Using Fenton Chemistry for Wastewater Treatment of Organic Recalcitrant Substances

Abel Mondelo Rodríguez[a], José M. Ameneiros Martínez[b] and Eduardo Marquez Canosa[b]

[a]Enterprise Group for Biopharmaceutical and Chemical Production LABIOFAM, Ave. Independencia Km 16½ Boyeros Ciudad de La Habana Cuba 17200 e-mail: abelmr1@yahoo.com

[b]Higher Politechnic Institute José A. Echeverría ISPJAE – CUJAE, Marianao Ciudad de La Habana, Cuba.

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Abstract:

The release of contaminants such as solvents and other volatile organic compounds (VOCs) into surface impoundment or through lk,kmother disposal practices has resulted in the contamination of a determined media. These organic contaminants were often introduced to the subsurface as a pure phase that was either lighter than or heavier than water. Those compounds heavier than water, such as solvents, are commonly known as DNAPLs (dense, non-aqueous phase liquids) when they are present as a separate phase. Those compounds lighter than water, such as gasoline, are commonly known as LNAPLs (light, non-aqueous phase liquids) when they are present as a separate phase. DNAPLs and LNAPLs in a media are difficult to remove by pump-and-treat methods, they can be difficult to detect and treat in situ, and act as significant sources of contamination continuously released to the ground water.

The chemical substances used in organic synthesis, or in inactivating of biological vaccines, generally are not degraded by conventional wastewater treatment process such as: aerobic, anaerobic treatment or chemical oxidation with chlorine or ozone.

The development of Advanced Oxidation Process (AOPs) and Fenton like Process, become a better choice for treating those substances. In this paper, a Fenton Process was performed for treating the residues of the inactivation of microorganisms used for vaccine production and its Quality Control (Potency, sterility, etc.). The yield of the reaction, based on the COD parameter, was very high in all cases. The laboratory scale studies were performed at 25 °C with hydrogen peroxide per iron II (ferrous) sulfate ratio of 5. In addition, the studies were performed after an aerobic and an anaerobic biological process. The comparison of all three cases were conducted for the yield, reagent spend and reaction time.

Introduction:

Direct Chemical Oxidation (DCO) is a non-thermal, atmospheric pressure, aqueous-based technology for the oxidative destruction of organic components of hazardous or mixed waste streams. The process has been developed for applications in waste treatment and chemical demilitarization and decontamination. It is applicable to the destruction of all virtually liquid or solid organics; including chlorosolvents, oils and greases, detergents, organic-contaminated soils or sludge, explosives, chemical and biological warfare agents and polichloride biphenyls (PCB´s)[1].

Applying destructive chemistry to contaminated sites reduce pollution levels by destroy undesirable chemical compounds, producing other innocuous[2]. Advanced oxidation processes (AOPs) for wastewater treatment are gaining more importance since biological treatment plants are often not sufficient for highly contaminated or toxic wastewater[3].

Fenton Chemistry.

The Fenton´s reagent methodology was first introduced in the 1890´s by H. J. Fenton, when he reported the oxidation of malic acid in a solution of ferrous iron and hydrogen peroxide. It has been shown that the Fenton´s reagent can oxidize many substrates, including organic matter, and this type of chemistry is know as “Fenton Chemistry”. The Fenton pathway is given as[2,4,5,6]:

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + OH^{\cdot} \qquad (1)$$

Fe^{2+} acts as a catalyst in the above reaction and is regenerated by the following reaction:

$$Fe^{3+} + H_2O_2 = Fe^{2+} + HO_2/O_2^- + H^+ \qquad (2)$$

$$Fe^{3+} + HO_2/O_2^- = Fe^{2+} + O_2 + H^+ \qquad (3)$$

The combination of hydrogen peroxide and ferrous iron produces the hydroxyl radical[2,4,5,6]. Hydroxyl radicals are very powerful, effective and nonspecific agents, approximately 106 to 109 times more powerful than oxygen or ozone alone[6].

Fenton Chemistry characterizes for oxygen liberation, accompanied by a radical hydroxyl flux. These last are a potent hydrogen atom abstractor, because of the O – H bond in water is particularly strong, 119.9 Kcal/mol, more stronger than almost all C – H bonds. Therefore, Fenton chemistry tends to the destruction of the organic matter and it is not so selective to be useful for the majority application in chemical reactions. Fenton Reagent can be formed by a mixture of a transition metal of low valent and a peroxide, per example: iron (II), copper (I), Cobalt (II), manganese (II) and hydrogen peroxide, an organic peroxide (alquil peroxide) or hypohalous acid (HClO)[7]. The use of iron is for toxicity reason, this is an element used by the nature for many redox catalyst[7].

