128	0.143	0.274
30	0.095	0.105	0.111	0.14
60	0.091	0.103	0.096	0.111

Note: 0.010 M of NB, 0.050 M of H_2O_2 , 0.001 M of Fe^{2+} , 100 g/l of Al_2O_3 and initial pH 2.8.

Table C.1b Nitrobenzene remaining with SiO_2 .

Time, min	Nitrobenzene , C/Co			
	free Cl^-	0.0015 M of Cl^-	0.02 M of Cl^-	0.2 M of Cl^-
0	1.000	1.000	1.000	1.000
2	0.846	0.793	0.865	0.874
5	0.595	0.521	0.52	0.782
10	0.349	0.277	0.376	0.536
20	0.267	0.158	0.201	0.234
30	0.165	0.131	0.185	0.194
60	0.161	0.118	0.183	0.155

Note: 0.010 M of NB, 0.050 M of H_2O_2 , 0.001 M of Fe^{2+} , 100 g/l of SiO_2 and initial pH 2.8.

Appendix D

pH optimization for Fluidized-bed Fenton process

Table D.1 pH optimization for Fluidized-bed Fenton process

Table D.1a Nitrobenzene remaining at pH 2.0.

Time, min	pH 2.0 Nitrobenzene remaining		
	Free Cl ⁻	0.02M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000
2	0.902	0.923	0.929
5	0.847	0.869	0.876
10	0.758	0.792	0.815
20	0.705	0.758	0.789
30	0.682	0.695	0.763
60	0.665	0.681	0.736

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.00025 M of Fe²⁺, 100 g/l of Al₂O₃.

Table D.1b Nitrobenzene remaining at pH 2.8.

Time, min	pH 2.8 Nitrobenzene remaining		
	Free Cl ⁻	0.02M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000
2	0.781	0.85	0.926
5	0.623	0.759	0.824
10	0.531	0.646	0.724
20	0.392	0.59	0.655
30	0.284	0.483	0.596
60	0.255	0.441	0.566

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.00025 M of Fe²⁺, 100 g/l of Al₂O₃.

Table D.1c Nitrobenzene remaining at pH 3.50.

Time, min	pH 3.5 Nitrobenzene remaining		
	Free Cl ⁻	0.02M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000
2	0.886	0.891	0.908
5	0.809	0.852	0.872
10	0.751	0.776	0.813
20	0.693	0.753	0.766
30	0.666	0.694	0.73
60	0.638	0.663	0.724

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.00025 M of Fe²⁺, 100 g/l of Al₂O₃.

Table D.1 pH optimization for Fluidized-bed Fenton process (continued)

Table D.1d Nitrobenzene remaining at pH 4.0.

Time, min	pH 4.0 Nitrobenzene remaining		
	Free Cl ⁻	0.02M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000
2	0.858	0.862	0.905
5	0.816	0.829	0.866
10	0.754	0.773	0.807
20	0.694	0.716	0.743
30	0.635	0.674	0.727
60	0.642	0.661	0.716

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.00025 M of Fe²⁺, 100 g/l of Al₂O₃.

Table D.1e Nitrobenzene remaining at pH 5.0.

Time, min	pH 5.0 Nitrobenzene remaining		
	Free Cl ⁻	0.02M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000
2	0.846	0.886	0.901
5	0.776	0.809	0.833
10	0.737	0.781	0.791
20	0.693	0.723	0.746
30	0.642	0.671	0.679
60	0.632	0.652	0.683

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.00025 M of Fe²⁺, 100 g/l of Al₂O₃.

Table D.1f Nitrobenzene remaining at pH 6.0.

Time, min	pH 6.0 Nitrobenzene remaining		
	Free Cl ⁻	0.02M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000
2	0.891	0.924	0.932
5	0.806	0.855	0.875
10	0.753	0.784	0.795
20	0.655	0.703	0.733
30	0.605	0.664	0.682
60	0.595	0.647	0.677

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.00025 M of Fe²⁺, 100 g/l of Al₂O₃.

Appendix E

Carriers size for Fluidized-bed Fenton process

Table E.1 Carriers size on the oxidation of nitrobenzene for Fluidized-bed Fenton process.

Table E.1a Nitrobenzene remaining with 3.50 mm of Al_2O_3 .

