Liquid Penetrant Degradation System

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Liquid penetrant testing is probably the most widely used non-destructive testing method for non-ferrous substrates. It is generally an oil base chemical solution of dye, either visible or fluorescent. Methods to remove the excess of penetrant depend on the type used and include water washable, post emulsifiable and solvent removable techniques. The wastewater generated by these processes contains fats, oils and greases exceeding the accepted limits. A fully automated degradation system combining an advanced oxidation process and coalescence has been developed. Total organic carbon concentrations as high as 1500 ppm are reduced to accepted level of 30 ppm or lower in less than 24 hrs. No additional waste streams are generated.

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Introduction

Liquid penetrant inspection is probably the most widely used NDT method for non-ferrous substrates. The test object or material is coated with a visible or fluorescent dye solution. The excess dye is removed from the surface and then a developer is applied. The developer acts like a blotter and draws penetrant out of imperfections, which open to the surface. With visible dyes, the vivid color contrast between the penetrant and the developer makes the bleed-out easy to see. With fluorescent dyes, an ultraviolet lamp is used to make the bleed-out fluoresce brightly, thus allowing the imperfections to be seen readily.

When water is used to rinse the parts, the resulting solution contains oils and greases concentration higher than the regulation permitted value to discharge into the sewer. Degradation of those chemical products can be achieved using an advanced oxidation process. The final products should be carbon dioxide and water if the reaction goes to completion. Thus, no additional waste streams are generated. The measure of the total organic carbon was selected as the easiest and most accurate technique to follow the degradation efficiency.

Gravimetric determination of oils and greases is not necessarily accurate to determine the concentration of the liquid penetrant present in the solution. TOC has proven its precision and linearity over a wide range of concentration.

Background of the Technology

Advanced oxidation processes use oxidants to reduce COD/BOD (Chemical Oxygen Demand/Biochemical Oxygen Demand) levels and to remove both organic and oxidizable inorganic compounds. The process should be able to oxidize completely organic materials to carbon dioxide and water. Although it is not always necessary or sometimes not possible to operate these processes until the complete reaction is over.

A wide variety of advanced oxidation processes are available: (a) chemical oxidation processes using ozone (O_3), hydrogen peroxide (H_2O_2), the combination of ozone and peroxide, catalytic ozonation, Fenton's reagent (Fe^{2+}/H_2O_2); (b) ultraviolet enhanced oxidation such as UV/ozone, UV/H_2O_2, UV/air; (c) wet air oxidation and catalytic wet air oxidation.

Advanced oxidation processes are particularly appropriate for effluents containing refractory, toxic or non-biodegradable materials. The processes offer several advantages over biological or physical processes including: process operability, unattended operation, the absence of secondary wastes, the ability to handle fluctuating flow rates and compositions.

Lab scale testing results were presented during AESF Week 2003 in Daytona Beach. A comparison between different processes was done. The conclusions of these previous tests were as follows:

Degradation of high concentrations of organic contaminants can be carried out using a combination of clean technologies. TOC levels as high as 3300 ppm could be reduced to less that 30 ppm in one day. Introduction of flocculation and coagulation decreased the process time to about 10 hours. Three processes proved to be equivalent considering their efficiency in TOC removal:

- ***O_3 + UV/H_2O_2**: The ozone followed by the TOC reduction using the combination UV/H_2O_2 does the color removal.*
- ***O_3 + Fenton reagent + coagulation + UV/H_2O_2**: The ozone removes the color. Then the combination Fenton reagent and coagulation removes most of the organic content. The remaining TOC is degraded using UV/H_2O_2.*
- ***Fenton reagent + coagulation + UV/H_2O_2**: The combination Fenton reagent and coagulation removes the color and most of the organic content. The remaining TOC is degraded using UV/H_2O_2.*

Unfortunately none of these results were completely in accordance with the client's requirements especially regarding the waste generation. Ideally, the process developed should generate no additional waste, be fully automated and require minimum maintenance.

Further tests ran at the lab scale showed the possibility to use UV/H_2O_2 combination to generate a phase separation. In that way, getting rid of more than half of the organic contaminant concentration could be easily achieved. The remaining liquid penetrant contaminated solution could be decomposed using UV (185 nm)/H_2O_2 combination in the pre-determined time (less than 24 hours). The reaction mechanism is as shown in figure 1.