Fenton reactions involve two components, in addition to the contaminated media, named catalyst and oxidizer. Iron catalyst could be ferrous or ferric salt, although, some researcher suggest that ferrous ion is preferred[2].

Hydroxyl generation begins when the hydrogen peroxide enters in contact with the ferrous sulfate. The reaction speed is limited by the speed of the hydroxyl radical generation. The perhydroxyl radical produced reacts with the ferric ion producing ferrous ion, so traces of iron 2+ catalyze big amounts of hydroxyl radicals[2,5,6]. The reaction is very dependent over the temperature, pH and hydrogen peroxide to ferrous iron ratio. Fenton's Reagent, general operation considerations include:

- pH of the system must be between 3 to 6.

- The rate of the reaction increases with the increasing temperature (although the efficiency declines above 40 to 50 ºC; because of the decomposition of the hydrogen peroxide become a strong competitive reaction over the hydroxyl radicals generation).

- For most application the valence of iron salts used doesn't matter (2+ or 3+) or doesn't matter a chloride or sulfate salt of iron is used[2,4,5,6].

Characteristic of the wastewater studied.

Wastewater generated in the experimental vivario through the inactivation of biological products used in potency or sterility test and other industrial fermentation process or in the cleaning and decontamination of the equipment, materials, work areas and animal areas have a poor or medium biodegradability. This behavior is produced by the substances used in those research and cleaning activities that are non biodegradable or recalcitrants to convenctional biological process or toxic:

- phenol
- formaldehyde
- benzalconium chloride
- detergent
- acetic acid
- cresol
- potassium permanganate
- etilenimine
- β - propiolactone
- ethylene oxide

This problem become more significative by the development of the pharmaceutic and biotechnological industries, were it is used many recalcitrant substances to convectional treatment. In addition, it is increased when biological risk III microorganism are used in a vaccine production process.

The degradation of such toxic or recalcitrant substances conduct to the introduction of new advanced process based over environmental restrictions and the incapacity of biological treatment to degrade it. Such new treatment include: supercritical water oxidation, wet (air) oxidation processes, incineration and advanced oxidation process. Each one of this processes are introduced depending over the concentration in the wastewater.

Methods.

Incoming wastewater was collected from the experimental vivario “La Granjita” from the Enterprise Group LABIOFAM, which it contain inactivating and decontaminating substances that are toxic or recalcitrant to biological processes. Two alternatives choices of the feed in Fenton Process were studied using the wastewater collected pre-treated through an aerobic and an anaerobic biological treatment. In addition, a wastewater containing PCE was also studied. Hydrogen peroxide and ferrous sulfate used were analytical grade reagent from Merck.

The reaction were conducted in an open vessel, at atmospheric pressure, with a water – ice bath to keep the temperature in 25 ºC or lower, and pH of the starting reaction system of 5 – 5.5. The regeneration of the iron catalyst was carry out at a pH ranging of 8 – 8.5. All analytical determination were conducted according to Standard Methods (APHA, AWWA & WEF 1992).

Preliminary experiments were performed for screening the input variables and identify the most important subset of factors affecting the reaction yield. The temperatures and hydrogen peroxide per ferrous sulphate concentration ratio remains as the most important input variables to find the better yield values. This procedure conducted to a factorial 2^3 experimental design for finding the better reaction condition. It was observed that the pH of the reaction declines through the reaction proceeds. Thus, the starting pH was fixed at a value of 5.0 to reach a reaction pH of 3.5 and lower. The iron catalyst was first added, and then the hydrogen peroxide addition was performed slowly, in 4 small volumes. This procedure conduces to moderate the rise in temperature as the reaction proceeds.

The temperature were studied at 24 – 35 °C, at three levels (table 1), because of an increase in temperature will increase the reaction yield, but at values of 40 or upper, the decomposition of the hydrogen peroxide will become the main reaction. There also was experimented the reaction at 40 °C and the reagent consumption was upper, as was expected. In addition, the concentration ratios between the hydroxyl radical promoters (hydrogen peroxide / ferrous sulfate) were setted at 2,00 – 5,00 values at three levels. The iron catalyst was used in both ferrous or ferric ions, so, traces of iron can generate indefinitely amounts of hydroxyl radicals.

