COMBINATION OF ADVANCED OXIDATION PROCESSE AND BIOLOGICAL TREATMENT OF INDUSTRIALWASTE WATER

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ABSTRACT

The aim of this work was to study the biotreatability of industrial waste water as well as application of AOP Of FACCO or effective pretreatment. Because industrial waste water expressed biodegradability (BOD5/C D ratio was 0.40), biological treatment was the first choice. At the same time, in preliminary ready biodegradability assessment test, diluted broth degraded 65% as well it was not toxic to mixed bacterial culture of activated sludge. However, we had considered additional pretreatment method to be able to enhance biotreatability. FACCO procedure was optimised in batch reactor using different concentrations of 0.5 Fe₂⁺, 0.2 H₂O₂, room temperatures. The highest treatment efficiency reached only 44% according to COD, but ready biodegradability of the sample increased (82%). FACCO was confirmed as possible method for pretreatment o industrial waste water for high COD contain, because it slightly enhanced biodegradability, it reduced organic pollution and formed products were nontoxic. We have focused our future work into a study on optimization of applied procedure for improving bio treatability of the industrial waste water.

Keywords : carbon; Facco process; hydrogen peroxide; Biodegradability; biological Treatment

Introduction

Traditionally, the attention received by biological treatment far exceeds that of other remediation processes, in part due to its low cost and versatility. However, the presence of toxic chemicals dramatically reduces the viability of biological processes. In this case, advanced oxidation processes (AOPs) can be a useful option (Esplugas et al.,2002) to prepare the effluents before the biological remediation. FACCO system is a pretreatment step to conventional biological treatment system. FACCO system helps to cleave (break down) the long chain organic molecules into simpler molecules .so that biodegradability of the chemical is increased. Aromaticity of

the organic compounds is eliminated. The objective of this work is to find a suitable oxidation technology a Fenton process in order to design an integrated chemical-biological system for industrial wastewater treatment. To follow this idea, the knowledge of the physical, chemical and biological properties of the oxidation intermediates and the extension of industrial waste water degradation in Fenton oxidation process are key points (Scott and Ollis, 1995). AC was used as catalyst since its low cost and high adsorption properties make it a suitable material for wastewater remediation through chemical oxidation processes (Stu"ber et al., 2005). Respirometric techniques have been applied to assess the bio degradability, toxicity or inhibitory effect of industrial wastewaters since they allow evaluation of the behavior of an activated sludge against different substrates (Guisasola et al., Water Science & Technology Vol.55, No-12, pp-221–227, O-IWA Publishing 2007 doi: 10.2166/wst.2007.412 2212003). Pharmaceuticals ind. has been chosen as model pollutant because it is one of the most prevalent forms of toxic and weakly biodegradable chemical pollutants from industrial activities.

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MATERIALS AND METHODS

(A) Methods

Materials

A provided analytical highly polluted industrial effluent. De ionized water was used to prepare all the solutions. Hydrogen peroxide (H_2O_2 - 0.5%) Take a 300 ml H_2O_2 solution and make with 30 lit. distilled water. Ferrous sulphate (FeSO₄- 0.2%): Take a 60 gm FeSO₄ solution and make with 30 lit. distilled water.The Carbon used as catalyst in and H_2O_2 processes was supplied by Merck_(reference #102518) in the form of 2.5mm pellets. Some characteristics of this C, prior to use, can be found elsewhere (Sua´rez-Ojeda et al., 2005).

The only exception is reacation, where under acidic conditions, a Fe_2^+ / $\text{H}_2\text{O}_2\text{mixture}$ produces hydroxide radicals in a very cost-effective manner (Reaction 1):

$$Fe_2^+ + H_2O_2 \rightarrow Fe^{3+} + OH^- HO^{\bullet}$$
 (1)
 $k = 76.5 \text{ mol}-1\text{s}-1$

Formed Fe(III) can react with H_2O_2 in the so called Fenton-like reactions (Reactions 2) regenerating Fe_2^+ and thus supporting the Fenton process:

$$Fe^{3+} + H_2O_2 \rightarrow Fe_2^{+} + HO_2 \cdot + H^+$$
 (2)
 $k = 2 \times 10-3 \text{ mol}-1\text{s}-1.$

$$Fe^{3+} + HO_2 \bullet \rightarrow Fe_2^+ + O_2 + H^+$$
(3)