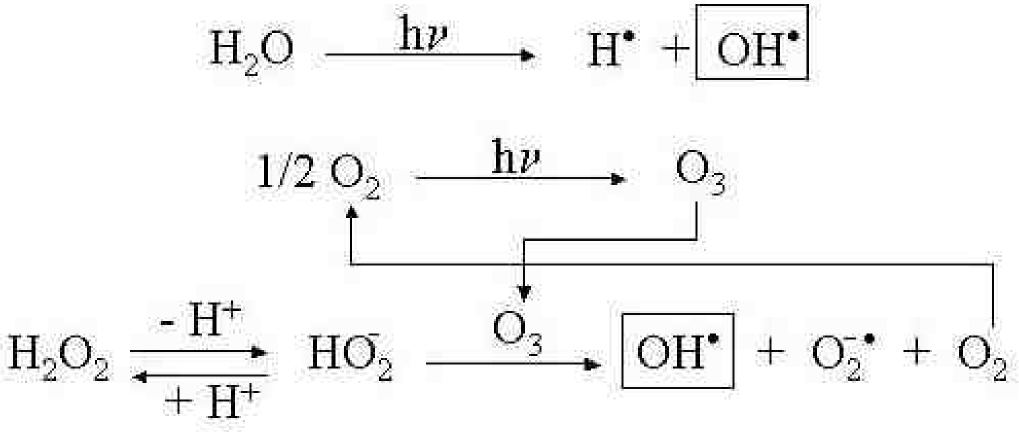

Figure 1. *UV (185 nm)/H_2O_2 Oxidation Mechanism*

Bactericide UV effects are well known and the radiation wavelength in that case is 254 nm. UV (185 nm) is in the ozone producing range as shown in the light spectrum below (Figure 2).

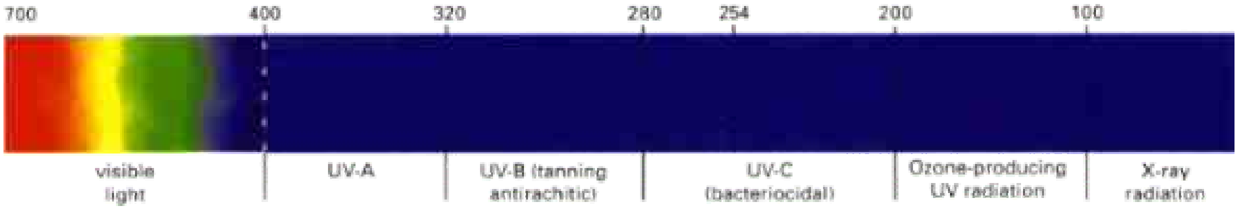

Figure 2. *Light Spectrum*

Total Organic Carbon Analysis

The total organic carbon (TOC) corresponds to the organic carbon content of a known sample. In order to determine that value, inorganic carbon (CO_2, HCO_3^- and CO_3^{2-}) must be purged out of the sample or measured using an acid analysis. In the present case, a known volume sample is injected into two different TOC analyzers. The first one is using thermal oxidation consisting in a platinum catalyst maintained at high temperature in an oxygen atmosphere to convert organic carbon into CO_2. The second apparatus performs that conversion by chemical oxidation using sodium persulfate and phosphoric acid. An infrared detector measures the amount of CO_2 produced for a known sample volume in both cases.

Many tests were made to validate the analysis method using the two different available TOC analyzers: a bench top apparatus using thermal combustion and an online equipment using chemical oxidation to decompose the total organic matter present in the samples. To control the process, the online analyzer was selected to be installed on the pilot unit. The comparison between the two analyzers was made to ensure that an appropriate determination of the contaminant concentration is made during the entire process including the low limit to be discharged to the sewer. A correlation between the TOC results and the approved gravimetric method results was also conducted.