The effluent of the wastewater containing PCE oxidation was analyzed by thin layer chromatography with hexane – ethyl acetate as movil phase, and observed under ultraviolet light before charring with sulfuric acid 5 % hydroalcoholic solution. It was analyzed too through HPLC with detection by ultraviolet light at 290 nm with an A_{max} of 1.0.

Results and Discussion.

The values of the input variables that showed better yield was 24 °C and a hydrogen peroxide per ferrous sulphate concentration ratio of 5.0. All experiments were performed at this values, removing the generated heat by water – ice bath. The yield reached in all cases shown values upper than 99 % based on the chemical oxygen demand. The reaction take place in 1 h for almost all experiences; except to the process performed after the aerobic treatment that takes place in 45 min.

The ability to pre-treat the feed in Fenton process reduces its chemical oxygen demand up to 99 % with a reduction in the reagent consumption in Fenton Process for both biological processes applied: aerobic and anaerobic treatment. In general form, the pH of the reaction declines through the reaction take place. It was more pronounced after the addition of the hydrogen peroxide. Besides, there was observed too a little decrease in pH for the feed pre-treated by an aerobic treatment. This change in pH indicates that the reaction proceeds as desired.

A hard stirring, where vortices formation was observed, was applied to permit a better oxygen transfer to reaction mixture. Only the process after the aerobic treatment was stirred more slowly because of this biological treatment supports enough oxygen to the Fenton reaction proceeds.

Table 1. Average Results of the Fenton Process Study.

Samples	6	6	6	6	1	4	A
H_2O_2 / $FeSO_4$	1.75	2.5	5.00	5.00	2.00	2.30	2.50
T (°C)	24	24	24	30	30	35	40
t (h)	1	0.75	1	1	1	1	1
H_2O_2 (mmol/L)	0.35	0.5	0.50	0.50	0.4	0.46	0.5
$FeSO_4$ (mmol/L)	0.20	0.20	0.10	0.10	0.20	0.20	0.20
% Rem.	95	99.5	99.9	99.9	99	99.00	99
DQOin	722	722	722	722	730	726	750
DQOout	36	3.5	0.7	7.2	7.3	7.3	7.5
V_{sample} (mL)	500	500	500	500	500	500	500

Important: *It was performed 4 additions of H_2O_2 and one addition of FeSO4*
Starting pH: 5 -6, reaction pH: 3 - 4, precipitation pH: 7,5 - 8,5.

The depurated water was microbiological tested. The laboratory results showed that It does not contain bacterial contamination, which it is according to the references.

The iron catalyst in the experiments was recovered by an increase of pH of the mixture and a filtration process. It also was re-used by acidifying the iron sludge to solubilizate it and sending it back to perform another experiment.

The Fenton process applied to the residues of perchloroethylene (PCE) showed a good reduction of it for all hydrogen peroxide per ferrous sulphate concentration ratio studied. After the process this substance was not detectable by TLC or HPLC; only for a ratio of 2.0 it show a small quantity of the substance in the effluent, upper values of it offer a best destruction of the substance, adding periodically small volumes of hydrogen peroxide. The process performed at 25 °C, atmospheric pressure and a ratio of 5,0 showed the best yield for PCE destruction. In all experiences was observed, as was expected, an increase in chloride concentration. It indicates the reaction proceeds as desired. The Fenton process for destroying PCE was only performed to the wastewater directly; it was not applied after any biological treatment (anaerobic or aerobic).

