Development of a combined Wastewater Treatment Process for Organic Recalcitrant Substances

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Key words: Biological treatment, anaerobic and aerobic processes, Fenton Chemistry, organic wastes, recalcitrant or toxic wastes and wastewater treatment

Abstract:

Biological wastewater treatments consist of a conglomerade of different microorganisms, mainly bacterias, that perform a continuous and sequencial attack over the organics in the wastewater. This process are the most commonly used, because of they are cost effective, efficients and do not generate contaminant byproducts.

Nevertheless, there are many substances that are recalcitrants or toxic to biological process. This problem become crucial for Pharmaceutical or Biotechnological Industries that use this type of substances in the production processes, in inactivating or decontaminating of areas or materials used or for the destruction of biological vaccines based on high risk microorganism. Thus, there is necessary the development of a wastewater treatment process able to degrade this organic contaminants and the microorganism elimination. The net effect in the full process must be directed to the environmental preservation.

In the present work, a combined stage by stage process was developed for the decontamination of the wastewater generated in the experimental vivario of the Enterprise Group for Biopharmaceutical and Chemical Production LABIOFAM; which apply a biological treatment and an advanced oxidation process. The study was perform in two choices that afford up to 99 % of COD reduction. The first choice is an anaerobic biological treatment and a Fenton Process. For the second choice, an aerobic biological treatment was implemented before the Fenton Process.

The comparison of this two methodologies, was performed for the yield of the process and the cost of the treatments.

Introduction:

Water quality regulations are becoming stricter in the late decades due to an increasing social concern on environment. This has provoque that Environmental Engineering becomes a very increasing field of work. So, a very interesting field of concern is: What to do with wastewater contains soluble organic compounds which are either toxic or just non-biodegradable?

Some of the products used in our modern society are too toxic to be disposed off without particular treatment. Nevertheless, not only the industry generates such kind of poisonous and hazardous wastes but also many household products fall under this category. If not disposed correctly, some cleaners, solvents, pesticides, paints, etc. can contaminate a landfill, leak into the ground-water or contaminate the ocean resulting in tremendous risk for the safety and health of human being. For the respect of our environment, the basis 3R´s rule (reduce, reuse, recycle) should prevail as a prevention instead of curing. Today treatment of hazardous wastes

includes biological treatment, chemical oxidation and reduction, neutralisation, stabilisation, incineration and energy recovery prior to landfill[1].
Treatment facilities simply compress the organic decomposition processes which take place in nature. This is performed by a combination of physical, biological and chemical treatment stages. Nature (receiving waters) can only accept small amounts of sewage before becoming polluted[2,3 4].

Industrial wastewater contains a vast array of pollutants in soluble, colloidal and particulate forms, both inorganic and organic. In addition, the requiered effluent standards are also diverse, varying with the industrial and pollutant class. Consequently, there can be no standard design for industrial water-pollution control[4].
Biological wastewater treatment process are based over the natural degradation process of organic substances in the nature. Watewater treatment process has been designed usually for removing traditional contaminants; that is, BOD and suspended solids.
Main biological Processes, based over the type of microorganism, are clasified as aerobic and or anaerobics. Aerobic processes requiere oxygen presence for the matter degradation and anaerobics does not requiere oxygen to be prensent.
Anaerobic degradation of organic matter is a complicated microbial process consisting of several interdependent consecutive and parallel reactions; which requiere the coordinated involvement of different bacterial species. All steps mantain a strong interaction; which results in the need for a strict control parameters[15].
In aerobic degradation, the biological depuration is carry out by an enormous amount of microorganisms that are grouped in flocules. Those microorganisms are, mainly, heterotrophic bacterias that use the organic contamination to produce new biomass cell and for reproducting themself.
Traditionally, anaerobic digestion has been used to treat wastewater with or without suspended solids as: animal manure, sludge provenient of biological or phisical – chemical treatment, etc.
The process of anaerobic digestion represent, definitelly, a favorable energetically process; because of it not only does not requiere energetic contribution but else it produce biogas, a fuel that can be used for different finalities.
Recently, there has been demonstrated that non-biodegradable organic byproducts will accumulate in a biological treatment process. Generally, this byproducts will be high molecular weight substances. Even, after long periods, non-biodegradable organic compounds and the byproducts remaining in the media[6]. Thus, an appropiated terciary wastewater treatment process will be needed for degrading this substances.