Time, min	Nitrobenzene , C/Co Al_2O_3 (3.50 mm, average size)			
	Free Cl^-	0.0015 M of Cl^-	0.02 M of Cl^-	0.2 M of Cl^-
0	1.000	1.000	1.000	1.000
2	0.801	0.856	0.895	0.936
5	0.73	0.786	0.814	0.852
10	0.629	0.658	0.762	0.813
20	0.435	0.509	0.635	0.719
30	0.352	0.409	0.501	0.616
60	0.332	0.348	0.457	0.572

Note: 0.01 M of NB, 0.050 M of H_2O_2 , 0.0025 M of Fe^{2+} , 100 g/l of Al_2O_3 and initial pH 2.8.

Table E.1b Nitrobenzene remaining with 2.50 mm of Al_2O_3 .

Time, min	Nitrobenzene , C/Co Al_2O_3 (2.50 mm, average size)			
	Free Cl^-	0.0015 M of Cl^-	0.02 M of Cl^-	0.2 M of Cl^-
0	1.000	1.000	1.000	1.000
2	0.781	0.802	0.85	0.916
5	0.623	0.701	0.759	0.794
10	0.531	0.598	0.646	0.694
20	0.392	0.471	0.59	0.635
30	0.284	0.342	0.483	0.596
60	0.255	0.287	0.441	0.57

Note: 0.01 M of NB, 0.050 M of H_2O_2 , 0.0025 M of Fe^{2+} , 100 g/l of Al_2O_3 and initial pH 2.8.

Appendix F

Comparison between Traditional Fenton and Fluidized-bed Fenton Processes

Table F.1 Comparison between Traditional Fenton and Fluidized-bed Fenton Processes.

Table F.1a Nitrobenzene remaining in Fluidized-bed Fenton Processes.

Time, min	Nitrobenzene, C/Co Fluidized-bed Fenton Processes			
	Free Cl ⁻	0.0015 M of Cl ⁻	0.02 M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000	1.000
2	0.798	0.807	0.838	0.856
5	0.405	0.393	0.589	0.719
10	0.279	0.28	0.301	0.503
20	0.092	0.102	0.118	0.25
30	0.067	0.078	0.085	0.112
60	0.063	0.076	0.07	0.082

Note: 0.01 M of NB, 0.050 M of H₂O₂, 0.001 M of Fe²⁺, 100 g/l of Al₂O₃ and initial pH 2.8.

Table F.1b Nitrobenzene remaining in Traditional Fenton Fenton Processes.

Time, min	Nitrobenzene, C/Co Traditional Fenton Fenton Processes			
	Free Cl ⁻	0.0015 M of Cl ⁻	0.02 M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000	1.000
2	0.801	0.798	0.863	0.9
5	0.73	0.762	0.732	0.777
10	0.629	0.65	0.662	0.708
20	0.435	0.28	0.364	0.493
30	0.352	0.153	0.167	0.22
60	0.332	0.12	0.133	0.21

Note: 0.01 M of NB, 0.050 M of H₂O₂, 0.001 M of Fe²⁺ and initial pH 2.8.

Appendix G

**Effect of chloride ions on the oxidation of nitrobenzene by
fluidized-bed Fenton process in the presence of ferrous concentration**

Table G. Effect of chloride ions on the oxidation of nitrobenzene by fluidized-bed Fenton process in the presence of ferrous concentration.

Table G.1a Effect of chloride ions at 0.001 M of ferrous.

Time, min	Nitrobenzene , C/Co Ferrous = 0.001 M			
	Free Cl ⁻	0.0015 M of Cl ⁻	0.02 M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000	1.000
2	0.804	0.813	0.843	0.861
5	0.423	0.411	0.601	0.728
10	0.3	0.301	0.321	0.519
20	0.119	0.128	0.143	0.274
30	0.095	0.105	0.111	0.14
60	0.091	0.103	0.096	0.111

Note: 0.01 M of NB, 0.050 M of H₂O₂, 100 g/l of Al₂O₃ and initial pH 2.8.

Table G.1b Effect of chloride ions at 0.0005 M of ferrous.

