

EFFECTS OF REACTION TIME AND pH ON FENTON'S BATCH PROCESS FOR THE TREATMENT OF LEACHATE

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Abstract

The effects of important parameters such as reaction time and pH on the Fenton's process were evaluated using a batch reactor. It was proven that organic materials and heavy metals in leachate could be successfully removed by Fenton's reagent. Favorable operation conditions were investigated.

It was observed that the reaction between ferrous iron and hydrogen peroxide with the production of hydroxyl radical was almost complete in 10 minutes. That is, the oxidation of organic materials by Fenton's reagent was so fast that it was complete in 30 minutes with batch experiments. With the formation of carbonic acid, pH of the batch reactor decreased to favorable acidic conditions without acid addition. The oxidation of organic materials in the leachate showed a pH dependence and was most efficient in the pH range of 2-3.

Keywords : leachate, Fenton's reagent, reaction time, pH, oxidation

Introduction

Solid waste disposal has always been a challenging task for engineers. According to the United States Environmental Protection Agency, nearly 208 million tons of municipal solid waste were generated in America in 1995, and this is projected to reach 218 million tons by 2000.¹ In the United States, most solid wastes (57% in 1995) are disposed of in landfills, a common practice in many countries as well. Landfilling is economically advantageous, minimizes adverse environmental effects, and allows waste to decompose into relatively inert and stabilized materials.² Nevertheless, one of the problems associated with this type of waste disposal is the generation of leachate due to the movement of moisture through solid wastes which may threaten the groundwater. Groundwater

pollution by sanitary landfills has been reported.^{3,4,5} Groundwater pollution is a serious problem in many counties where groundwater is their major source of drinking water. In addition, the adverse impacts to surface water and wildlife or habitats also are major problems.⁵ As a result, leachate disposal is one of the most environmentally sensitive issues facing the landfill operator.

Three landfill leachate disposal methods have been using: discharge to a publicly owned treatment works (POTW), land application of pre-treated leachate, and discharge to surface waters following full treatment.⁶ Most landfills send their leachate to POTW because it is usually cheaper than providing on-site treatment. On-site treatment of landfill leachate is usually carried out by a combination of biological and physical-chemical methods. It is

known that biological processes are effective for readily biodegradable leachates with a high biological oxygen demand (BOD)/chemical oxygen demand (COD) ratio.⁷ However, some materials in landfill leachate, in particular toxic organic materials, are not readily biodegradable but require longer retention times that are not economically feasible. Some refractory and/or toxic materials can not be treated by biological process. Moreover, the fluctuation in leachate amount and characteristics often poses an obstacle to the biological treatment process.

Various physical/chemical processes have been applied to leachate treatment. Physical/chemical processes are particularly useful in treating leachates from older landfills whose organic content is negligible, or as a polishing step for leachates previously treated by biological methods.⁷ Physical/chemical processes include the addition of chemicals to precipitate, coagulate, or oxidize inorganic and organic fractions. Typical physical/chemical processes are adsorptions by activated carbon and ion exchange resins, treatment by reverse osmosis membrane techniques, and chemical oxidation. Ho et al.⁸ have demonstrated that precipitation with lime is effective in the removal of iron and other multivalent ions, color, suspended solids, and COD. Keenan et al.⁹ found that lime treatment alone provided removal efficiencies of approximately 50% of organic materials, 75% of suspended solids, 50% of mercury and cadmium, and at least two-thirds of other heavy metals. Pohland¹⁰ reported good results using a combination of cationic and anionic exchange resins, removing many ionic species as well as dissolved solids and nutrients. Carbon treatment has been studied by many researchers. Carbon treatment of raw young leachates generally yields poor TOC removal due to the poor affinity of carbon for free volatile fatty acids. But it is very effective on poorly biodegradable organics, solvents, pesticides, and humic acids. Chian

and DeWalle¹¹ found that reverse osmosis was the most effective method of removing COD. It is currently used great success for leachate treatment in Rastatt, Germany.¹² Other utilization of the reverse osmosis process has distinct advantages for primary biological treatment prior to reverse osmosis. However, fouling of the membrane and the disposal of highly concentrated liquids produced are still problems. Chemical oxidation is one of alternatives for the wastewater treatment that is either non-biodegradable or toxic. Chemical oxidation was shown to be reasonably effective in removal of COD, iron and color⁸, though only at high concentrations of the oxidizing reagent such as chlorine, calcium hydrochlorinate, potassium permanganate, and ozone. Chemical oxidation processes are slightly more successful than chemical coagulation and precipitation processes for COD removal, but removal efficiencies have been too low to be practical.¹³ Land application of leachate through spray irrigation or overland flow is another possible treatment alternative. Compared with high technologies it has advantages such as low operation costs and maintenance. Fuller¹⁴ investigated leachate pollutant attenuation by soils, and suggested that soil attenuate ability depended largely on its clay and silt content, hydrous oxides of iron, and pH. The advantages of land application are that fluctuating flow rates and water quality may be easily accommodated. Since the soil is the media in which the treatment is to take place, careful consideration must be given to selecting a site with soil properties suitable for the retention and degradation of the leachate to be treated. However, some problems such as discoloration of the grass and ponding were reported.¹⁵ Consequently, better treatment methods which can remove these refractory and/or toxic materials must be found.

Recently, advanced oxidation technologies using Fenton's reagent have been reported as

powerful and cost effective to remove a variety of refractory and/or toxic materials. In this study, an advanced oxidation process using Fenton's reagent was investigated to treat landfill leachate. The objective was to develop a feasible leachate treatment process using Fenton's reagent. Important factors such as reaction time, solution pH were studied.

Methods and Materials

Sample Preparation

Leachate samples were taken with polyethylene bottles from the Central Solid Waste Management Center (CSWMC) at Sandtown, Delaware. Samples taken were preserved in refrigerator at 4C in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA, 1992). Leachate characteristics such as COD, TOC, heavy metals (cobalt, copper, lead and nickel), ferrous iron, and alkalinity were analyzed (Table 1). Prior to the experiments, large particles and debris were removed by centrifuge to minimize particulate effects in oxidation reactions. The leachate samples were centrifuged for 10 minutes at 10,000 rpm (centrifuge force of 16,000 dyne).

Stumm and Morgan¹⁶ expressed the average oxidation state of organic carbon in the wastewater mixture with COD and TOC as:

$$\text{Oxidation state} = [4(\text{TOC}-\text{COD})/\text{TOC}] \quad (1)$$

The amount of oxygen converted to carbon dioxide can be determined from TOC, whilst the ratio of COD to TOC is defined as the average

oxidation state of the carbon that was related to the degree of change in the structure of the organic compounds after oxidation.