The best oxidation efficiency is achieved when neither H₂O₂ nor Fe2+ is overdosed, so that the maximum amount of OH• radicals is available for the oxidation of organic. For industrial waste water usually Fe₂⁺ / H₂O₂ mass ratio from ½ to 1/10 is found to be the most effective one. The Fenton reaction has a short reaction time among all advanced oxidation processes and it has other important advantages. Iron and H2O2 are cheap and non-toxic, there is no mass transfer limitations due to its homogenous catalytic nature, there is no energy involved as catalyst and the process is easily to run and control. It has been widely used for treatment of highly polluted textile and paper mill wastewaters, as well as industrial waste water . Depending upon their excretion rate, they are released into the effluent and reach sewage treatment plant. If they are not degraded, they could enter the environment, where little is known about their fate and effects. They usually have two characteristics, which declare them as environmental hostile: they are stable and biologically effective .For these reasons optimization of production processes and effective biological treatment is necessary to avoid broad contamination of receiving environment due to the industrial waste water.

(B) FACCO experiments protocol

Effluent ,after secondary treatment from selected industrial units are Collected pH, COD ,BOD, and TOC are analyzed soon after receipt. The Collected , effluent sample 30 lit. is acidified to pH 3.2-3.5 with sulfuric acid . 60 mg $\,$ FeSo_4 added and mixed thoroughly. 300 ml $\rm H_2O_2$ added and mixed thoroughly. Flow rate about 96ml /min. After 15 hours of run/ flow through a sample is collected for the analysis of parameter After every batch back wash thoroughly with tap w after acidified to pH 3.0 with sulfuric acid +100 mg/L FeSo_4+0.08 ml/L $\,$ H_2O_2 and mixed well. (Hamidi Abdul Aziz , "Chemical Oxidation Of Treated Textile Effluent Using Hydrogen Peroxide And Fenton Process" (ICERT 2008).

Biodegradability testing

Respirometry:

Objective: The main objective of performing respirometry is to know the biodegradability of the effluent in less time period. Principle: Respirometry is a scientific method of communication with microbial communities; A technology that monitors and measures the respiration of micro-organisms and the oxidative degradation process of the effluent.

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Methodology:

Collect 2 liter samples from FACCO Members/CETP Plant/ Member Units etc .Neutralized the efffluent if required. Effluent mixed with 30% RAS (i.e. 700 ml Effluent + 210 ml RAS). Aerate it for 15 min. Reactor Kept on Magnetic stirrer inserted With DO sensor. Finally observe the respire meter graph.

Time taken for DO Uptake	Conclusion
in seconds	
100-200	degradable
200-400	Partially degradable
400-1000	difficult degradable

RESULTS AND DISCUSSION

The results and discussion are divided into two sections. In the first one, the performance f each AOP is discussed by means of the COD removal

.Also, the main detected intermediates in each process are examined. In the second section, the determination of the effluents biodegradability parameters is presented.

(A)Carbon Efficency Test Of Fresh Carbon

TRIAL	COD (mg/l)	COD(mg/l)	COD % Reduction		
	Inlet	Outlet			
Trial 1	2480	368	85.16		
Trial 2	2560	480	81.25		
Trial 3	2720	384	85.88		
			84.09		

Carbon Efficency Test Of used Carbon

TRIAL	COD (mg/l)	COD(mg/l)	COD %	
	Inlet	Outlet	Reduction	



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Trial 1	2240	1280	42.85
Trial 2	2560	1600	37.50
Trial 3	2400	1632	32.00
			37.45

(B) Bellow the result of different unit which is treating FACCO and given results for under control of GPCB Norms.

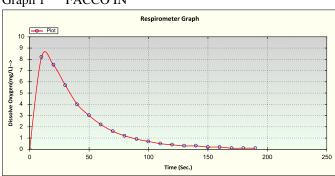
NORMS FOR GPCB COD 250 mg/lit BOD 30 mg/lit

(C) Biodegradability enhancement

(Table is presented at last)

Once the biodegradability parameters (OUR) obtained, the fraction of readily biodegradable COD (%COD) can be calculated (Sua´rez-Ojeda et al., 2007). The total biodegradable COD is the sum of the readily and the slowly (CODS) biodegradable fractions ,therefore COD is always lower than the total biodegradable COD. The determination of CODS requires different experiments that are extremely time-consuming; therefore the COD can be used as a fast method to compare the biodegradability enhancement reached from the different oxidation treatments graph respect to the initial effluent solution, which has 0% of COD.

Graph 1 FACCO IN

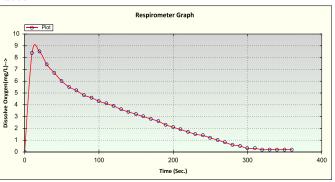


Interpretation of results: Time taken for DO Uptake is between 100-200sec, so sample is Biodegradable.