Time, min	Nitrobenzene , C/Co Ferrous = 0.0005 M			
	Free Cl ⁻	0.0015 M of Cl ⁻	0.02 M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000	1.000
2	0.777	0.797	0.821	0.902
5	0.563	0.652	0.722	0.79
10	0.392	0.471	0.53	0.597
20	0.174	0.223	0.261	0.35
30	0.109	0.126	0.145	0.229
60	0.061	0.069	0.108	0.204

Note: 0.01 M of NB, 0.050 M of H₂O₂, 100 g/l of Al₂O₃ and initial pH 2.8.

Table G. Effect of chloride ions on the oxidation of nitrobenzene by fluidized-bed Fenton process in the presence of ferrous concentration (continued).

Table G.1c Effect of chloride ions at 0.000375 M of ferrous.

Time, min	Nitrobenzene, C/Co Ferrous = 0.000375 M			
	Free Cl ⁻	0.0015 M of Cl ⁻	0.02 M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000	1.000
2	0.786	0.809	0.855	0.9
5	0.498	0.66	0.757	0.769
10	0.352	0.518	0.613	0.634
20	0.211	0.302	0.395	0.453
30	0.109	0.195	0.265	0.414
60	0.08	0.081	0.125	0.254

Note: 0.01 M of NB, 0.050 M of H₂O₂, 100 g/l of Al₂O₃ and initial pH 2.8.

Table G.1d Effect of chloride ions at 0.00025 M of ferrous.

Time, min	Nitrobenzene, C/Co Ferrous = 0.00025 M			
	Free Cl ⁻	0.0015 M of Cl ⁻	0.02 M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000	1.000
2	0.781	0.802	0.85	0.926
5	0.623	0.701	0.759	0.824
10	0.531	0.598	0.646	0.724
20	0.392	0.471	0.59	0.655
30	0.284	0.342	0.483	0.596
60	0.255	0.287	0.441	0.566

Note: 0.01 M of NB, 0.050 M of H₂O₂, 100 g/l of Al₂O₃ and initial pH 2.8.

Appendix H

Kinetic Determination for Fluidized-bed Fenton Process

Table H. Kinetic Determination for Fluidized-bed Fenton Process

Table H.1 Effect of ferrous.

Time, min	Nitrobenzene , C/Co Ferrous			
	0.00025 M of Fe ²⁺	0.000375 M of Fe ²⁺	0.0005 M of Fe ²⁺	0.001 M of Fe ²⁺
0	1.000	1.000	1.000	1.000
2	0.926	0.9	0.902	0.861
5	0.824	0.769	0.79	0.728
10	0.724	0.634	0.597	0.519
20	0.655	0.453	0.35	0.274
30	0.596	0.414	0.229	0.14
60	0.566	0.254	0.204	0.111

Note: 0.01 M of NB, 0.050 M of H₂O₂, 0.2 M of Cl⁻, 100 g/l of Al₂O₃ and initial pH 2.8.

Table H.2 Effect of hydrogen peroxide.

Time, min	Nitrobenzene , C/Co hydrogen peroxide			
	0.025 M of H ₂ O ₂	0.050 M of H ₂ O ₂	0.075 M of H ₂ O ₂	0.100 M of H ₂ O ₂
0	1.000	1.000	1.000	1.000
2	0.875	0.916	0.862	0.959
5	0.808	0.794	0.816	0.833
10	0.685	0.694	0.694	0.698
20	0.615	0.635	0.655	0.661
30	0.589	0.596	0.596	0.6
60	0.575	0.57	0.587	0.588

Note: 0.01 M of NB, 0.00025 M of Fe²⁺, 0.2 M of Cl⁻, 100 g/l of Al₂O₃ and initial pH 2.8.

Table G.1d Effect of chloride ions.

Time, min	Nitrobenzene , C/Co Ferrous = 0.00025 M			
	Free Cl ⁻	0.0015 M of Cl ⁻	0.02 M of Cl ⁻	0.2 M of Cl ⁻
0	1.000	1.000	1.000	1.000
2	0.781	0.802	0.85	0.926
5	0.623	0.701	0.759	0.824
10	0.531	0.598	0.646	0.724
20	0.392	0.471	0.59	0.655
30	0.284	0.342	0.483	0.596
60	0.255	0.287	0.441	0.566

Note: 0.01 M of NB, 0.00025 M of Fe²⁺, 0.050 M of H₂O₂, 100 g/l of Al₂O₃
and initial pH 2.8.

