



EG0000248

**T-33**

## **Treatment of Some Hazardous Industrial Pollutants by Simple Oxidation Techniques**

**N.M. Abd El-Rahman**

*Department of Pesticide Chemistry National Research Center, Dokki, Cairo 12622,  
Egypt*

### **ABSTRACT**

Central treatment of Industrial wastewater requires pretreatment of some specific pollutants which may be not effectively degraded in down stream processes in central treatment unit.

Some of the hazardous pollutants in industrial wastewater including acrylonitrile, pesticides and some commonly used dyes (active and acid dyes) have been subjected individually to oxidation using hydrogen peroxide catalyzed by ferrous ions in acidic solution.

Treatment efficiency was monitored by chemical oxygen demand (COD) removal using a specially developed concentration/COD curves.

Initial concentrations (in terms of COD) were 910 PPM, 1348 and 530ppm and the respective COD reductions were 91, 98 and 99%, for the pesticide, acrylonitrile and the reactive dye.

Oxidative degradation of polared and acid green also reduced COD by 99 and 100% respectively.

The obtained results confirm the appropriateness of oxidative degradation as a pretreatment for some hazardous pollutants prior to treatment in central facilities or municipal activated sludge stations.

*Key words: Central treatment, Dyes, Pesticide, Acrylonitrile, Oxidation, Pretreatment*

### **INTRODUCTION**

Central treatment of industrial wastes is one of the cost-effective approaches for environmental management in industrial zones. Central treatment approach requires unification of treatment methods for all incoming streams. Presence of soluble hazardous chemicals may inhibit the efficiency of the central treatment units (e.g. activated sludge). Further, the hazardous chemicals may be refractory and pass to the receiving water body with no significant degradation. Thus, onsite treatment of some hazardous chemicals prior to down stream treatment in the central facility is mandatory in numerous cases. Also, some of the organic compounds which are difficult to treat biologically demand modified treatment including biodegradation, stripping, sorption or combinations of these processes. Systems with preozonation assist may be also included (1). Refractory organics require chemical or oxidative degradation to render them available for secondary treatment process.

Three common pollutants generally found in industrial wastewater namely dyes, pesticides and acrylonitrile have been chosen for oxidative degradation as a pretreatment step prior to any down stream treatment. The selection of the dye stuff is justified by the enormous size of the textile sector in Egypt. The presence of coloring material would reduce colour transmission in recipient water bodies. Further, toxicity of numerous dyes will significantly affect the present aquatic life (2).

Pesticides generated from manufacturing processes, pesticides packaging in addition to pesticides normally present in agricultural run off will affect water, fish and may get into the food chain (3,4).

Acrylonitrile as one of the chemicals used in the manufacture of polymer composites, packaging materials and numerous industrial and household chemicals may cause substantial threat to health and environment (disorders related to skin, nervous system and probably cancer) unless properly treated or disposed of (5,6).

Numerous physicochemical and biological methods could be used for the treatment of many dye stuffs. Ozone, ion exchange, membrane separation, adsorption, chemical precipitation may be used separately or in combination for the treatment (2,7,8).

Also, pesticides may be treated by appropriate oxidation system, e.g. ozonation, UV, ozone/UV and UV/ H<sub>2</sub>O<sub>2</sub> (3,9-14).

Powdered activated carbon and ozone assisted activated sludge treatment show promising indicators for the removal of toxic organic compounds including acrylonitrile (1).

Acrylonitrile (120mg/l) was 99.1% removed in a batch system comprising combination of stripping and biodegradation. Ozonation decreased the biodegradability of acrylonitrile (15). Acrylonitrile was not readily oxidized by ozone (16). Wastewater discharged from the production of acrylonitrile is treated by activated carbon adsorption. The wastewater may be subjected to preliminary oxidation (17,18).

A mobile treatment system including mediafilter, activated carbon, chlorination, coagulation and physical-chemical methods can handle a spilled hazardous materials including acrylonitrile(19).

Chemical wastes such as those generated from the production of acrylonitrile can be treated by any of three basic two steps systems including wet air oxidation followed by biological treatment, physical treatment followed by wet air oxidation and wet air oxidation with biophysical treatment (20). Organic nitriles (e.g. acrylonitrile) can be hydrolyzed into amide by the action of hydrogen peroxide in alkaline medium (21). Ozone is used to decompose the organic nitrogen contained in acrylonitrile. The initial

pH and the alkalinity seem to affect the degradation rate of organic nitrogen. At low initial pH (e.g. 4) the acrylonitrile has a shorter  $t_{1/2}$  of 18.9 min. (22). Membranes may be used to transfer the ozone nondispersively into wastewater streams containing acrylonitrile (23,24).