At the present day, Advanced oxidation process (AOPs) for wastewater treatmert are gaining more importance since biological treatment Plants are often not sufficient for highly contaminated or toxic wastewaters[7].
AOPs makes use of (Chemical) oxidants to reduce COD / BOD levels and to remove both organic and oxidisable inorganic components. The process can completely oxidise organic materials to carbon dioxide and water, although it is often not necessary to operate to this level of treatment.
A wide variety of advanced oxidation process are available:
- Chemical oxidation processes using peroxide, ozone, combined peroxide & Ozone, hypochlorite, Fenton´s reagent, ect.
- Ultra-violet enhanced oxidation such as UV / ozone, UV / hydrogen peroxide, UV / air.
- wet air oxidation and catalytic wet air oxidation (where air is used as the oxidant).

Advanced oxidation processes are particularly appropiate for effluents containing refractory, toxic or non-biodegradable materials[8]. Its principles is based over the hydroxyl radicals, a very powerful oxidising agents for degrading the organic recalcitrant matter.
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)[9]. Iron catalyst is preferred due to toxicity reason. This element is used by nature in many redox reactions[17].

Methods

The wastewater studied were collected from the experimental vivario of the Enterprise Group LABIOFAM. It contain Some substances that are toxic and / or non-biodegradable (recalcitrant) to the biological process. The BOD / COD analysis and all the laboratory scale studies were performed in the Enterprise of Laboratories of Quality Control of he Enterprise Group LABIOFAM. All analytical determination were conducted according to the Standard Methods (APHA, AWWA & WEF 1992).

The study was carry out in four experimental stages:
First, biodegradability determination through the BOD / COD ratio and the anaerobic biodegradability method.
Second, Biological treatment processes study of the wastewater.
Third, Chemical oxidation study through the fenton Process.
Four, Combination of the Biological and chemical methods (aerobic plus Fenton and anaerobic plus fenton).

All analytical reagent are puriss p.a. from Merck Company. Catalyst solution of 100 ppm ferrous sulfate, pH range of 4 – 6, and hydrogen peroxide of 500 ppm were applied. For recovering the iron catalyst, an increase in pH up to 8 were applied.

For the Fenton Process Study, a 3^3 factorial experimental design were applied for screening the main variables and reach the better reaction parameters. In the biological treatment process, just the wastewater characteristic was influenced by using a bactericidal detergent in the cleaning and decontamination activities for reducing the amount of formaldehyde used in those activities.

Results:

The investment and operation cost for Fenton Process are higher than the cost for biological process, thus, in order to find out the most efficient and cheap process, it was developed a stage by stage wastewater treatment process, which include a biologic method before the chemical oxidation through Fenton Process.

An aerobic and an anaerobic process were introduced as a pre-treatment method to the fenton process. This choices offer a reduction in the reagent comsuption in the chemical process. The aerobic process showed a little increase in the hydrogen peroxide/ferrous sulfate comsuption refering to the anaerobic choice. This last method offered an interest choice because of generate an renovable resource and lesser sludge generation than the aerobic method, besides, an acceptable reaction yield. Fenton reagent has been chosen as the active media for oxidizing this kind of substances. This method shows to be a powerful oxidizing agent, Iron was selected as catalyst for toxicity reason, it is used in nature for many redox reaction. The study of the fenton process were carry out for the samples collected in the vivario with and without biological pre-treatment. For this study, the temperature, hydrogen peroxide/ferrous ion ratio and pH are the main parameter to reach better yield.

For carrying out this study, an anaerobic and other aerobic process were experimented as a pre-treatment step. By this way, the COD was removal in 60 to 70 %. In addition, there was applied a bactericidal detergent for reduce the formaldehyde used in the cleaning and decontamination activities. This choice did permit improve both biological process, and in the anaerobic choice, it did improve the reaction yield and the gas generation.

In general way, the puntual samples collected in the vivario, did show a low or middle biodegradability based over the BOD / COD ratio (ranging between 0.15 to 0.3). This behavior is due to the substances used in the cleaning and decontaminating activities. Nevertheless, mixturing and homogenizing this puntual samples, it was reached acceptable anaerobic biodegradability levels, obtaining an average 56 to 60 % of COD removal. The medium volume of gas generated was 75 and 110 ml for both choices: 1) anaerobic process of the wastewater generated in the vivario and 2) anaerobic process of the wastewater generated after the use of the bactericidal detergent.