Appendix I

Effect of carriers on the oxidation of nitrobenzene in fluidized-bed reactor

Table I.1 Effect of initial amount of aluminium oxide media on the oxidation of nitrobenzene in FBR.

Time, min	10 g of aluminium oxide			25 g of aluminium oxide		
	NB	H ₂ O ₂	Fe ²⁺	NB	H ₂ O ₂	Fe ²⁺
0	1.000	1.000	1.000	1.000	1.000	1.000
2	0.759	0.749	0.41	0.815	0.773	0.377
5	0.525	0.658	0.905	0.533	0.662	0.854
10	0.144	0.409	0.925	0.164	0.372	0.901
20	0.091	0.114	0.935	0.09	0.12	0.911
30	0.075	0.048	0.936	0.082	0.045	0.925
60	0.064	0	0.941	0.078	0	0.93

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.001 M of Fe²⁺ and initial pH 2.8.

Table I.1 Effect of initial amount of aluminium oxide media on the oxidation of nitrobenzene in FBR (continued).

Time, min	50 g of aluminium oxide			75 g of aluminium oxide		
	NB	H ₂ O ₂	Fe ²⁺	NB	H ₂ O ₂	Fe ²⁺
0	1.000	1.000	1.000	1.000	1.000	1.000
2	0.686	0.783	0.375	0.711	0.779	0.336
5	0.336	0.655	0.752	0.513	0.679	0.663
10	0.152	0.437	0.822	0.229	0.426	0.721
20	0.091	0.198	0.825	0.089	0.184	0.757
30	0.072	0.033	0.831	0.075	0.048	0.775
60	0.058	0	0.84	0.061	0	0.792

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.001 M of Fe²⁺ and initial pH 2.8.

Table I.1 Effect of initial amount of aluminium oxide media on the oxidation of nitrobenzene in FBR (continued).

Time, min	100 g of aluminium oxide		
	NB	H ₂ O ₂	Fe ²⁺
0	1.000	1.000	1.000
2	0.804	0.808	0.254
5	0.423	0.657	0.559
10	0.31	0.414	0.682
20	0.119	0.112	0.734
30	0.095	0.034	0.753
60	0.091	0.024	0.773

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.001 M of Fe²⁺ and initial pH 2.8.

Table I.2 Effect of reusability of aluminium oxide media on the oxidation of nitrobenzene in FBR.

Time, min	Cycle 1			Cycle 2		
	NB	H ₂ O ₂	Fe ²⁺	NB	H ₂ O ₂	Fe ²⁺
0	1.000	1.000	1.000	1.000	1.000	1.000
2	0.73	0.918	0.425	0.714	0.883	0.518
5	0.613	0.825	0.629	0.601	0.81	0.764
10	0.337	0.676	0.635	0.319	0.664	0.75
20	0.114	0.305	0.659	0.084	0.376	0.759
30	0.069	0.111	0.645	0.063	0.115	0.723
60	0.06	0	0.665	0.057	0	0.727

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.001 M of Fe²⁺, 100 g/l of Al₂O₃ and initial pH 2.8.

Table I.2 Effect of reusability of aluminium oxide media on the oxidation of nitrobenzene in FBR (continued).

Time, min	Cycle 3			Cycle 4		
	NB	H ₂ O ₂	Fe ²⁺	NB	H ₂ O ₂	Fe ²⁺
0	1.000	1.000	1.000	1.000	1.000	1.000
2	0.758	24.213	0.894	0.787	0.91	0.355
5	0.537	62.981	0.851	0.601	0.843	0.599
10	0.34	66.037	0.678	0.375	0.704	0.761
20	0.087	91.283	0.33	0.095	0.333	0.787
30	0.065	93.523	0.135	0.078	0.1	0.782
60	0.058	94.165	0	0.064	0	0.771

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.001 M of Fe²⁺, 100 g/l of Al₂O₃ and initial pH 2.8.

Table I.2 Effect of reusability of aluminium oxide media on the oxidation of nitrobenzene in FBR (continued).