In view of the stated indicators concerning the treatment of the three target pollutants, an additional work is still needed to simplify oxidative degradation using Fenton reagent under appropriate conditions.

This paper outlines the results of oxidative treatment for the target pollutants using the  $H_2O_2/Fe^{++}$  system in acidic medium.

## MATERIALS AND METHODS

To prepare the simulated wastewater 3 dyes namely polared, acid green and reactive dye were purchased from the local market (Hoxet). Acrylonitrile was supplied by Fluka >99% (GC) and pyrociel is a local pesticide manufactured by El Naser Intermediate Chemicals.

The concentration of the synthetic dye wastewater was adjusted to 250 PPM. Likewise, synthetic solutions for pesticide-containing wastewater has been prepared using commercial locally produced pesticide (pyroceil). The concentration was adjusted to 500 PPM. Acrylonitrile wastewater of 500 PPM concentration was prepared similarly.

The experimental program adopted numerous oxidation runs based on samples of the simulated solutions (50 ml each).

Each sample was acidified to pH 3-4 prior to the slow addition of hydrogen peroxide and the ferrous salt.

Details of the oxidation are described in earlier publications (2,25). The plan of work included exploring the impact of oxidant quantity and retention time on the efficiency of oxidation in terms of COD reduction. COD was evaluated using Hach DR 2000 Spectrophotometer and standard test kits 0-1500 vials. Further, dye concentration was monitored using developed light absorption curves.

## RESULTS AND DISCUSSION

### A. OXIDATION OF DYES

Oxidation of dye solution using Fenton reagent showed significant colour removal and COD reduction. Typical values for dye concentration and COD reduction are shown in *Table (1)* and *Figures (1,2)*. The estimated reduction corresponds to the given oxidant dose and chosen retention time.

Hydrogen peroxide oxidation has been carried out for polared (acid dye), acid green and reactive dyes. Addition of Hydrogen peroxide to polared removes the colour almost completely (99-100%). COD decreased from 528 mg/l to 30 mg/l after 15 minutes. The colour of the acid green dye has been removed completely using 0.4 ml H<sub>2</sub>O<sub>2</sub>. COD value decreased from 470 to 20 mg/l after 15 min. Full COD removal was observed after 30 min using 0.7 ml of the peroxide. Colour removal of the reactive dye approached 99%. Also, COD decreased from 530 mg/l to 10 mg/l after 45 min.

*Table (1) Effect of time on COD reduction of dyes*

dye	COD (mg/l)		time (min)	10% H <sub>2</sub> O <sub>2</sub> (ml)
	Initial	Final		
Polared	528	30	15	1
		30	30	
		25	45	
		20	60	
Acid green	470	20	15	0.72
		10	30	
		ND	45	
		ND	60	
Reactive dye	530	20	15	1
		10	45	
		ND	60	

## **B. OXIDATION OF PYROCIEL**

Oxidation results reveal full removal of COD using about 2 ml of H<sub>2</sub>O<sub>2</sub>. About 98% COD reduction could be achieved using 1 ml of H<sub>2</sub>O<sub>2</sub> *Fig. (3)*. These results suggest the adequacy of Fenton oxidation as a pretreatment stage for the removal of some pesticides.

## **C. Oxidation of Acrylonitrile**

The concentration of acrylonitrile (expressed as COD) decreased by about 91% using 4 ml of H<sub>2</sub>O<sub>2</sub> (10% conc.). COD removal reflects linear dependence on hydrogen peroxide dose as shown in *fig. (4)*.

The COD value decreased from 1348 to 46 mg/l after 60 min. using 4 ml of H<sub>2</sub>O<sub>2</sub>. The oxidation efficiency is about 91%. Increasing the time of oxidation from 15 to 60 min increased the oxidation efficiency from 89.5% to 91%. Thus, 15 min was considered appropriate for the oxidation of acrylonitrile, *Fig. (5)*. Additional work is still needed to identify residual oxidation products.

## **OXIDATIVE PRETREATMENT FOR THE ACTIVATED PROCESS**

A proposed treatment scheme for the integrated oxidation/Activated sludge/Powdered activated carbon (PACT) is proposed, *Fig. (6)*. The integrated complex may incorporate additional chemical precipitation if needed.

## **CONCLUSION**

Central treatment of industrial wastewater may be an appropriate option within some industrial complexes. Realization of sustainable central treatment system requires unification of the principal treatment technology. Thus, an appropriate pretreatment should be employed to destroy organic wastes, which affect the efficiency of down stream treatment operations. Fenton oxidation may be regarded as an appropriate option to be applied for in situ treatment. Results of this work confirmed the adequacy of Fenton oxidation for degradation and removal the colour of polared, acid and reactive dyes.