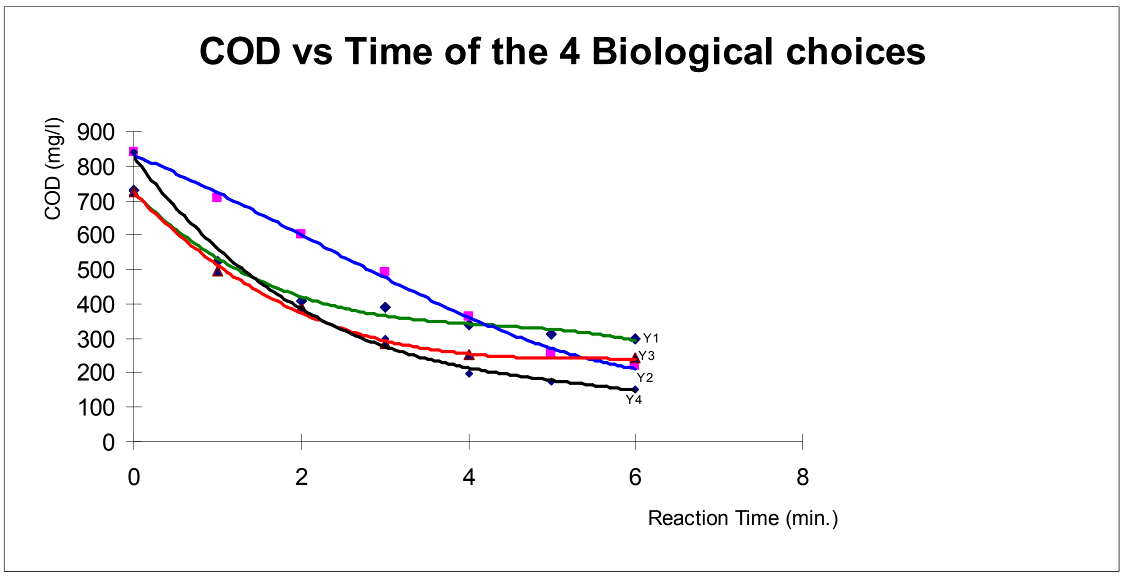

Fig. 1: Comparison of the four biological experimental choices studies. Y1- anaerobic treatment of the incoming residual, Y2- aerobic treatment of the incoming residual, Y3- anaerobic treatment after apply bactericidal detergent, Y4- aerobic treatment after apply bactericidal detergent.

The solids retained after filtering the samples, were mixtured and homogenized with sludge generated in the biological processes, residues of the BIORAT production and wastes of fermentation process; following its degradation by anaerobic digestion. The stabilized sludge was expanded in a flat surface for drying, exposed to direct sunlight for at least 72 hours. It was characterized for stabilization level, pH and pathogenicity(reference); determining that it have no presence of pathogenic microorganism. Thus, it can be used as organic fertilizer.

The anaerobic biodegradability was relatively higher (69 to 76 %) for the choice in which the bactericidal detergent was used for reducing the amount of formaldehyde in the cleaning and decontaminating activities. The gas generation for this choice was also higher as we expected.