Experiments

Batch experiments were performed in a 1 L double jacket spherical plastic reactor with four baffles to minimize vortexing and rotational flow. Mixing was provided by a variable speed motor connected to an epoxy-coated steel shaft and teflon standard three blade propeller. It was vertically mounted above one propeller diameter from the reactor bottom. Mixing speed was about 1,750 rpm. With this speed, it could turn over liquid in the reactor two times per minute. The acidic condition on the reactor was controlled with an automatic pH controller (New Brunswick Scientific Co., Model pH-2). Concentrated sulfuric acid (98 %) was used to bring down the pH to near pre-selected acidic condition. After that, the pH of the reactor was controlled using 1 M sulfuric acid and 10 M sodium hydroxide. The reactor temperature was maintained by a water circulator at 25±1 °C.

Leachate samples were diluted to the desired COD strengths with distilled water, and transferred to the reactor. pH and temperature were adjusted to a desired value. A selected amount of ferrous sulfate was dissolved, and hydrogen peroxide was added. Samples were taken at pre-selected time intervals with 20 mL syringe. Residual hydrogen peroxide and ferrous ion were measured after filtering with a 0.45×10⁻⁶ m filter. Separate aliquots without filtration were taken at the same intervals, and

Table 1. Leachate Characteristics.

	COD (mg/L)	TOC (mg/L)	COD/TOC (mM O ₂ /mM C)	Oxidation state	Alkalinity as CaCO ₃ (mg/L)
Range	8,298-8,894	2,040-2,207	1.45-1.60	(-2.4)-(-1.8)	3,500-4,600
Average	8,589±270	2,134±69	1.4±0.07	-2.1±0.27	4,275±525

(* Number of samples analyzed: 11.)

neutralized to about pH 7.5-8.0 with 10 M and 3 M sodium hydroxide and 1 M sulfuric acid. They were mixed for 10 minutes with magnetic stirred bar. After leaving alone for 20 minutes, the supernatant was centrifuged for 10 minutes at 15,000 rpm (centrifuge force of 27,000 dyne). COD, TOC, heavy metals, hydrogen peroxide, ferrous iron, and total iron in the supernatant were then measured.

One favorable condition was selected through the investigation of one factor effect at a fixed experimental condition. Other factors were tested one by one under the favorable condition selected.

Analytical Methods and Chemicals

Chemical Oxygen Demand (COD)

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content in a sample susceptible to oxidation by a strong chemical oxidants. Most types of organic matters are oxidized by a boiling mixture of chromic and sulfuric acids added to carbon dioxide and water.

COD were determined by both Hach vials and a closed reflux, colorimetric method at 600 nm with Hach spectrophotometer (Hach DR/2000, Loveland, CO) according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1992). The COD testing reagents were prepared as follows:

a) Digestion solution preparation: Added to about 500 mL distilled water 10.216 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103°C for 2 hours, 167 mL concentrated H_2SO_4 , and 33.3 g $HgSO_4$. Dissolved, cooled to room temperature, and diluted to 1000 mL.

b) Sulfuric acid reagent preparation: Added Ag_2SO_4 , reagent grade, to concentrated H_2SO_4 at the ratio of 5.5 g Ag_2SO_4 /kg H_2SO_4 . Let stand 1 to 2 day to dissolve Ag_2SO_4 .

1.5 mL of digestion solution and 3.5 mL of sulfuric acid reagent solution were mixed with 2 mL of aliquot of the sample into a test vial.

With these reagents, COD equivalents between 20 and 1000 mg O_2 /L could be measured. The vial cap was tightly replaced and inverted gently several times to mix the contents. The COD vials were placed into the COD reactor preheated to 150°C and heated for 2 hours. They were cooled to room temperature, and their absorbances were measured. The CODs of the samples were calculated using the linear regression equation obtained from the standard curve.

Hydrogen Peroxide (H_2O_2)

The concentration of hydrogen peroxide was analyzed using a titanium sulfate, $Ti(SO_4)_2$, spectrophotometric method¹⁷ with a visible range spectrophotometer (Hach DR/2000, Loveland, CO). In the presence of hydrogen peroxide under acidic conditions, titanium (IV) forms a yellow complex. The titanium testing reagent was prepared as follows: 0.504 g of $Ti(SO_4)_2$ and 1.6 g of $(NH_4)_2SO_4$ were added into 50 mL of concentrated H_2SO_4 . This solution was boiled on a hot plate at 90°C for one hour to completely dissolve the $Ti(SO_4)_2$. Its volume was then adjusted to 1 liter with distilled water. 9 mL of the titanium reagent was mixed with 1 mL aliquot of the sample in a test tube. The sample was then heated to 60 ± 3 °C in a constant temperature water bath for 10 minutes before cooling to room temperature. The absorbance was measured using a visible range spectrophotometer at 410 nm. The calibration curve was linear in accordance with the Beer-Lambert Law over the range of 10-300 mg/L. Using the linear regression equation of a standard curve at 410 nm, residual hydrogen peroxide was measured.

Ferrous Iron [Fe(II)] and Total Iron

Ferrous iron [Fe(II)] was determined using a 1,10-phenanthroline colorimetric method with a visible range spectrophotometer (Hach DR/2000, Loveland, CO) according to the Standard

Methods for the Examination of Water and Wastewater (APHA, 1992). The ferrous iron forms a reddish complex with 1,10-phenanthroline. The analysis procedure was as follows: 5 mL of aliquot was added to 2 mL of 1,10-phenanthroline monohydrate (0.01 M) solution and 1 mL of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (3 M) solution and 2 mL of HCl (0.5 M) solution, and shaken vigorously. After 6 minutes, the intensity of the red color was measured with a visible range spectrophotometer at 510 nm. Total iron was measured with the flame atomic absorption spectrophotometric method, using AA spectrophotometer (Perkin-Elmer Co., Model 5000), according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1992). To reduce interference of organic matter and to convert metal associated with particulates to the dissolved metal, the samples were digested with concentrated HNO_3 .