Further, oxidation of pyrociel (local pesticide) and acrylonitrile approached 98% and 91% (expressed as COD) reduction respectively. Additional research is still needed to identify residual oxidation.

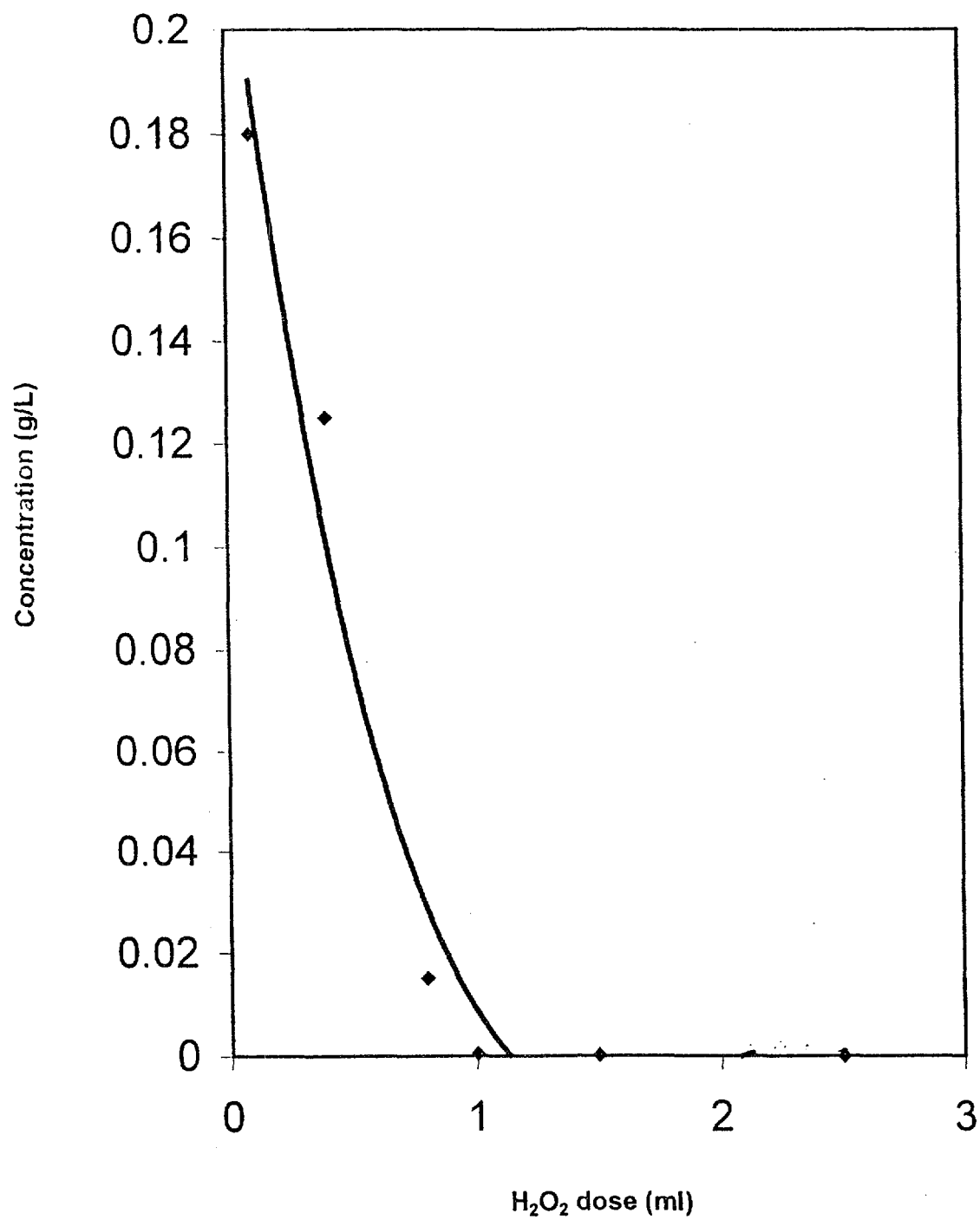
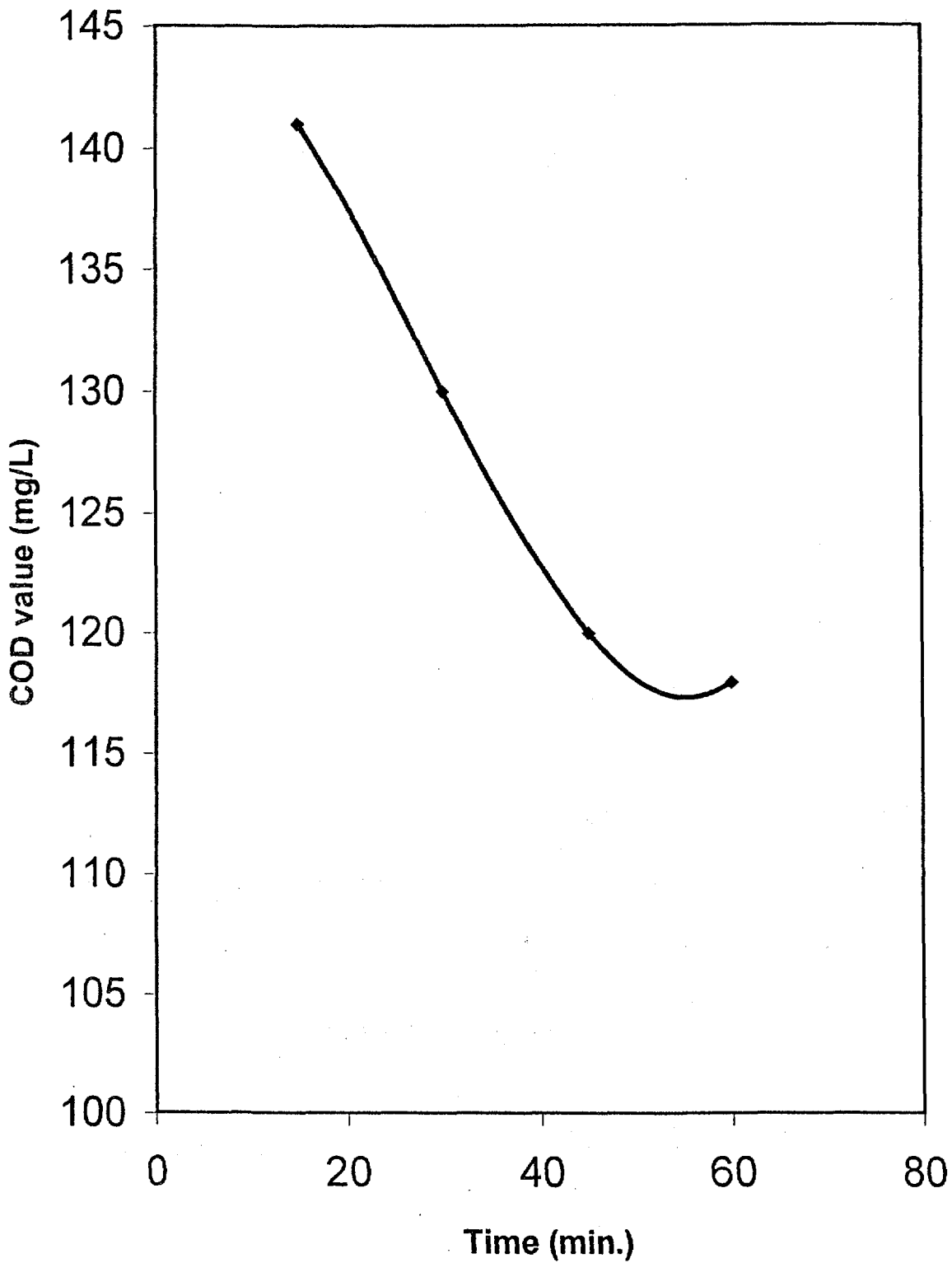
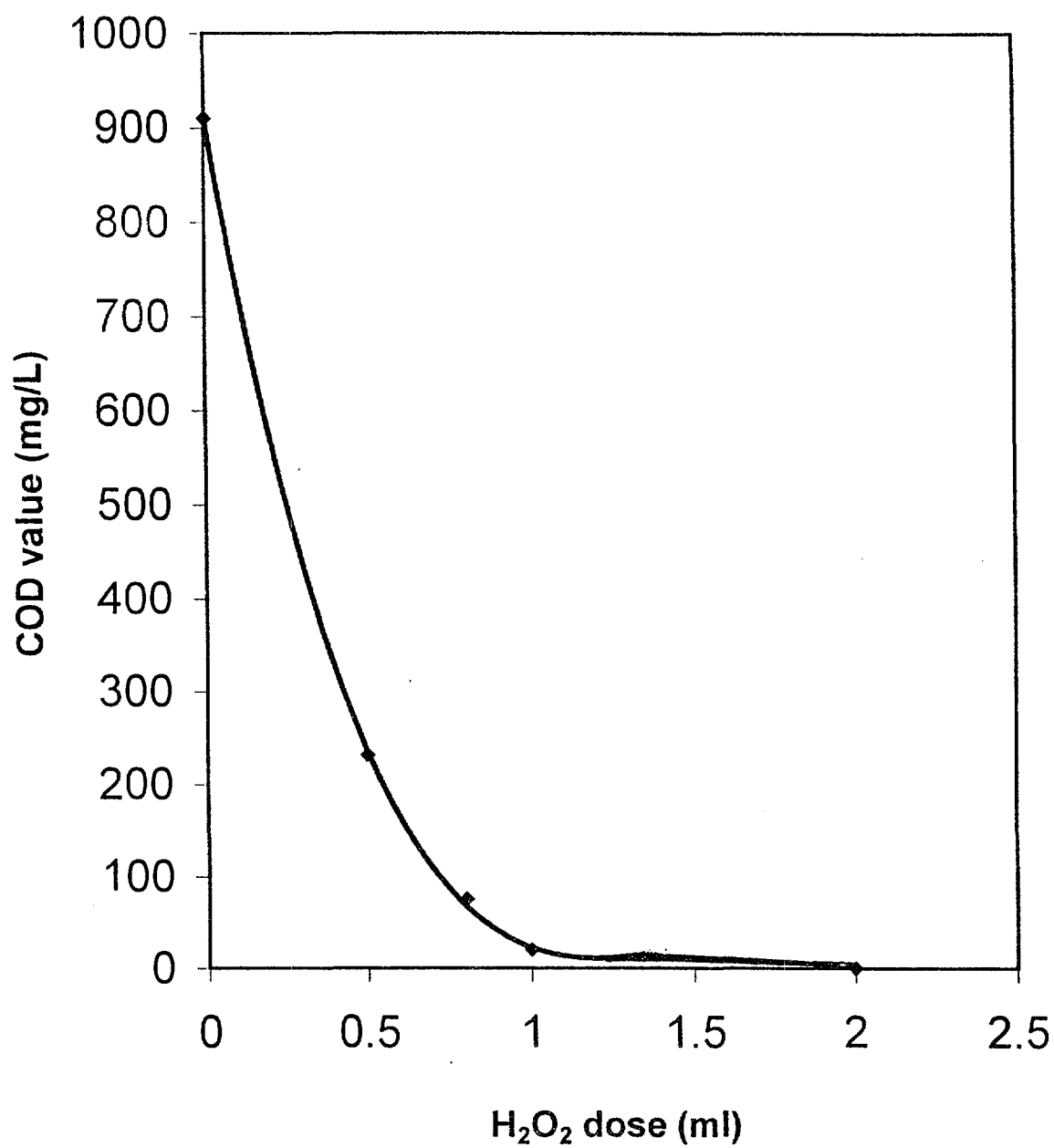