Figure 3 compares the degradation curves obtained using two different oxidation techniques to follow the reaction. It is the same solution analyzed using two different apparatuses. From these curves, it is obvious that the liquid penetrant is not easily oxidized since the difference between chemical oxidation and thermal oxidation should normally be within 10%. In fact, only the thermal oxidation technique can degrade the total amount of organic contaminants present in the solution at high concentrations. The oxidation of the organic matter in the wastewater is incomplete using chemical oxidation. When the organic concentration reaches a certain value, the difference between the two-oxidation techniques is getting smaller. It proves that even if the values obtained using the chemical oxidation are quite different from those obtained using thermal oxidation at high TOC values, the chemical oxidation technique used to decompose the organic matter in the online apparatus is reliable enough to control the lower TOC limit acceptable to discharge the solution into the sewer.

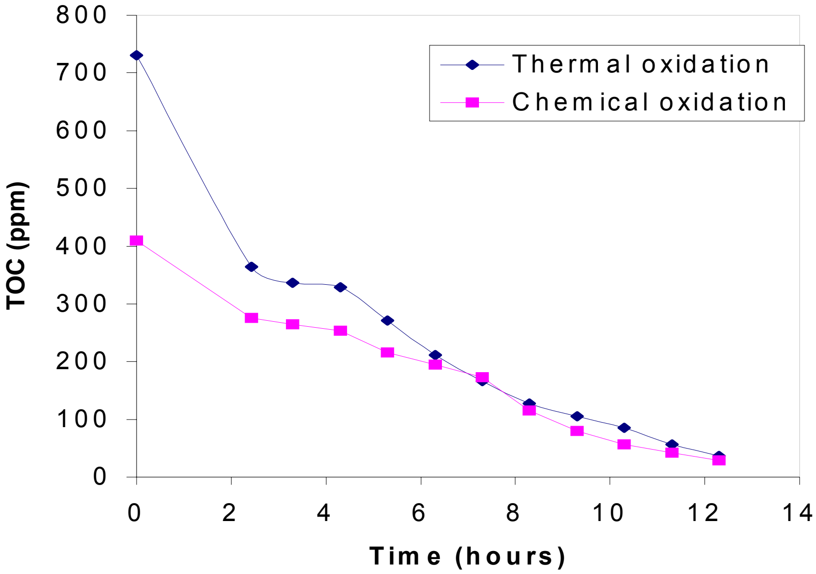

Figure 3. *100 Litres of Solution, 730 ppm 1000 ml of Peroxide to get the Phase Separation, 100 ml per Hour After Separation.*

Results Obtained Using the Pilot Unit

The pilot scale unit was built to correspond to a production of about 200 litres of contaminated rinse water per day (~ 50 US gallons). Figure 4 shows the schematic representation of the oxidation process. The rinse tank is the starting point. The solution is then transferred to the transition tank via a 50-micron bag filter and a coalesceur. The transition tank is big enough to contain few days of wastewater production. It gives a back up container allowing the possibility to shutdown the unit for preventive maintenance and/or repair. Batches of 200 litres are transferred to tank 1 and the treatment starts. Depending on the initial concentration of liquid penetrant in the rinsing water, two different processes can be selected by the PLC as described in Figure 5.

When the initial TOC value is lower than 600 ppm (value established according to the bench top equipment using thermal oxidation), the oxidation process is a single-phase treatment. A combination of UV irradiation and periodical addition of hydrogen peroxide can oxidize the organic contaminants until the concentration reaches the TOC value of 15 ppm. Then the solution can be discharged into the sewer.

When the solution contains more than 600 ppm of organic contaminants, a two-step treatment starts. In the first part of the treatment a phase separation is induced using specific concentrations of hydrogen peroxide combined with UV irradiation. The solution is then allowed to rest for a separation time. The aqueous phase is kept to continue the treatment. The oily phase ends in the used oils and greases container which content will be sent for external disposition (energy recovery). The aqueous phase will undergo the same treatment as in the case of low TOC concentration until it reaches the acceptable limit to be discharged into the sewer.

Figure 6 shows two different views of the actual advanced oxidation pilot unit. Most operations are automated. Alarms are generated in different situations including high level, empty peroxide reservoir, UV reactor problems, etc. This way the operator knows when an intervention should be made.