Total Organic Carbon (TOC)

The combustion-infrared method using TOC analyzer (Rosemount Dohrmann, Model-190) was used for TOC measurement. TOC was determined by the difference between TC and IC according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1992). The aliquots were injected into total carbon (TC) channel of the analyzer preheated to 950°C , and all carbonaceous materials in the sample were converted to CO_2 . After the conversion, a continuous flow of carrier gas conveyed the resultant detection cloud of CO_2 to the flow-through sample cell of an infrared analyzer for detection of CO_2 . The same aliquots were injected into inorganic carbon (IC) channel of the analyzer preheated to 150°C , and all inorganic carbonates were converted to CO_2 by phosphoric acid.

Heavy Metals

The analysis of the three heavy metals selected (cobalt, copper, lead and nickel) was

performed by the inductively coupled plasma method (ICP, Spectro Analytical Instruments, Spectrum EOP, Germany) according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1992). An aliquot of the sample was injected to ICP. A sample aerosol was generated in an nebulizer and spray chamber, and was carried into plasma through an injection tube within the torch, subjecting the constituent atoms to temperatures of about 6000 to 8000K. The high temperature of plasma excited atom emission efficiently. Ionization of a high percentage of atoms produced ionic emission spectra. The polychromator simultaneously monitored all configured wavelengths using a computer-controlled readout system.

Chemicals

All chemicals used were ACS (American Chemical Society) certified grade and obtained from Fisher Scientific Company, Springfield, NJ, or Aldrich Chemical Company, Milwaukee, WI.

Results and Discussion

Reaction Time Effect

As it is known well, the formation of hydroxyl radicals is the rate limiting step, and the consecutive oxidation reactions are very fast. At first, reaction time effects for the Fenton's treatment were tested to choose an experimental condition for further research at a fixed condition. Oxidation of organic materials in leachate was conducted with 1000 mg/L COD. Ferrous iron sulfate (0.05 M) and hydrogen peroxide (0.075 M) were added and temperature was controlled at $25 \pm 1^\circ\text{C}$. In order to check the effect of pH control, two test runs were performed under the same conditions: (1) pH was not controlled and monitored pH changes throughout the experiment; (2) pH was controlled at $\text{pH } 2.5 \pm 1$.

Figure 1 and Figure 2 showed the decrease of

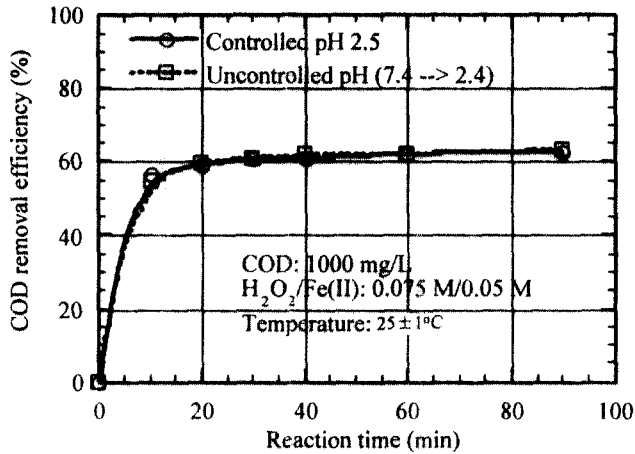


Fig. 1. The changes of COD removal efficiencies at uncontrolled pH and controlled pH 2.5 by batch reactor.

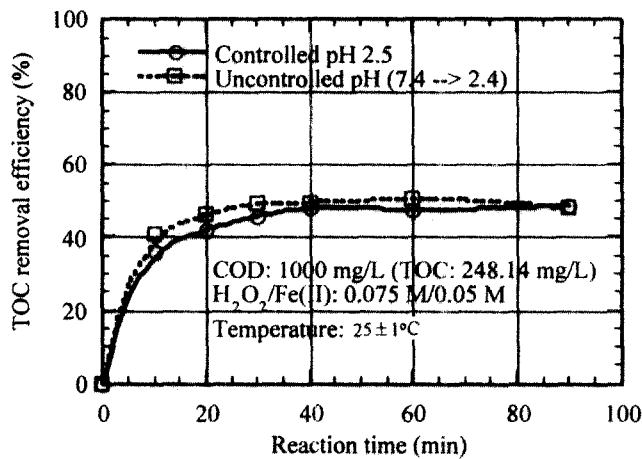


Fig. 2. The changes of TOC removal efficiencies at uncontrolled pH and controlled pH 2.5 by batch reactor.

organic materials as a function of reaction time. The results demonstrated that organic materials were rapidly degraded by Fenton's reagent. Most organic removal occurred in the first 20 minutes. After 20 minutes, the change of residual COD became insignificant. Similar results were obtained by Lin and Peng¹⁸ and Keating et al.¹⁹. Lin and Peng found that drastic COD decrease occurred within 40 minutes of reaction time with textile wastewater.

Keating et al. found that the reaction between hydrogen peroxide and phenol was essentially completed in 30 minutes when ferrous iron was present as catalyst.

Whether pH was controlled or not, it did not give any effect on COD removal efficiencies through the whole reaction times tested (Figure 1), while controlled pH 2.5 gave better TOC removal efficiency than uncontrolled pH run (Figure 2). It means that a low, favorably

controlled pH could provide a better condition for complete oxidation of organic materials in leachate.

The changes of pH in the uncontrolled pH test are shown in Figure 3. It was initially pH 7.4, but decreased to less than pH 3 in a few minutes. Murphy et al.²⁰ found a similar trend when they treated formaldehyde with Fenton-like reagent. They confirmed that formaldehyde oxidized to carbon dioxide by way of formic acid, and that the greatest change in pH occurred during the time that formic acid was being oxidized most rapidly. Keating et al.¹⁹ recommended selecting a slightly higher starting pH to compensate for pH drop. They used a starting pH of between 5 and 6 rather than the optimum pH that was between 3 and 4 during the oxidation of phenol. Eisenhauer²¹ found that the initial pH in the range of 3 to 7 did not affect on the efficiency when 50 mg/L of phenol were treated with the optimum concentration of Fenton's reagent. The pH of the system dropped rapidly to 2.4 to 3.7. The reasons for pH drops can be explained by two types of chemical reactions and nitrification: protonation of carbonate species and formation of organic acids^{22, 23}; nitrification of ammonia²⁴.