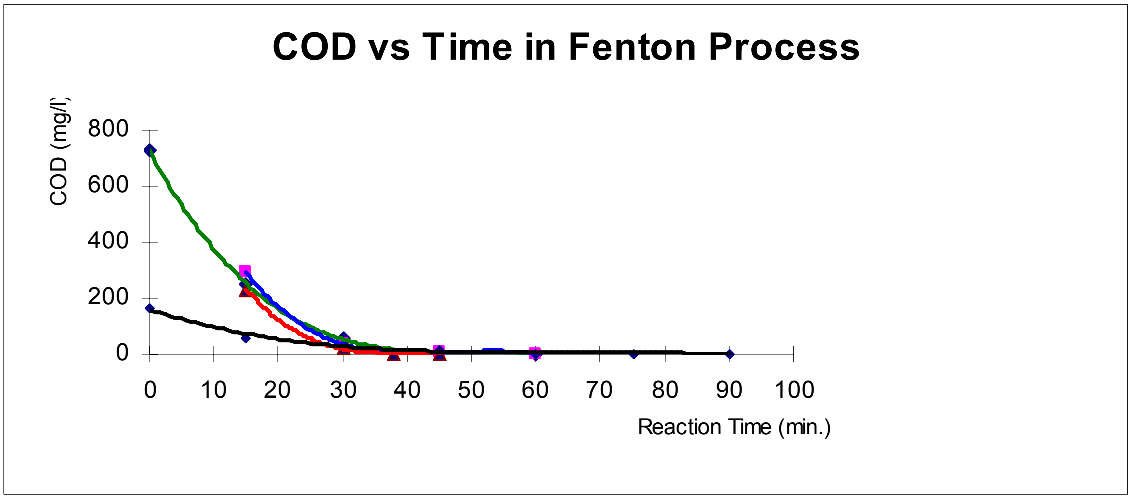

Fig. 1: Fenton Process for the all experimental choices studies.

Conclusion.

The Fenton process was studied for several choices of the feed, including one case for a wastewater containing PCE. All the experiences performed at 24 °C, atmospheric pressure and a ratio of 5.0 showed a good yield of the oxidation reaction. The mineralization of the incoming wastewater was obtained in all cases, and an increase of chlorides ions was observed for the wastewater containing PCE, as was expected.

The process applied to the feed pre-treated with a biological treatment showed a reduction in the reagent consumption. Besides, it influences in the cost of the whole treatment process.

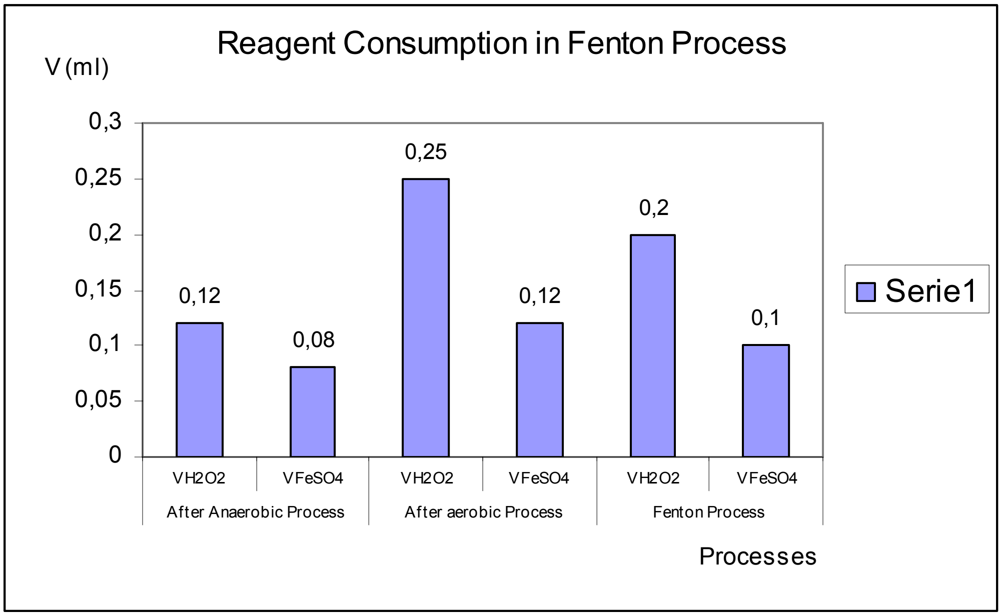

Figure. 2: Reagent consumption in Fenton Process.

All depurated water do not show bacterial contamination, thus it have a good bactericidal activity and permit to reduce the biological risk in the aquifer or any other body receptor. In addition, it can be used for decontaminating materials or for the destruction of biological vaccines not in use with high risk microorganism.

Recommendations

Further studies must be performed applying techniques for detecting organic radicals that could be generated and it does not detectable by COD analysis. This studies will be performed in collaboration with the Universidad Complutense de Madrid, performing gas chromatography, HPLC and mass spectrometry analysis to detect any organic radical generated in the process.

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