In order to meet environmental compliance, the pH should be adjusted in the range of 5.5 to 9.5 before the wastewater can be discharged into the sewer. From previous experiments, it was expected that adjusting the pH would have a positive effect on the efficiency of the degradation process. From Figure 7, it is obvious that the liquid penetrant oxidation is faster when the pH is maintained around 7. Otherwise, the pH goes down to a value of about 2.3. Adjusting the pH during the treatment has an economical impact since the oxidation rate is increased consequently resulting in a shorter total treatment time. An automatic pH adjustment system was then incorporated in the process for two reasons, i.e. to meet the regulation and to increase the contaminant degradation rate.

Conclusions

An easily maintained fully automated degradation system combining an advanced oxidation process and coalescence has been developed. Total organic carbon concentrations as high as 1500 ppm are reduced to the accepted level of 30 ppm or lower in less than 24 hrs. Minimal amount of used oils and greases are generated from the phase separation with highly contaminated water effluents. No additional waste streams are generated. The end result of the degradation system is a compliant wastewater stream without any sludge or fouling membranes. The system is easily adaptable to any production rate. Many components can be adjusted (tank and UV reactor sizes, etc) depending on the plant specific needs.

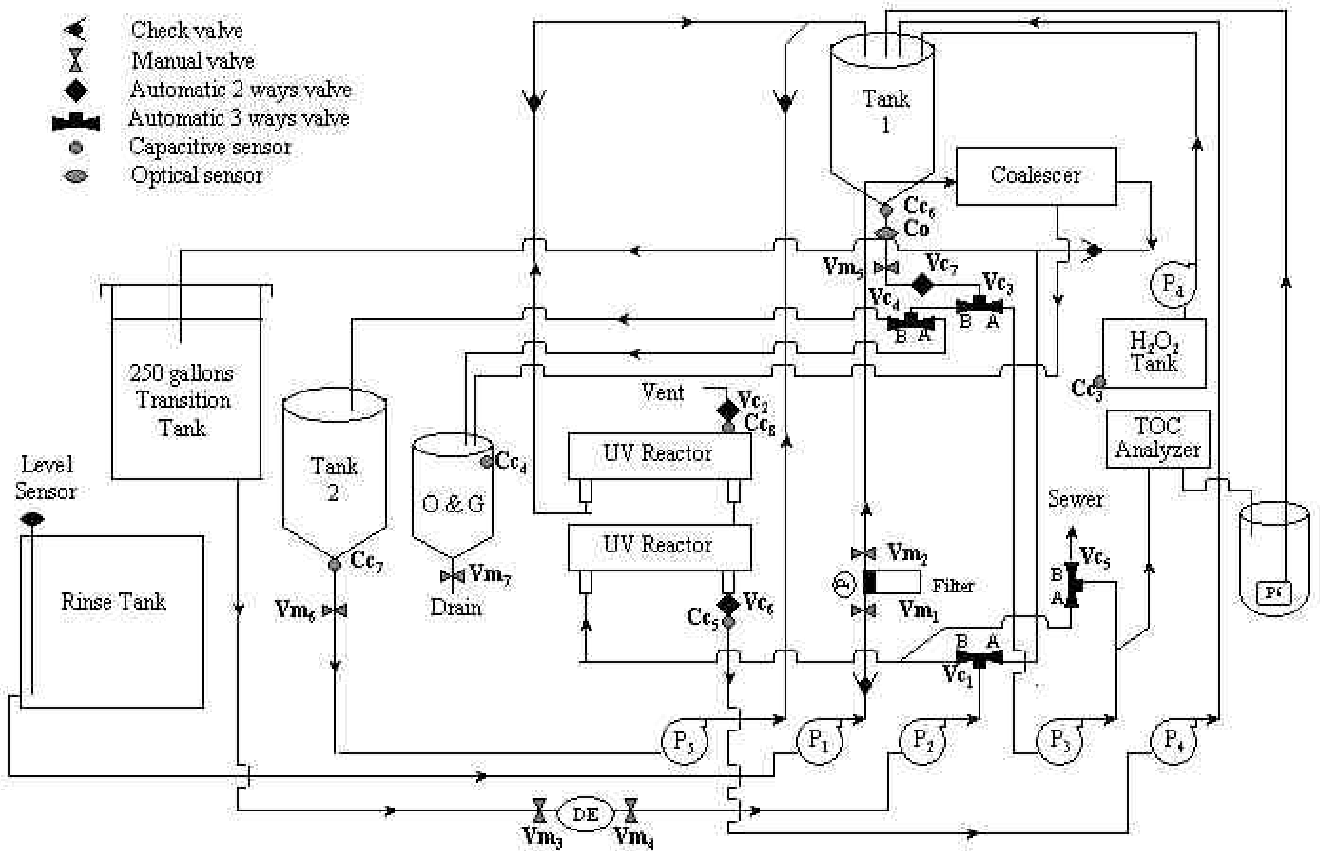

Figure 4. *Advanced Oxidation Process Scheme*

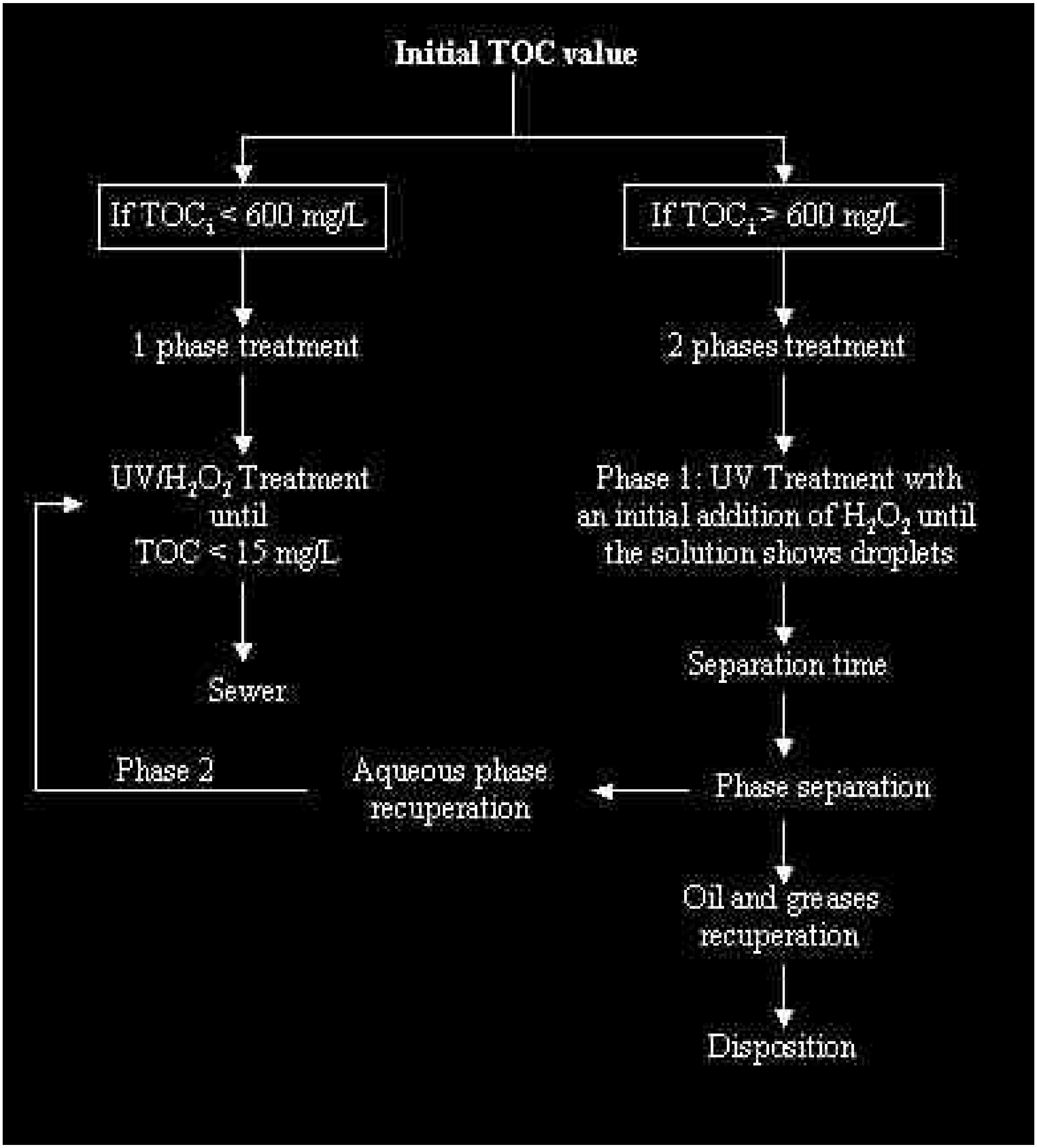

Figure 5. *Treatment Option Diagram*

Figure 6. *Two Different Views of the Oxidation Unit.*

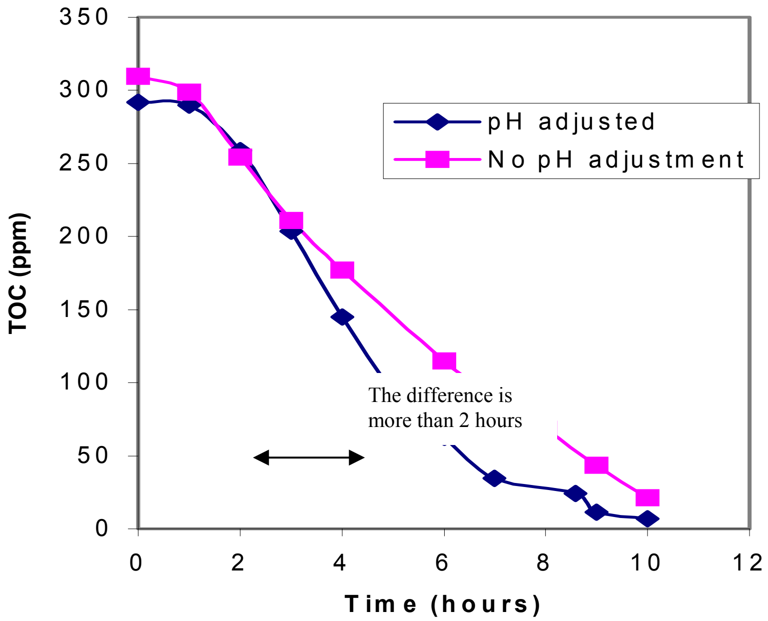

Figure 6. *pH Maintained around 7 from 3 Hours of Treatment to the End (blue line), 80 Litres of Solution, 300 ppm, 250 ml at t=0, 100 ml per Hour.*

References

1. M. Doré, *Chimie des oxydants et traitement des eaux*, Technique et Documentation - Lavoisier, Paris, France, 1989.

2. R. L. Droste, *Theory and Practice of Water and Wastewater Treatment*, John Wiley & Sons Inc., New York, NY, 1997.

3. D. Miousse and F. Biasotto, *Advanced Oxidation Process to Decompose Oils & Greases*, AESF Week 2003, February 3-6, Daytona, FL.

4. J. Dallan, *Ultraviolet Light in TOC Reduction*, Water Conditioning & Purification, 36-37, June 2002.