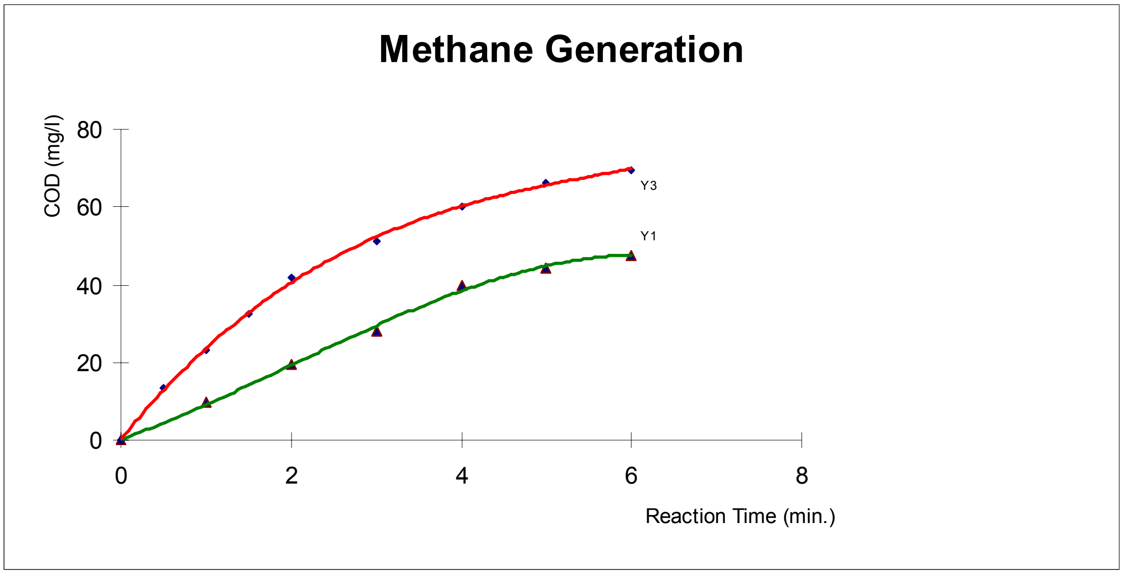

Fig. 2: Methane Generation.

Nevertheless, there is a fraction in the biological process which it is not degraded. It contain the substances that are toxic or recalcitrant to the biological degradation. This fraction can be accumulated in the discharge, if it is not treated.

The chemical oxidation (Fenton Process) was carried out during 1 hour, keeping the tempearture in 25 to 35 °C, by removing the generated heat in the reaction with a water – ice bath.

The reaction yield in all the experiences were higher than 99 % of COD removal. The iron catalyst were recovered increasing the pH up to 8.0, by adding a sodium hydroxide solution.

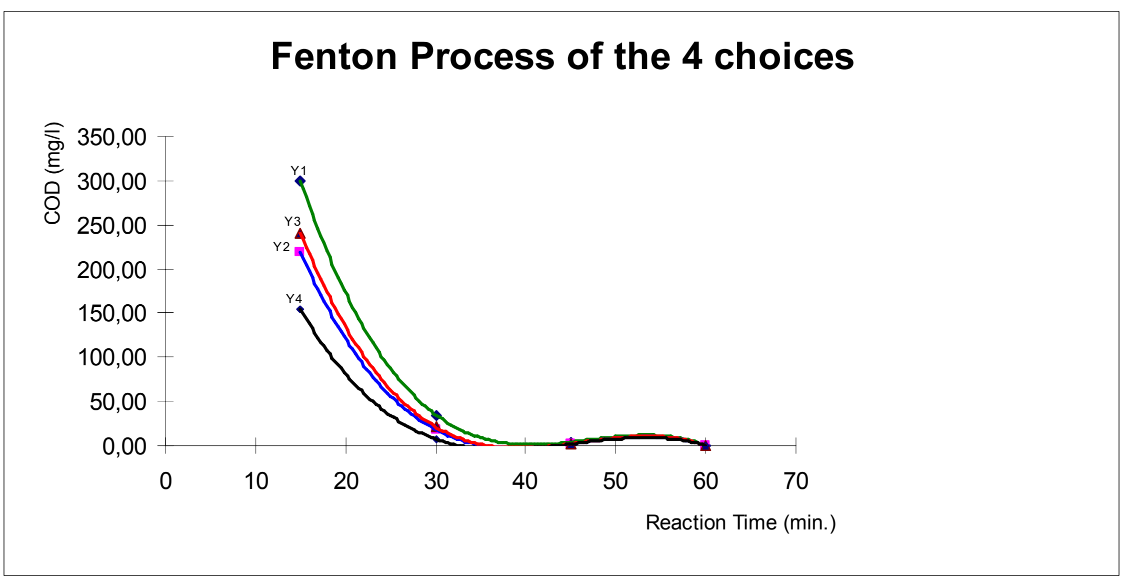

Fig. 3: Fenton Process for the four experimental choices studies. Y1, Y2- after the aerobic treatment of the incoming residual, Y3- after the anaerobic treatment (wastewater after apply bactericidal detergent), Y4- after the aerobic treatment (wastewater after apply bactericidal detergent).

Reagent consumption in the Fenton process decrease for the samples pre-treated anaerobically, where the bactericidal detergent was applied for reducing the amount of formaldehyde used. It must be because the toxicity of the formaldehyde was lower and the anaerobic digestion was more efficient.
Contrariarly, for the samples aerobically pre-treated, the reagent consumption was higher (fig. 4). This choice showed a lot of suspended solids in the effluent; thus, it must need a clarifier for removing this solids. This option increase the investment cost for this choice. The reaction time was lower than the other choices (45 minutes) it must be, due to the higher oxygen concentration in the effluent of the aerobic process. Oxygen concentration is beneficious for the Fenton Reaction(ref).