Time, min	Cycle 5		
	NB	H ₂ O ₂	Fe ²⁺
0	1.000	1.000	1.000
2	0.798	0.916	0.389
5	0.652	0.834	0.448
10	0.412	0.664	0.769
20	0.154	0.325	0.781
30	0.095	0.124	0.788
60	0.087	0.002	0.785

Note: 0.010 M of NB, 0.050 M of H₂O₂, 0.001 M of Fe²⁺, 100 g/l of Al₂O₃ and initial pH 2.8.

Table I.3 Effect of ferrous concentration on the oxidation of nitrobenzene in FBR;
iron crystallization.

Time, min	Remaining , C/Co ²⁺ 0.001 M of Fe			
	NB	H ₂ O ₂	Fe ²⁺	Total iron
0	1.000	1.000	1.000	1.000
2	0.856	0.867	0.527	0.773
5	0.719	0.792	0.702	0.575
10	0.503	0.655	0.719	0.512
20	0.25	0.354	0.737	0.355
30	0.112	0.139	0.743	0.337
60	0.082	0.033	0.749	0.328

Note: 0.01 M of NB, 0.050 M of H₂O₂, 0.2 M of Cl⁻, 100 g/l of Al₂O₃ and
initial pH 2.8.

Table I.3 Effect of ferrous concentration on the oxidation of nitrobenzene in FBR;
iron crystallization (continued).

Time, min	Remaining , C/Co ²⁺ 0.0005 M of Fe			
	NB	H ₂ O ₂	Fe ²⁺	Total iron
0	1.000	1.000	1.000	1.000
2	0.902	0.89	0.285	0.787
5	0.79	0.789	0.421	0.706
10	0.597	0.682	0.478	0.617
20	0.35	0.51	0.546	0.555
30	0.229	0.337	0.546	0.564
60	0.204	0.079	0.546	0.526

Note: 0.01 M of NB, 0.050 M of H₂O₂, 0.2 M of Cl⁻, 100 g/l of Al₂O₃ and
initial pH 2.8.

Table I.3 Effect of ferrous concentration on the oxidation of nitrobenzene in FBR;
iron crystallization (continued).

Time, min	Remaining , C/Co ₂₊ 0.00025 M of Fe			
	NB	H ₂ O ₂	Fe ²⁺	Total iron
0	1.000	1.000	1.000	1.000
2	0.916	0.86	0.1	0.711
5	0.794	0.831	0.09	0.613
10	0.694	0.803	0.05	0.607
20	0.635	0.789	0.04	0.609
30	0.596	0.773	0.02	0.61
60	0.57	0.764	0.01	0.682

Note: 0.01 M of NB, 0.050 M of H₂O₂, 0.2 M of Cl⁻, 100 g/l of Al₂O₃ and
initial pH 2.8.

Appendix J

**Effect of inorganic ions on the oxidation of nitrobenzene in
fluidized-bed reactor**

Table J.1 Effect of dyhydrogen phosphate on the oxidation of nitrobenzene in FBR.

Time, min	Nitrobenzene , C/Co (dyhydrogen phosphate)			
	Free H_2PO_4^-	0.0015 M of H_2PO_4^-	0.02 M of H_2PO_4^-	0.2 M of H_2PO_4^-
0	1.000	1.000	1.000	1.000
2	0.798	0.721	0.775	0.795
5	0.405	0.689	0.721	0.755
10	0.279	0.626	0.677	0.698
20	0.092	0.548	0.601	0.637
30	0.067	0.509	0.559	0.587
60	0.063	0.493	0.535	0.551

Note: 0.01 M of NB, 0.050 M of H_2O_2 , 0.001 M of Fe^{2+} , 100 g/l of Al_2O_3 and initial pH 2.8.

Table J.2 Effect of nitrate on the oxidation of nitrobenzene in FBR.

Time, min	Nitrobenzene , C/Co (nitrate)			
	Free NO_3^-	0.0015 M of NO_3^-	0.02 M of NO_3^-	0.2 M of NO_3^-
0	1.000	1.000	1.000	1.000
2	0.798	0.672	0.799	0.743
5	0.405	0.559	0.499	0.475
10	0.279	0.287	0.284	0.316
20	0.092	0.098	0.116	0.112
30	0.067	0.072	0.087	0.09
60	0.063	0.065	0.064	0.076

Note: 0.01 M of NB, 0.050 M of H_2O_2 , 0.001 M of Fe^{2+} , 100 g/l of Al_2O_3 and initial pH 2.8.