5. Yabe et al., *Dissociation Energies for Interatomic Bonds in Organic Substances*, http://www.trojanuvlogic.com/UV_Applications/diss_toc.html

6. *Municipal Water Disinfection and Destruction of Toxic Organic Compounds in Wastewater*, http://www3.sympatico.ca/csatari/index5.htm

7. *BOD and COD Reduction Using Hydrogen Peroxide*, http://www.h2o2.com/applications/ industrial wastewater/bodcod.html

8. *Advanced Oxidation Technologies*, www.hydroxyl.com

9. R. P. Donovan, R. P. Timon, J. G. Chavez, R. V. Jones and D. M. Rogers, *Photolytic Destruction of TOC in Spent Rinse Waters by H_2O_2/UV Radiation*, Ultrapure Water, 28-35, February 2002.

10. C. G. Namboodri, W. K. Walsh, *Ultraviolet Light/Hydrogen Peroxide System For Decolorizing Spent Reactive Dyebath Waste Water*, American Dyestuff Reporter **3**, 15-22, 1997.

11. *Source Reduction of Pollutants from Textile Processing Waste Water*, National textile Center Annual Report, 29-38, 1994.

12. J. C. Edwards, *Investigation of Color Removal by Chemical Oxidation for Three Reactive Textile Dyes and Spent Textile Dye Wastewater*, M. Sc. Thesis, Virginia Polytechnic Institute and State University, July 2000.