Fig.(1) Effect of H<sub>2</sub>O<sub>2</sub> dose on Polaredconcentration

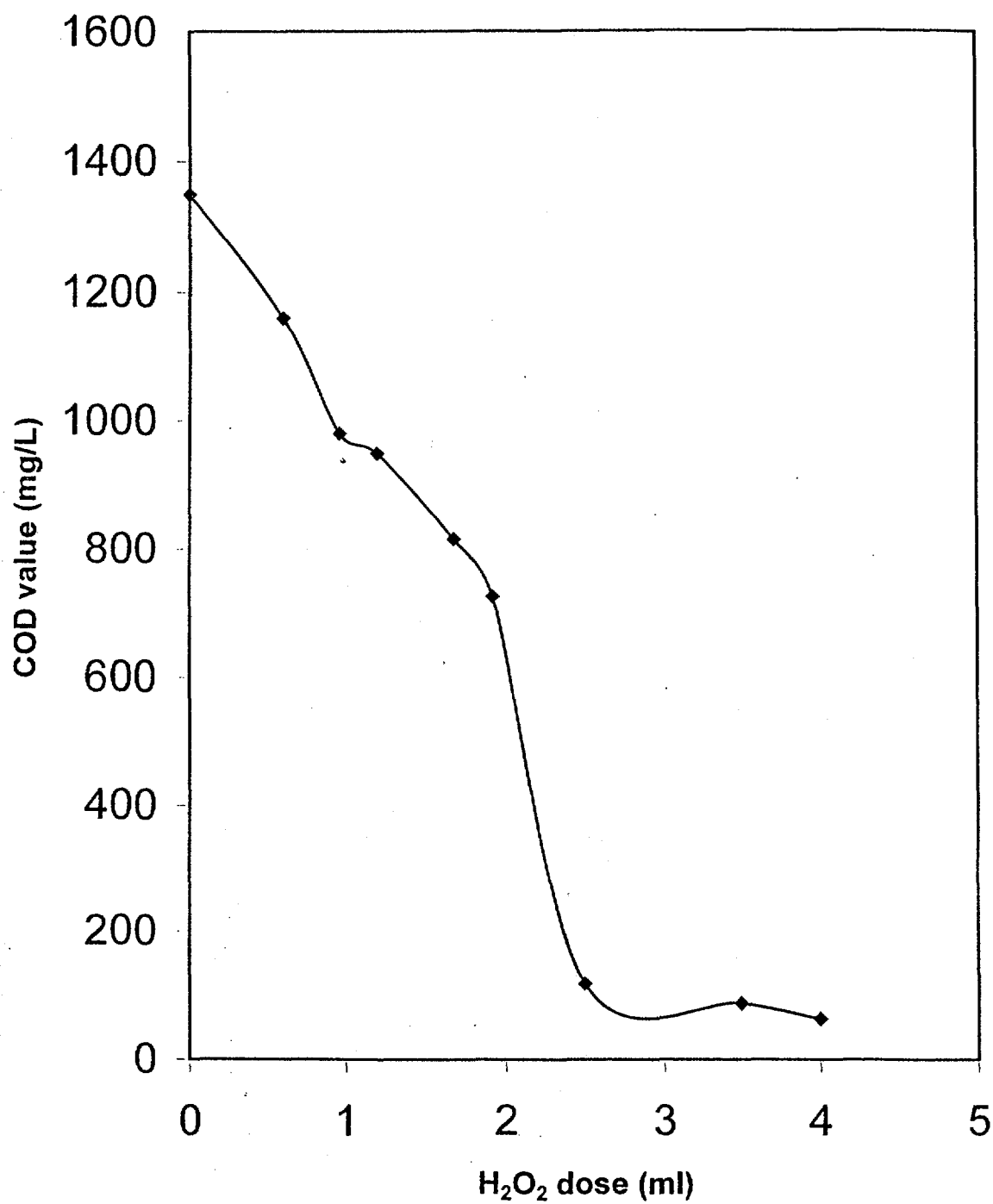


**Fig.(2) Effect of retention time on COD for simulated Polared solution**

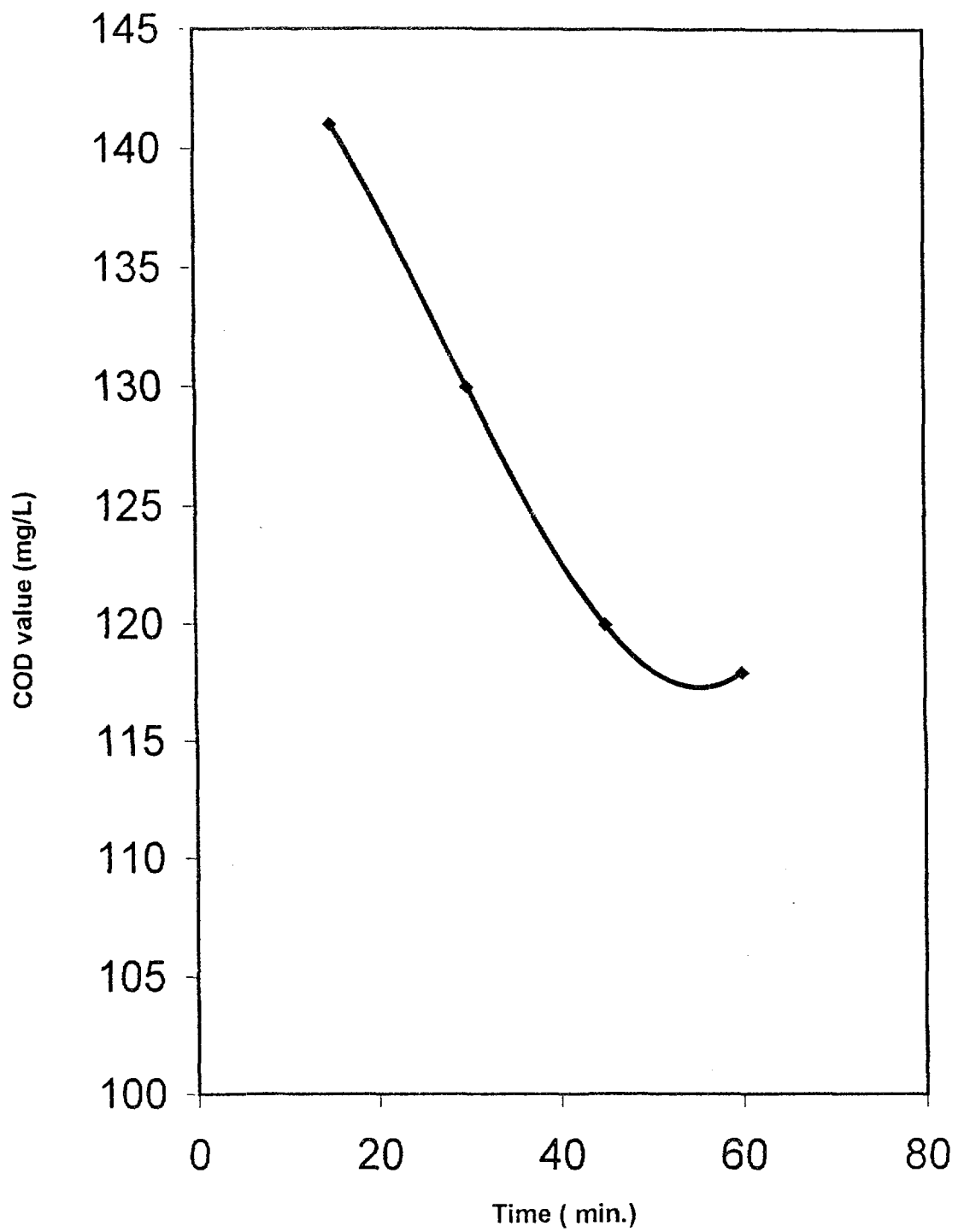


**Fig.(3) Effect of H<sub>2</sub>O<sub>2</sub> dose on COD for simulated Pyrociel solution**





**Fig.(4) Effect of H<sub>2</sub>O<sub>2</sub> dose on residual COD for Acrylonitrile solution**



**Fig.(5) Effect of retention time on residual COD for simulated Acrylonitrile solution.**

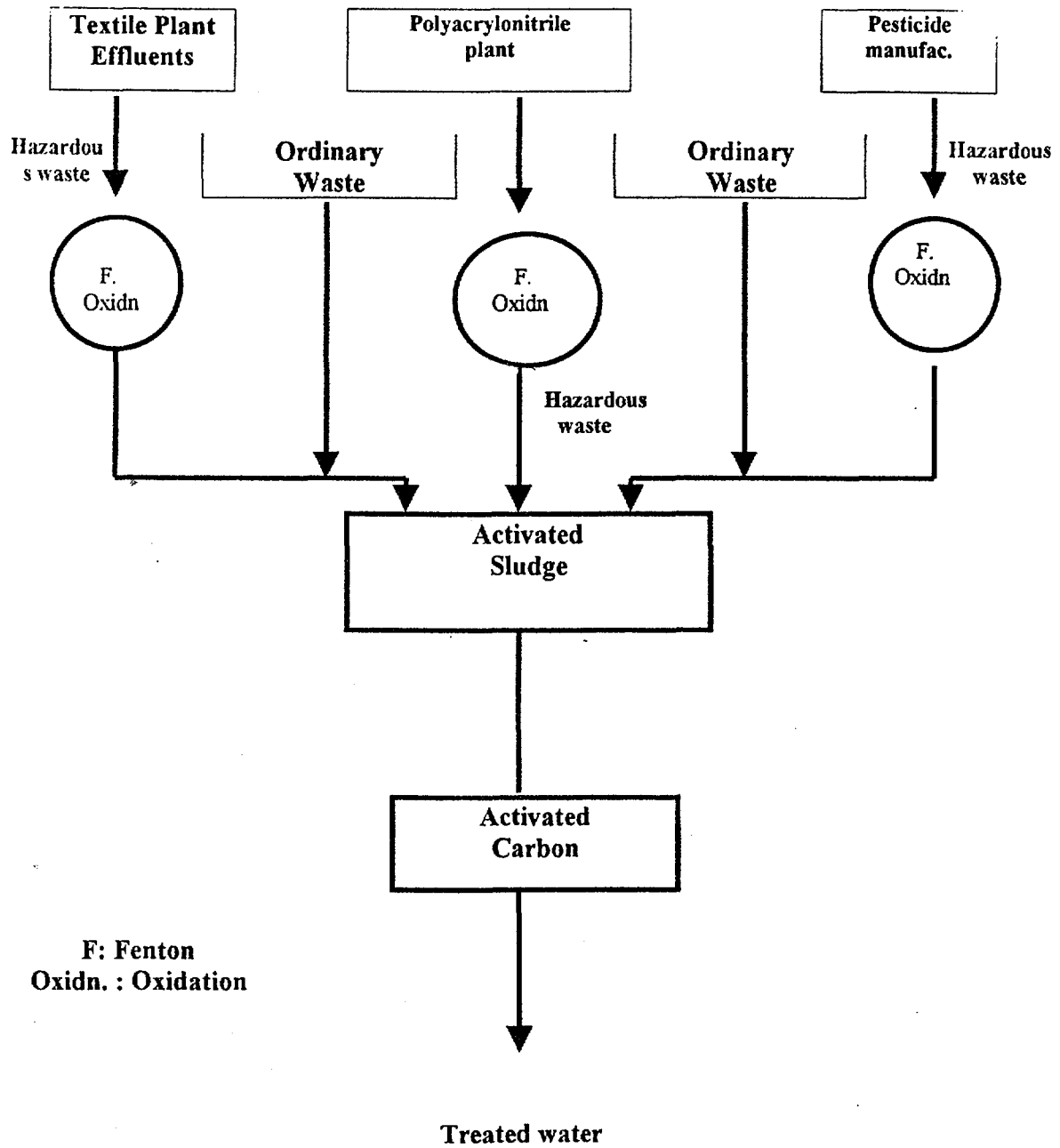


Fig (6) Proposed Oxidation / Activated Sludge / Activated Carbon Treatment Plant

## REFERENCES

- 1- EL., Stover; A. Fazel; and D.F. Kincannon, *Ozone Science and Eng.*, 7(3), 191-203 (1985).
- 2- W.G. Kuo, , *Water Res.*, 26 (7) PP.881-886 (1992).
- 3- U.S. EPA SOCs and IOCs. Final Rule. *Fed. Reg.* 57, 31776 (1992).