More foam was observed on the top layer of

leachate as the oxidation proceeded. This was evidence of carbon dioxide formation. The foam finally disappeared in about 30 minutes. Carbon dioxide formation can be explained as: initial TOC, and alkalinity were 248 mg/L (0.021 M of carbon), and 390 mg/L as CaCO₃ (10^{-2.409} M of carbon), respectively. After 30 minutes of reaction time, residual TOC decreased to 125.5 mg/L (0.01 M of carbon) for controlled pH 2.5, 134.4 mg/L (0.011 M of carbon) for uncontrolled pH, respectively. Net decreased organic carbon was about 0.01 M to 0.011 M. It turned to inorganic carbon. Also, inorganic carbon concentration of untreated leachate was 246 mg/L (10^{-2.253} M), and turned from bicarbonate ions to carbonic acids as the pH changed to acidic. Both of these carbonic acids would dissolve in liquid or escape to air as carbon dioxide making foam.

However, the decrease of pH was not only the formation of carbonic acids. Inorganic carbon concentration of untreated leachate that was 246 mg/L (10^{-2.253} M) was a little bit more than alkalinity (10^{-2.409} M). It means that other materials diminished alkalinity. The concentration of ammonia in untreated leachate was high (37 mg/L, 10^{-2.66} M), enough to contribute to alkalinity. As a result, ammonium

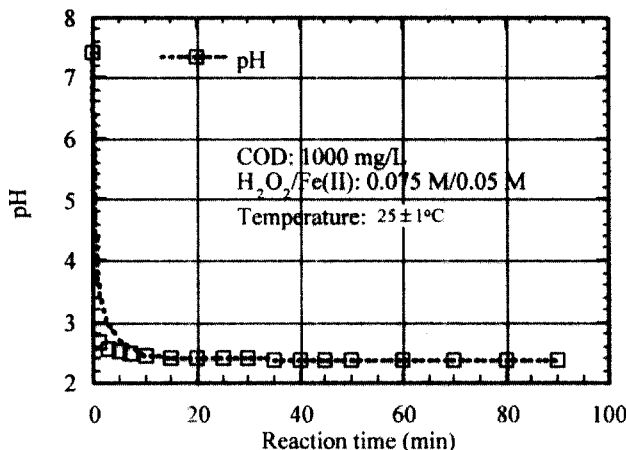


Fig. 3. The change of pH versus reaction time plot by batch reactor.

ion has to be added to the equation of alkalinity. Finally, the alkalinity, the acid-neutralizing capacity of the solution, is defined as:

$$[\text{Alk}] = C_B - C_A$$

$$= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] - [\text{NH}_4^+] \quad (2)$$

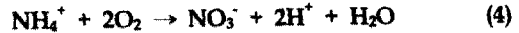
In acidic condition, this equation is simplified:

$$[\text{Alk}] = [\text{HCO}_3^-] - [\text{H}^+] - [\text{NH}_4^+]$$

$$= [\text{H}_2\text{CO}_3^*] \frac{k}{[\text{H}^+]} \quad (3)$$

Where, k is the acidity constant of carbonic acid.

Some ammonia was consumed by nitrification reaction. A ratio of 7.14 mg/L of alkalinity is destroyed per mg of ammonia nitrogen oxidized by the following reaction:



All of these terms must be monitored to calculate their contribution to alkalinity. However, final ammonia and nitrate concentrations were not measured, so that the contribution of nitrification to the alkalinity could not be calculated stoichiometry.

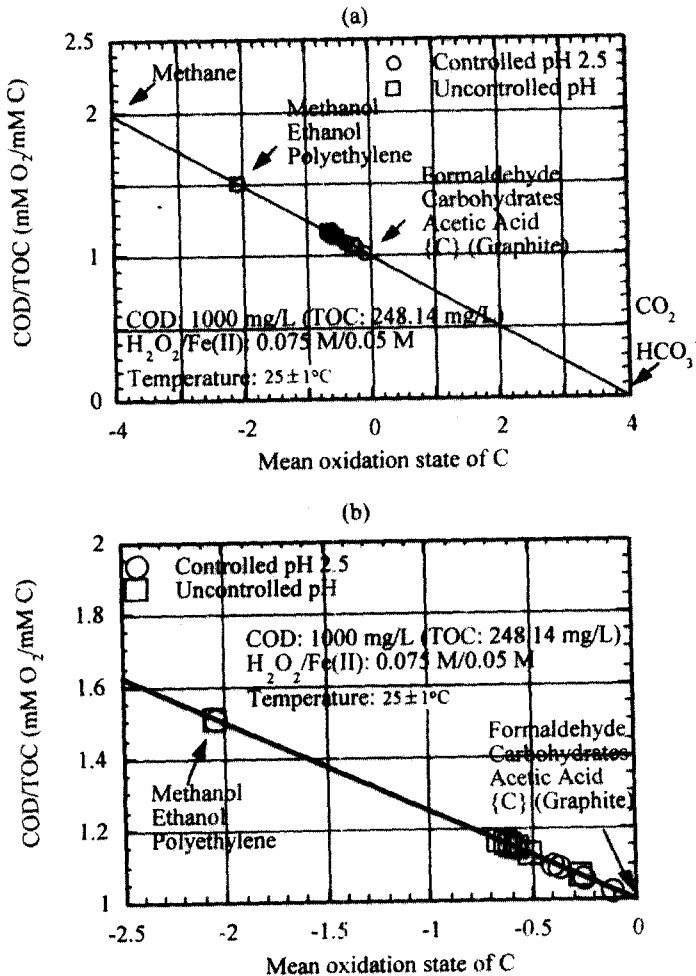


Fig. 4. Oxygen demand and mean oxidation state of organic C in uncontrolled pH and controlled pH 2.5 by batch reactor: (a) all range; (b) narrow range.

Figure 4 showed the change of oxygen demand (COD/TOC ratio) and mean oxidation state of organic C. The COD/TOC ratio was converted to mean oxidation state for each reaction time using the equation (1). In mean oxidation state of organic carbon C, (-)4 oxidation state corresponds to methane, (+)4 oxidation state corresponds to inorganic carbon (CO₂), respectively. In the COD/TOC ratio, (+)2 corresponds to methane, (0) corresponds to inorganic carbon (CO₂), respectively. Mean

oxidation state of organic carbon C and COD/TOC of raw leachate were (-)2 and 1.51, respectively. After treating with Fenton's reagent, COD/TOC ratio decreased in the range of 1.02 to 1.17 (Figure 5), but mean oxidation state of organic carbon C increased in the range of (-)0.66 to (-)0.11 (Figure 6). The COD/TOC ratio decreased rapidly by 10 minutes of reaction time, but kept almost same level after 20 minutes. The increase of mean oxidation state of organic C showed similar trends (Figure