Appendix K

Effect of ferrous by COD analysis on the oxidation of nitrobenzene

Table K.1 Effect of ferrous by COD analysis on the oxidation of nitrobenzene.

Time, min	COD remaining , C/Co (Ferrous)		
	0.00025 M of Fe ²⁺	0.0005 M of Fe ²⁺	0.001 M of Fe ²⁺
0	1.000	1.000	1.000
2	0.8361	0.8003	0.7606
5	0.8137	0.7914	0.7461
10	0.7975	0.7906	0.7024
20	0.7853	0.7858	0.6742
30	0.7742	0.7651	0.6614
60	0.7626	0.7172	0.655

Note: 0.01 M of NB, 0.050 M of H₂O₂, 0.2 M of Cl⁻, 100 g/l of Al₂O₃ and initial pH 2.8.

Appendix L

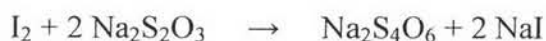
Analysis of Hydrogen Peroxide

Appendix L

Standard iodometric

Principle

Hydrogen peroxide oxidizes iodide to iodine in the presence of acid and molybdate catalyst. The iodine formed is titrated with thiosulfate solution, incorporating a starch indicator as demonstrated in the following equation:



Interferences

Other oxidizing agents will also produce iodine, whereas reducing agents (and unsaturated organics) will react with the liberated iodine. The contribution from other oxidizing agents can be determined by omitting the acid and molybdate catalyst.

Reagents

1. potassium iodide solution (1 % w/v): dissolve 10 gram KI into 1 l of RO water.
2. Ammonium molybdate solution: dissolve 9 grams ammonium molybdate in 10 ml 6N NH_4OH , add 24 grams NH_4OH_3 and dilute to 100 ml with RO water.
3. Sulfuric acid solution (1:4 N_2SO_4): carefully add one part N_2SO_4 98% to four parts RO water.
4. Starch indicator
5. Sodium thiosulfate solution (0.0125 N)

Apparatus

1. Analytical balance (+/- mg/l)
2. Small weighing bottle (<5 ml)
3. 250 ml Erlenmeyer flask
4. 50 ml burette (Class A)
5. Medicine dropper

Procedure

1. Transfer sample to Erlenmeyer flask.
2. Add to Erlenmeyer flask 50 ml of RO water. Next, 10 ml of sulfuric acid solution and 15 ml of potassium iodide were added. Then two drops ammonium molybdate solution was added.
3. Titrate with 0.0125 N sodium thiosulfate to faint yellow or straw color. Swirl or stir gently during titration to minimize iodine loss.
4. Add about 2 ml starch indicator, and continue titration until the blue color just disappears.
5. Repeat steps 2-4 on a blank sample of water.
6. Note ml of 0.0125 N $\text{Na}_2\text{S}_2\text{O}_3$ for samples and blanks analysis.

Calculation

$$\text{H}_2\text{O}_2, \text{ mg/} = \frac{(\text{A} - \text{B}) \times \text{N} \times 17 \times 1000}{\text{ml.sample}}$$

Where: A = ml of $\text{Na}_2\text{S}_2\text{O}_3$ for sample

B = ml of $\text{Na}_2\text{S}_2\text{O}_3$ for blank

N = Normality of $\text{Na}_2\text{S}_2\text{O}_3$

Appendix M

Analysis of Ferrous Ions

Appendix M

Analysis of Ferrous Ions

Background

The 1,10-phenanthroline complex with iron (II) was first discovered by Blau. Aspectrophotometric determination of iron dependent on the formation of the iron(II)-1,10-phenanthroline complex was developed by Fortune Mellon. The iron(II)-1, 10-phenanthroline complex reddish orange in color.

Apparatus

1. Colorimetric Equipment; Spectrophotometer (Shimadzu UV-1201). The absorbance used for ferrous (Fe^{2+}) analysis was 510 nm.
2. Acid-washed Glassware. All glass wares were washed with conc. HCl and rinsed with DI water to remove deposit of iron oxide.
3. Membrane Filter: a 0.45 μm membrane filter was used to filter the sample to remove precipitation particle on solution.
4. Reagents:

All of reagents were prepared by distilled water. Reagents were stored in glass bottles. The HCL and ammonium acetate solutions were stable indefinitely if they were tightly closed the bottles. The standard ferrous ion (Fe^{2+}) solutions were not stable, it was prepared daily.