- 4- S.Ro. Kyoung and A.L. Judy, *Water Envir. Research*, 67(4), 548-552 (1995).
- 5- U.S. EPA, *Pollution Prevention and Toxics*, "Acrylonitrile fact sheet", 749-F95-001 (1994).
- 6- F. Hund, U.S. EPA, Report No./440/1-89/104 (1989).
- 7- C. Prat,, M. Vicente, and S. Esplugas , *Wat. Res.*, 22(6), 663-668 (1988).
- 8- A. Reife, and H.S. Freeman, Eds., *John Wiley & Sons*, 1996.
- 9- F.J. Beltran; J.F. Garcia-Araya and B. Acedo, , *Wat. Res.*, 28(10), 2153-2164(1994).
- 10- K. Harda; T. Hisanaga, and K. Tanaka, *Wat. Res.*, 24(11), 1415-1417 (1990).
- 11- E. Gal; P. Aires; E. Chamarro and S. Esplugas, *Wat. Res.*, 26(7), 911-915 (1992).
- 12- F.J. Beltran; J.F. Garcia-Araya and B. Acedo, *Wat. Res.*, 28(10), 2165-2174(1994).
- 13- J.J. Pignatello and Y. Sun, , *Wat. Res.*, 29(8), 1837-1844 (1995).
- 14- F.J. Benftez; J. Beltran-Heredia and T. Gonzalez, *Ind. Eng. Chem. Res.*, 33, 1264-1270 (1994).