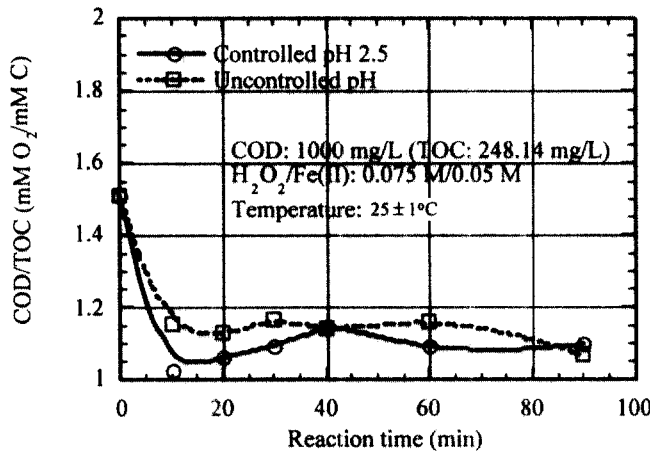


Fig. 5. Oxygen demand versus reaction time plot in uncontrolled pH and controlled pH 2.5 by batch reactor.

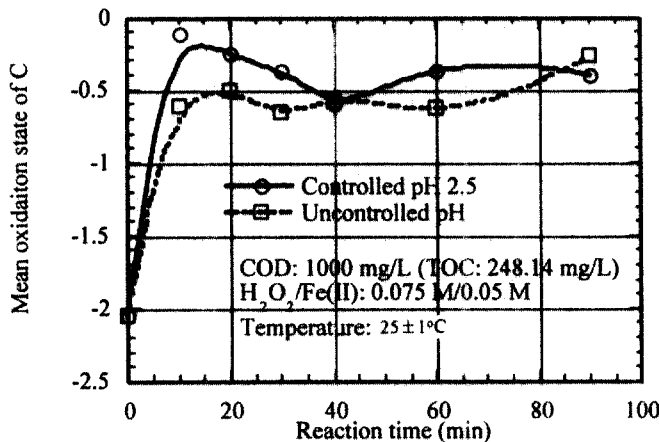


Fig. 6. Mean oxidation state versus reaction time plot in uncontrolled pH and controlled pH 2.5 by batch reactor.

6). The original organic materials were drastically changed by Fenton's reagent to other more highly oxidized byproducts. However, ultimate conversion of organic carbon to inorganic carbon was not completed. They mean that early oxidation reactions were both partial oxidations (primary degradation and/or acceptable degradation) and ultimate conversion to inorganic carbon with an abundant amount of hydroxyl radicals but further reactions with residual hydroxyl radicals prevailed partial

oxidations rather than ultimate conversion. Figure 5 and Figure 6 also show that a lower pH condition is favorable to get higher oxidation. As mentioned earlier, foam formation in the early period of reaction time and its disappearance observed on the top layer of leachate seems evidence of the ultimate conversion of organic materials.

Figure 7 and Figure 8 showed the changes of residual ferrous iron and hydrogen peroxide. In first 10 minutes, most of the Fenton's reagent

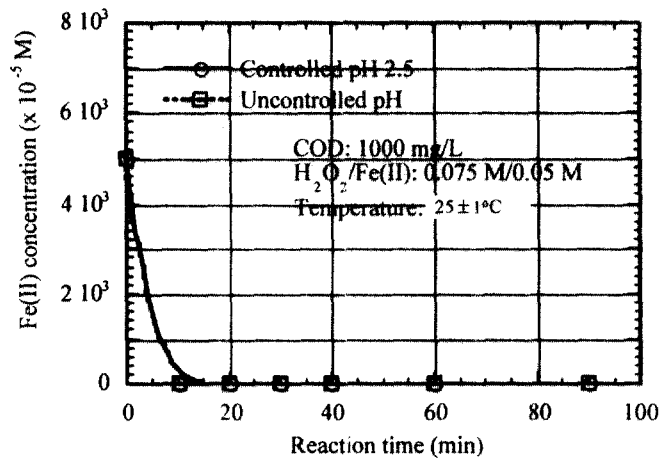


Fig. 7. Residual Fe(II) concentration versus reaction time plot by batch reactor.

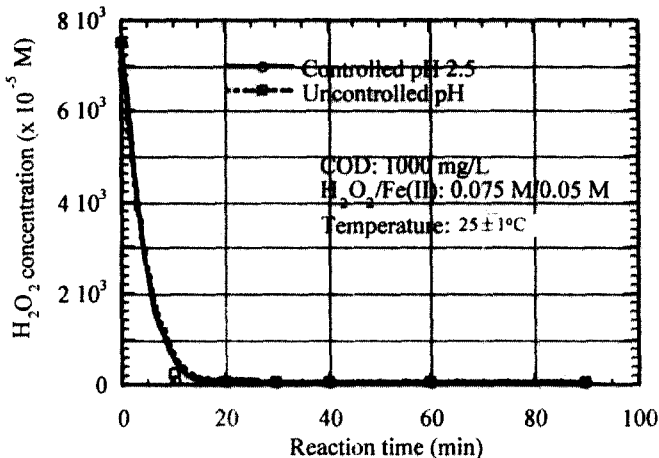


Fig. 8. Residual H₂O₂ concentration versus reaction time plot by batch reactor.

was consumed. Residual ferrous iron and hydrogen peroxide decreased from 5×10^{-2} M to about 10^{-5} M, and from 7.5×10^{-2} M to about 10^{-3} M, respectively. This means that the reaction between ferrous iron and hydrogen peroxide with the production of hydroxyl radical was almost complete in 10 minutes. Based on the results, the reaction time for the Fenton's treatment with batch reactor was determined to be 30 minutes for further experiments.

Effect of pH

As mentioned by Walton²⁵, oxidant applications have a typically sharp, preferred pH region in which they are optimally operated. The pH affects the activity of both the oxidant and the substrate (organic substances tend to be more reactive in their ionized states), the speciation of iron, and hydrogen peroxide decomposition. Detailed kinetic studies on the effects of Fe(II) and Fe(III) on the decomposition of hydrogen peroxide under acidic conditions have been interpreted in terms of free radical

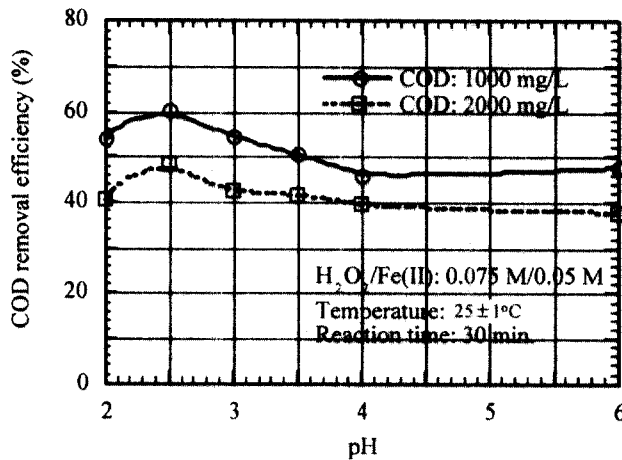


Fig. 9 COD removal efficiencies at different reaction pH values by batch reactor.