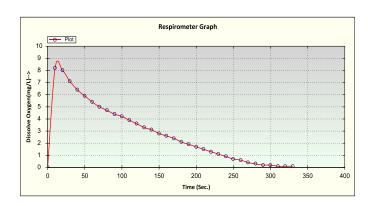
FACCO OUT

Graph 2

Facco in



FACCO OUT



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Interpretation: Time taken for DO Uptake is between 100-200sec, so sample is Biodegradable.

Effect of Iron Type (Ferrous or Ferric)

For most applications, it does not matter whether Fe^{2+} or Fe^{3+} salts are used to catalyze the reaction -- the catalytic cycle begins quickly if H_2O_2 and organic material are in abundance. However, if low doses of Fenton's Reagent are being used (e.g., < 10-25 mg/L H_2O_2), some research suggests ferrous iron may be preferred. Neither does it matter whether a chloride or sulfate salt of the iron is used, although with the former, chlorine may be generated at high rates of application.

It is also possible to recycle the iron following the reaction. This can be done by raising the pH, separating the iron flock, and re-acidifying the iron sludge. There have been some recent developments in supported catalysts that facilitate iron recovery and reuse.

Effect of Temperature

The rate of reaction with Fenton's Reagent increases with increasing temperature, with the effect more pronounced at temperatures <20 deg-C. However, as temperatures increase above 40-50 deg-C , the efficiency of $\rm H_2O_2$ utilization declines. This is due to the accelerated decomposition of $\rm H_2O_2$ into oxygen and water. As a practical matter, most commercial applications of Fenton's Reagent occur at temperatures between 20-40 deg-C.

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(2) Adel Al Kdasi, "Treatment of Textile Waste Water by Advanced Oxidation Processes", Int. J.Vol 6, No 3, pp 222-230, 2004

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- Applications of Fenton's Reagent for pre treating high strength wastes may require controlled or sequential addition of $\rm H_2O_2$ to moderate the rise in temperature which occurs as the reaction proceeds. This should be expected when $\rm H_2O_2$ doses exceed 10-20 g/L. Moderating the temperature is important not only for economic reasons, but for safety reasons as well.
- (3) Susana Cortez, "Fenton's oxidation as post-treatment of a mature municipal landfill leachate," .2009

CONCLUSIONS

- (4) A. Rubalcaba *, "Advanced oxidation processes coupled to a biological treatment,"
- 1. Fenton's reagent, a mixture of hydrogen peroxide and ferrous iron, is capable of releasing hydroxyl radicals which may take part in oxidation of dissolved organics in wastewater.
- (5) Metcalf & Eddy, "Waste water Engineering, Treatment and Reuse," Tata McGraw Hill Publication, Fourth Edition 2003.
- 2. Advanced Oxidation Processes represent a powerful treatment for refractory and/or toxic pollutants in textile wastewaters. Hydrogen peroxide and UV different AOP techniques have been developed .thus allowing to make choice the most appropriate for the specific problems. Taking into consideration that the efficiency of AOPs is compound specific, the final choice of the AOP system can be made only after preliminary laboratory tests.
- (6) Hamidi Abdul Aziz , "Chemical Oxidation Of Treated Textile Effluent Using Hydrogen Peroxide And Fenton Process" (ICERT 2008).

0/

Total

3. The	efficiency	of dif	ferent	candidates	'process	under
different	controlle	d con	ditions.	Identif	ication	of
intermed	iates and	by prod	ucts an	d their toxic	ity.	

Cr Darameter Industrial

Sr	Parameter	Industrial								1 otal
No		effluent		FACCO Treatment					Removal	%
				Tim	ne 0 min t	o1 hr			(in	Removal
									facco)	by
									,,,,	FACCO+8
										hr
										biological
				1	1	ı	ı	ı		treatment
			10	20	30	40	50	60		
1	рН	6.75	3.5	3.5	3.6	3.5	3.53	3.5		
2	TDS(mg/L)	20250	19800	17500	16689	14502	13989	13500	31.81	35.09
3	COD(mg/L)	21120	16660	15586	13689	11503	9317	7120	66.02	94.05
K	BOD(mg/L)	4200	3170	2240	1320	680	200	79	98.11	98.95
5	NH₃(mg/L)	117	103.2	92.17	81.14	71.12	63.02	59.2	49.40	53.02

ES (1)

REFE RENC

Rama

ni and G. Sekaran * Fenton activated carbon catalytic oxidation (FACCO) system for the treatment of soak liquor for reuse application," Department of Environmental Technology, Central Leather Research Institute, Adyar, Chennai.