- 15- D.F.Kincannon; E.L. Stover;; V. Nichols, and D. Medley, *J. of the Water Pollution Control Federation*, 55(2), 157-163 (1983).
- 17- H.E. Alford and K.L. Bigler, , *US Patent, No.*, 4,141,826 (1979).
- 18- Y. Tagashira,; H. Takagi, and K. Inagaki, *US Patent, No.*, 4,203,835 (1980).
- 19- M.K. Gupta, *US EPA, Report No.*, EPA-600/2-76-109 (1976).
- 20- A.R. Wilhelmi and R.B. Ely, *Chemical Eng.* , 83(4), 105-109 (1976).
- 21- J.P. Zumbunn, , *US Patent, No.*, 3,715,309 (1973).
- 22- C.N. Chang,; J.G. Lin ; A.C. Chao; B.C. Chao and R.F. Yu, , *Pretreatment of Industrial Wastewaters II*. Andreadakis, A. (Ed.), 401 (1997).

- 23- P.V. Shanbhag; A.K. Guha and K.K. Sirkar, , J. Hazard. Mater., 41(1), 95-104 (1995).
- 24- A.K. Guha; P.V. Shanbhag and K.K. Sirkar, Aiche. J., 41(8), 1998-2003 (1995).
- 25- N.M. Abd El-Rahman, "Parametric Evaluation of Phenol Degradation", Submitted for Publication in Environ. Sci. & Technol., 1998.