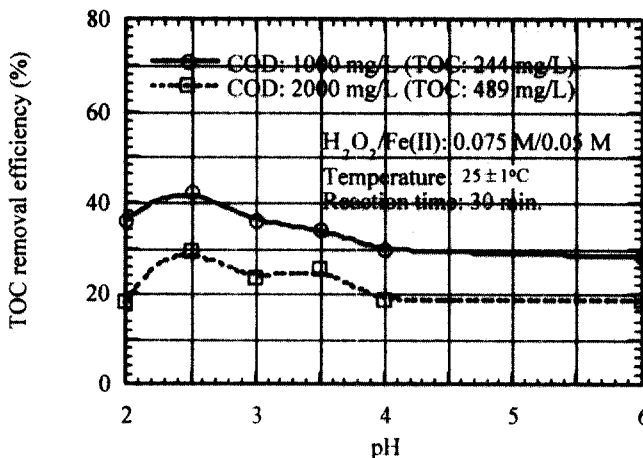


Fig. 10. TOC removal efficiencies at different reaction pH values by batch reactor.

mechanism.²⁶ Sedlak and Andren²⁷ explained higher hydroxyl radical product yields in the pH range of between 2 and 4 by a reaction involving the organometallic complex where either hydrogen peroxide is regenerated or reaction rates are increased. If pH is too high, the iron precipitates as $\text{Fe}(\text{OH})_3$ and catalytically decomposes hydrogen peroxide to oxygen.²⁵ Haber²⁸ noted that the chain reaction length was increased at lower pH values meaning that the propagation cycle was extended before termination. Haag and David Yao²⁹ found that

precipitation did not occur at pH 3.6 in an experiment with 1 mM $\text{Fe}(\text{III})$, but that precipitation became detectable and oxidation became less efficient at pH 4.3. Also, it is better to remove inorganic carbons from wastewater because they can scavenge hydroxyl radicals.³⁰ Inorganic carbons can be easily removed by controlling the pH to the acidic condition.

pH effects were tested at six different pH values (2, 2.5, 3, 3.5, 4, and 6) at a fixed dosage of Fenton's reagent (0.05 M of ferrous iron and 0.075 M of hydrogen peroxide) for 30 minutes

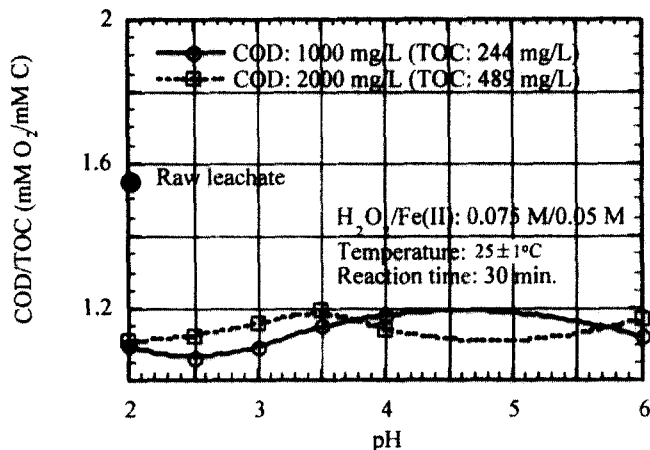


Fig. 11. Oxygen demand versus reaction pH value plot by batch reactor.

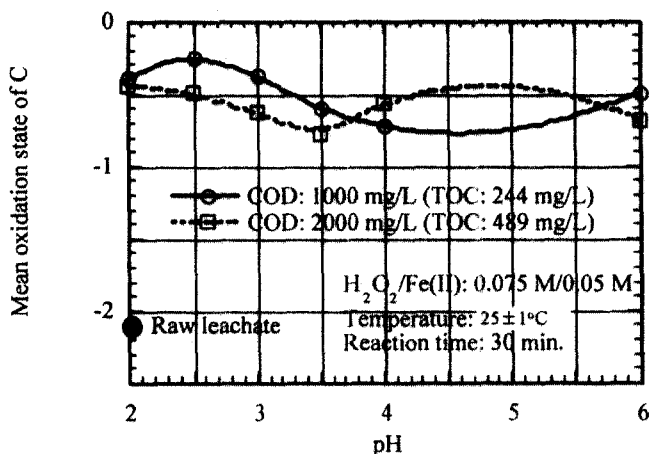


Fig. 12. Mean oxidation state versus reaction pH value plot by batch reactor.

of reaction time at temperature 25 ± 1 °C. Figure 9 and Figure 10 showed the effect of pH on the COD removal efficiency and the TOC removal efficiency, respectively. They showed similar trends. Figure 11 and Figure 12 showed the change of oxygen demand (COD/TOC ratio) and mean oxidation state of organic carbon C. Low pH of between 2 and 3 has been found effective for Fenton's reagent, and best removal efficiency was obtained at pH 2.5. These results

agree with other studies on the oxidation of organic compounds in wastewaters (Table 2).

Residual ferrous iron concentration and ferric iron concentrations are shown in Figure 13. Most ferrous irons were consumed by the reaction with hydrogen peroxide in all tested pH values. Small amount of ferrous irons remained between pH 2 and pH 3. Ferric irons generated by the oxidation of ferrous irons rapidly increased by pH 3 remaining in soluble

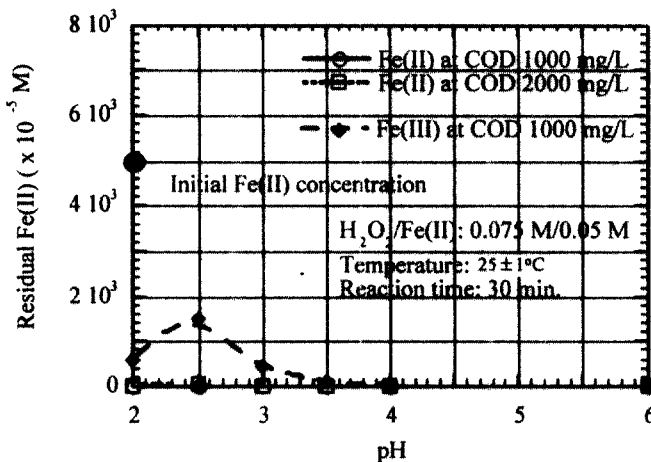


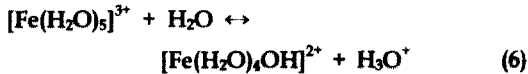
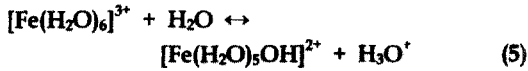
Fig. 13. Residual Fe(II) and Fe(III) concentrations versus reaction pH value plot by batch reactor.