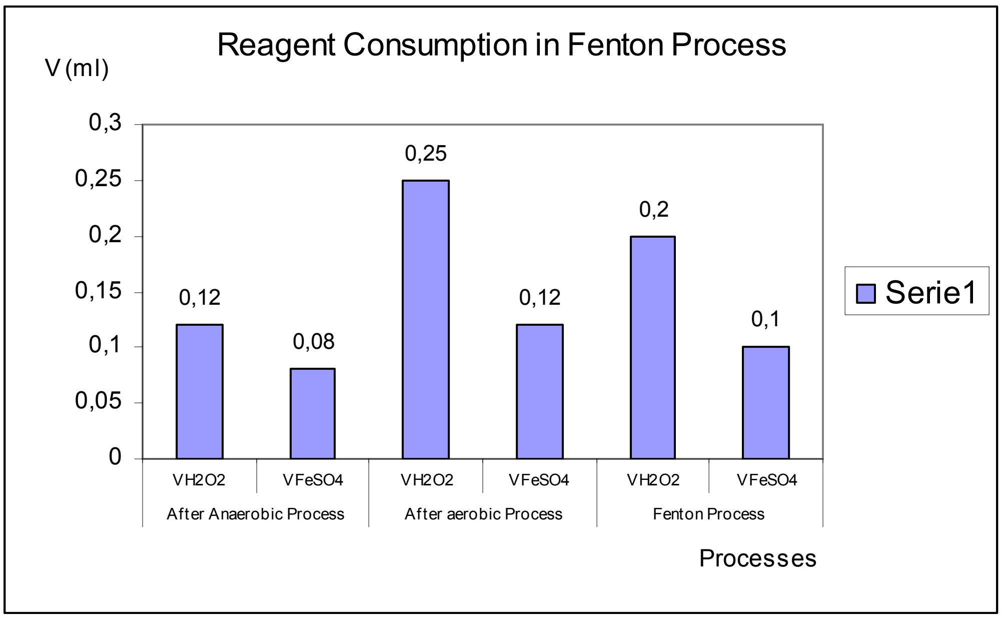

Figure. 4: Reagent consumption in Fenton Process.

In all cases, the water mineralization was observed. The disolved oxygen was upper than 6.1 mg/l and there was no presence (detection) of viable microorganism, neither pathogenic microorganism in the purified water.
The vortice formation in Fenton process guarranty a better oxygen mass transfer to the reaction mixture.

The combined use of Fenton Proccess, after a biological wastewater treatment process has proven reliable for degrading organic recalcintrant substances and biological byproducts produced in the anaerobic or aerobic process. In all experimentals, a COD reduction up to 99 % was observed (fig. 5). Nevertheless, using an anaerobic process before Fenton process allow to produce a renewable resource that can be used as fuel for electricity generation, heat generation, cooking, or other activities. This biogas can be purified for increasing its calorific value; thus, allowing a better yield in those processes and decresing the corrosion and atmospheric pollution in addition to the human risk reduction.

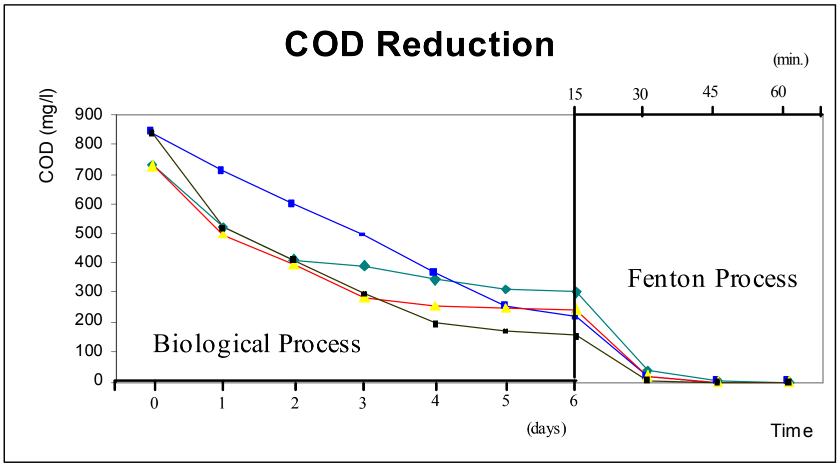

Figure. 5: COD removal for the combined wastewater treatment process.

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.

Acknowledgement

We want to thank to the Enterprise Group LABIOFAM for the financial support for the experiments. We also want to thank to the Enterprise of Quality Control of the Enterprise Group LABIOFAM for their help in all analysis techniques.

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