HCl: 20 ml of concentrated hydrochloric acid was diluted to 1000 ml with DI water.

Ammonium Acetate Buffer Solution: 500 g of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ was dissolved in 300 ml of DI water. Then, 1400 ml of concentrated acetic acid was filled up to the mark of 2000 ml.

Phenanthroline Solution: 5 g of 1,10-phenanthroline monohydrate, $C_{12}H_8N_2H_2O$, was dissolved and 1 ml of concentrated hydrochloric acid was added. Then, DI water was used to make the mark of 1000 ml.

Stock Ferrous Ion Solution: 20 mo of concentrated H_2SO_4 was slowly added to 25 ml DI water. Then 5 ml of stock ferrus ion solution was diluted to 50 ml with DI water. The standard solution was 50 mg/l as Fe^{2+} .

Procedure

1. Sample preparation for calibration curves: The satandard ferrous (Fe^{2+}) solution was prepared in the range 0 to 10 mg/l as Fe^{2+} . 25 mo of HCl from stock solution was prepared in six 50 ml volumetric flasks. Then, 10 ml of phenanthroline solution and 5 mo of ammonium acetate solution were added with vigorous stirring. 1, 2, 3, 4, 5 and 10 mo of 50 mg/l as Fe^{2+} standard solution were pipetted, respectively. After that, the samples were diluted to 50 ml with DI water, mixed thoroughly.

2. Ferrous Ion analysis: To determine ferrous ion, 25 mo of HCl from stock solution was prepared in 50 ml volumetric flask. Then, 10 ml of phenanthroline solution and 5 ml of ammonium acetate solution were added with vigorous stirring. 2 ml of sample was filled and diluted to 50 ml with DI water. After that, it had to stand for 30 min. Do not expose to sunlight. (Color development was rapidly in the presence of excess phenanthroline.)

Calculation

$$y = 5.0694x - 0.1313$$

Where: $y = \text{Fe}^{2+}$, mg/l, $x = \text{absorbance at 510 nm}$.

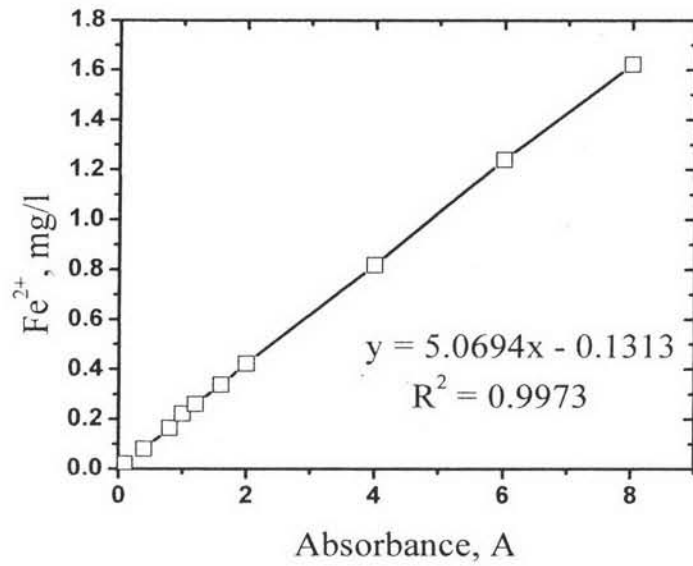


Figure M.1 Ferrous vs. Absorbance

BIOGRAPHY

Mr. Somboon Chintitanun was born on June 9th, 1981 in Bangkok, Thailand. He graduated Bachelor's degree in Civil Engineering from the Faculty of Engineering, South-East Asia University 2003. He pursued his Master Degree in Engineering Program in Environmental Engineering Department of Environmental Engineering Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand on May, 2004. He had attended to oral presentation and submitted a publication with his advisor, Associate Professor Chavalit Ratanatamskul and co-advisor Professor Ming-Chun Lu, in the subject of "Effect of Chloride Ions on the Oxidation of Nitrobenzene by Fluidized-bed Fenton Process", the international conference on Environmental Quality Concern, Control and Conservation on June 29th, 2006 in Tainan, Taiwan.