Table 2. Optimum pH conditions by other researchers.

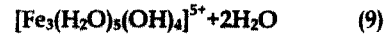
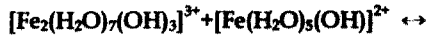
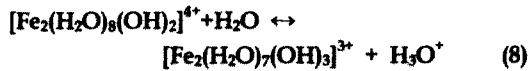
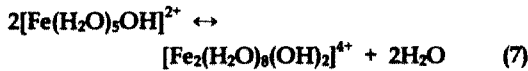
Organics/wastewater	Reactor	Optimum pH	References
Landfill leachate	CSTR	3 ^a	Kim et al. ³¹
Textile wastewater	CSTR	3.5 - 4 ^a	Lin & Peng ¹⁸
Halogenated phenols	Batch	2 - 3	Dong ³²
Dye wastewater	Batch	1 - 3	Kuo ³³
Toxic/refractory wastewaters	Batch	3.5	Bowers et al. ³⁴
Hydroxylmethanesulfonic acid	-	2	Martin et al. ³⁵
Municipal wastewater	Batch	3 - 5	Bishop et al. ³⁶
Phenolic waste	-	3 - 4	Eisenhauer ²¹

(a : untreated leachate/wastewater.)

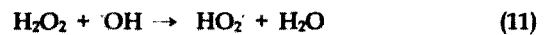
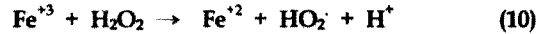
species. Further increase of pH showed drastic decrease of total soluble species. Considering the added total iron concentration, most irons precipitated as Haag and David Yao²⁹ found, and oxidation became less efficient. The hydrolysis of ferric iron is a function of pH and total ferric iron concentration.¹⁶ It is known that the solution with 0.05 M of soluble iron concentration becomes oversaturated with respect to Fe(OH)₃ (s) around pH 2.5, and additional polynuclear hydrolysis species occur. Kuo³³ explained this phenomena with ferric hydroxo complexes with hydroxide ions as:



These complexes have a pronounced tendency to polymerize at pH 3.5-7, as equations (7) - (9)¹⁶:



As a result coagulation would occur. Remaining organic materials could be coagulated and precipitated. It could make up for the disadvantage of the oxidation and minimize the amount of sludge after treatment.³³ Figure 14 showed the change of residual hydrogen peroxide concentration. It is known that the production of organic acids and other oxidation products, and the possibilities for the variation may be responsible for the variation in the behavior of the hydrogen peroxide decomposition rate.³⁶ Initial ferrous irons added reacted rapidly with hydrogen peroxide to produce hydroxyl radicals. The residual hydrogen peroxide was then slowly decomposed by ferric irons. The decomposition of more than the stoichiometric reduction in hydrogen peroxide was attributed to the reactions both between ferric irons generated and hydrogen peroxide (10), and between the hydroxyl radicals produced and the hydrogen peroxide (11).



Maximum decomposition of hydrogen

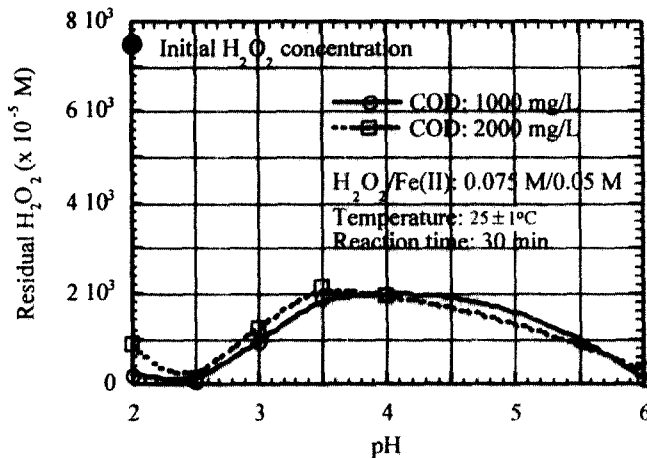
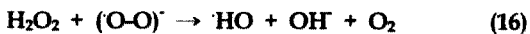
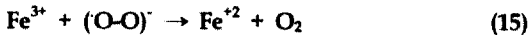
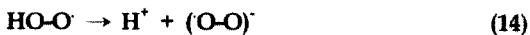
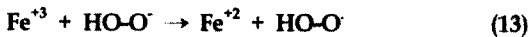
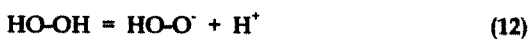


Fig. 14. Residual H₂O₂ concentration versus reaction pH value plot by batch reactor.

peroxide occurred at pH 2.5. As pH increased above that pH value, residual hydrogen peroxide concentrations increased by pH 4, then rapidly decreased at pH 6. More soluble irons were available in acidic condition so that they could accelerate the decomposition of hydrogen peroxide whether the decomposed hydrogen peroxide produced hydroxyl radicals or was only consumed by other competitive reactions.

Therefore, low residual hydrogen peroxide concentrations were observed at less than pH 2.5. Meanwhile, as pH increased above pH 2.5, the amount of soluble irons reacting with hydrogen peroxide was decreased by precipitation resulting higher residual hydrogen peroxide concentration. However, above pH 4, more hydrogen peroxide was decomposed without improving oxidation even though soluble iron concentration was so low. It indicated a change in decomposition mechanism. Hydrogen peroxide was decomposed to oxygen without producing hydroxyl radicals.³⁷ The reaction arises from the nature of hydrogen peroxide, which is an extremely weak acid. In the presence of ferric iron, oxygen is evolved through the following steps:



It is interesting that both maximum decomposition of hydrogen peroxide and maximum oxidation occurred at pH 2.5. It means that the rate of hydrogen peroxide decomposition and the efficiency of hydroxyl radical production which related to the activity of predominant species in soluble and concentration were best at this pH condition. It is known that more soluble ferric irons are available at below pH 3.¹⁶ Below a pH range of

3, the predominant soluble ferric iron species is hydrated ferric iron $\{[\text{Fe}(\text{H}_2\text{O})_4]^{+3}\}$ and in the 3 to 4 pH range, the hydrated ferric iron complex $\{[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{+2}\}$.

Bowers et al.³⁴ provided a method evaluating the efficiency of the reaction process according the fraction of the ultimate hydrogen peroxide used during the oxidation as follows:

$$f = [\Delta\text{H}_2\text{O}_2 / 2.13 (\text{COD}_0)] \quad (17)$$

where

f = fraction of ultimate hydrogen peroxide used
 $\Delta\text{H}_2\text{O}_2$ = hydrogen peroxide actually consumed during reaction

COD_0 = initial COD of the wastewater

2.13 = the conversion factor for O_2 demand to H_2O_2 demand.

However, this method gave contradictory results when decomposition mechanism changed such as at pH 6 (Figure 15). More rapid decrease of residual hydrogen peroxide than the decrease of COD removal efficiency pretended that higher fraction of hydrogen peroxide was used for oxidation. However, some of the hydrogen peroxide decomposed without contributing oxidation, resulting lower removal efficiencies. Instead of this method, the oxidation efficiency (O. E.) of the oxidation process suggested by Bishop et al.³⁶ seems a better method. The changes in COD and hydrogen peroxide concentration were combined to determine the oxidation efficiency of the oxidation process as follows:

O. E.

$$= [\text{COD (mg/L)/available O}_2 \text{ (mg/L)}] \times 100 \quad (18)$$

The available oxygen was the theoretical amount of reactive oxygen in the added hydrogen peroxide based on two oxygen equivalents per mole of hydrogen peroxide. Here, the oxidation efficiency was the ratio of

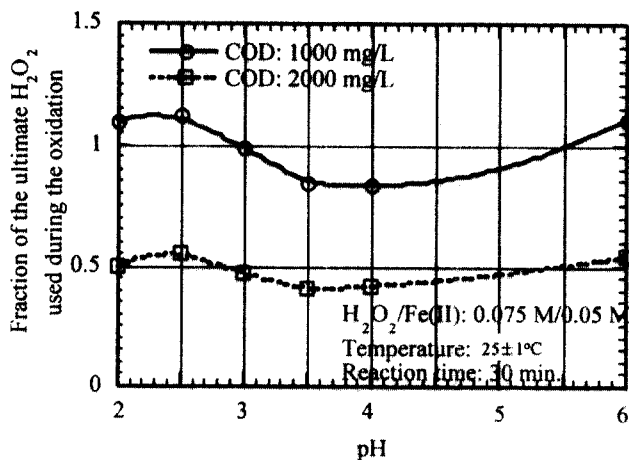


Fig. 15. The fraction of the ultimate H₂O₂ used during the oxidation versus reaction pH value plot by batch reactor.

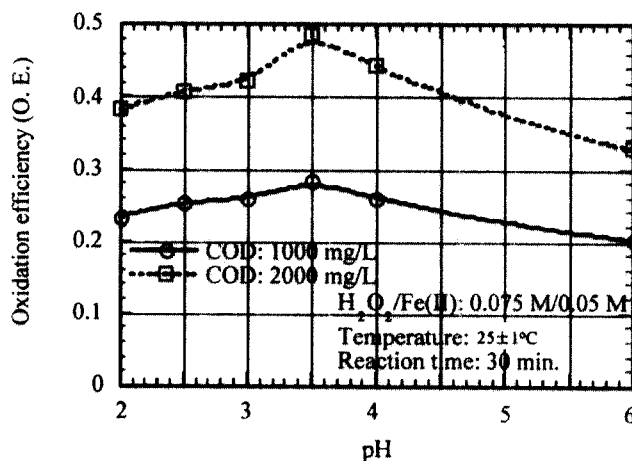


Fig. 16. Oxidation efficiency of H₂O₂ versus reaction pH value plot by batch reactor.

the amount of oxidation of the wastewater substrate as measured by its change in COD to the maximum amount of oxidation possible from hydrogen peroxide. Best oxidation efficiency was obtained at pH 3.5 (Figure 16). Even though better oxidation efficiency could be achieved at pH 3.5, the rate of hydrogen peroxide decomposition was worse than pH 2.5. Sedlak and Andren²⁷ got optimal oxidation efficiency at pH 2-3, and explained it with the formation of substrate-Fe-H₂O₂ complex in reaction.

The selection of a pH condition for further experiments was pH 2.5, based on organic removal efficiencies and reaction rates instead of oxidation efficiency.

Table 3 shows the results of heavy metal removals. The concentrations of cobalt, copper, lead and nickel in untreated leachate were so low that most of them decreased to below detection limit, although tested conditions were not optimum condition. Further test for heavy metals was not performed.

Table 3. Heavy metal removals at different pH values.

(Unit : $\mu\text{g/L}$)

	pH		COD 1000 mg/L			COD 2000 mg/L		
	Co	Ni	Cu	Pb	Co	Ni	Cu	Pb
Initial	0.99	5.34	5.30	8.76	1.97	10.67	10.61	17.52
2.1	<0.98	1.21	2.30	<3.67	<0.98	1.21	2.30	<3.67
2.5	<0.98	<1.12	<1.67	<3.67	<0.98	1.19	1.84	<3.67
3.0	<0.98	<1.12	<1.67	<3.67	<0.98	<1.12	<1.67	<3.67
3.5	<0.98	<1.12	3.24	<3.67	<0.98	4.55	2.10	<3.67
4.0	<0.98	<1.12	1.77	<3.67	<0.98	1.85	<1.67	<3.67
6.0	<0.98	<1.12	<1.67	<3.67	<0.98	2.94	<1.67	<3.67

Conclusion

The effects of important parameters such as reaction time and pH on the Fenton's process were evaluated using a batch reactor. It was proven that organic materials and heavy metals in leachate could be successfully removed by Fenton's reagent. Favorable operation conditions were investigated. The oxidation of organic materials by Fenton's reagent was so fast that it was complete in 30 minutes with batch experiments. With the formation of carbonic acid, pH of the batch reactor decreased to favorable acidic conditions without acid addition. The oxidation of organic materials in the leachate showed a pH dependence and was most efficient in the pH range of 2-3.

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