EFFECT OF HYDROGEN PEROXIDE ON INDUSTRIAL WASTE WATER EFFLUENTS: A CASE STUDY OF WARRI REFINING AND PETROCHEMICAL INDUSTRY

J. SOJI ADEYINKA and A. RIM-RUKEH
Department of Chemical Engineering, University of Port Harcourt, P.M.B. 5323, Choba, Port Harcourt, Nigeria

(Received 17 April 1997; accepted in revised form 16 September 1998)

Abstract. This paper assessed the composition of waste water effluent generated by a Petrochemical industry and a treatment system developed to improve the quality of the discharge water. Parameters as pH, COD, TSS chloride and lead ions were analysed and treated comparatively using hydrogen peroxide. At pH 8.0 post treatment analysis showed a COD – 96 mg/l TSS – 48 mg/l Cl – 798.75 mg/l and Pb^{2+} – 2 mg/l for treatment D where 40 g/l of alum was used on 30% solution of H_2O_2 compared to systems A-C. Process treatment included activated clay with sodium ion resin which at pH 6.8 had COD – 52 mg/l, TSS – 10 mg/l, Cl – 510 mg/l and Pb^{2+} – 0.070 mg/l. This system has an overall efficiency of 79.0% TSS, 45.83% COD, 97.5% Pb^{2+} and 36.1% Cl reduction. Characteristics obtained for the study has a higher efficiency compared with FEPA and WHO standard for similar industrial water treatment.

Keywords: alum, effluent, environment, hydrogen peroxide, oxygen demand, suspended particles

1. Introduction

Natural water is the habitat for active and diversified biotic community closely linked with non-biotic organism. Presence of pollutants affect natural water, alters the quality and often destroys aquatic life. Unpolluted environment is healthly for the aquatic life, this also will contribute to human health who depend on biotic life for both water and nutrition.

Water contaminants can be classified into chemical, physical and biological sources. All these sources of pollution introduced foreign matters such as organic compounds which on oxidation/reduction depletes oxygen level of the water. Use of disolved oxygen (DO) in the water for biological degradation of organic compounds leads to oxygen deficiency in the environment and the biota. These dissolved oxygen is needed by fish and other aquatic life to survive. Such dissolved oxygen should normally be maintained above 5 mg/l (US Dept. of Interior, 1968). Pollution caused by the presence of inorganic compounds leads to toxic effects by reducing available oxygen in the waters' DO; also due to the chemical characteristics of such inorganic compounds, a cation exchange reaction may take place by one metal displacing a less electropositive metal from a soluble salt (precipitation of insoluble salts) especially sulphates of calcium and barium. Also cation

Environmental Monitoring and Assessment **59:** 249–256, 1999.

exchange reaction exists in the salts of heavy metals (Cd, Pb, Cr, Cu, Hg and Zn). Presence of such elements even in trace quantities can lead to negative effect on the biotic. Presence of cadmium and lead had been reported to have a negative effect on bone deformation in fish while mercury polluted water had been reported to give permanent neurological impairment amongst people eating fish from such mercury polluted water (Gold, 1971). Treatment of waste prior to its discharge into the environment is desirable to avoid pollution.

Discharging a relatively warm water from an industrial plant into the aquatic water can cause physical changes leading to temperature change of the receiving water, reduction of water density and viscosity which will cause suspended solids to settle faster at local spots. Also temperature variation (increased temperature) leads to faster assimilation of waste and leads to faster oxygen depletion with turbidity and colour changes arising from the dissolution of suspended particles in such water (Hodges 1973).

Hydrogen peroxide has been used in different experiments to improve the oxygen supply and oxidation rate of suspended and disolved particles that causes pollution in such water effluent. (Chen *et al.*, 1996) reported use of hydrogen peroxide (30%) in metal speciation. Also, use of hydrogen peroxide as oxidizing auto catalyst for treatment of halogenated hydrocarbon in waste water exists (Muganlinskii, 1985; Adeyinka *et al.*, 1986; Adeyinka *et al.*, 1997). From such works, hydrogen peroxide showed good ability in reducing bonded chlorides in both organic and inorganic compounds present in the waste water treated.

Untreated or incompletely treated industrial waste contain algal nutrients, non-bio-degradable organics, heavy metals and other toxicants that deteriorate the receiving stream. For the purpose of treating such water, there is need to device and carry out research into various methods for reduction of such wastes. These methods can be grouped under conventional and advanced treatment categories. Conventional methods are biological in approach, and are used specifically to romove suspended solids, biodegradable organics and micro-organisms from waste water. The principal processes in advanced methods are chemical treatment using activated carbon, filteration processes, reverse osmosis and electrodialysis either used singly or combination of two or more of these processes in a single plant set (Adeyinka, 1996). Demand for high quality water calls for further investigation into alternative methods for treatment which are dynamic in approach and complete in practice, such that the various waste water of modern technology can be treated adequately for save discharge into environment or reused as recycled water for industrial purposes. Eckenfelder *et al.*, 1973, used physico-chemical methods to treat waste water and found that such properties affect reduction of organic matter in effluent treatment. In the work of (Rebhum *et al.*, 1974) on municipal waste water treatment in Israel, physico-chemical properties was used to reduce suspended solids, biological oxygen demand and COD. This process was used for domestic sewage treatment in Nigeria (Ademoroti *et al.*, 1979) where a final effluent free of suspended solids bacteria and non bio-degradable organics was

TABLE I
Characterization of the effluent waste water

Parameter	Value
pH	8.0
TSS	48 mg/l
COD	96 mg/l
Cl^-	798.75 mg/l
Pb^{++}	2 mg/l

obtained. The treated water was odourless, colourless and non turbid. This results shows a high quality waste effluent treatment. Major problem of the process was due to deposition of trapped solids which required back-flushing of the plant with dilute acids to regenerate the column.

This paper presents a study of hydrogen peroxide treatment developed for industrial waste water using data and available chemicals to carry out an easy to operate technology with a view of good economic advantage.

2. Material and Method

Industrial effluent from Warri refining and petrochemical was obtained both at the point of discharge into the main stream and from the receiving stream. The samples were analysed for pH Cl^-, Pb, COD and TSS for reduction purposes since the refining has a waste water treatment unit using urea as active reagent.

Sample of waste effluent was taken from a stream carrying waste water from the plant. Materials used for sample collection were pretreated by washing the container with dilute hydrochloric acid and later rinsed with distilled water. The containers were later dried in an oven for 1 h at 105 ± 5 °C and allowed to cool to ambient temperature. At the collection point, containers were rinsed with samples twice and then filled with sample and then corked tightly. All samples were taken to the laboratory for treatment and analysis. Pre-treatment analysis of the water is shown in Table I.

3. Experimental procedure

Based on the degree of pollutants in the water, samples of the effluent was divided into four portions of equal volume (500 ml). The first portion was then divided into three equal volumes (150 ml). Each of the volume was treated with 50 ml of standard alum solution of varying concentrations (10 ml/1, 20 ml/l, and 40

TABLE II

Quality of effluent obtained from alum clarification passed through a bed of activated clay and sodium-ion exchange resin

Parameter	Alum concentration (mg/l)		
	10	20	40
pH	7.4	7.2	7.1
TSS	10	10	10
COD	80	77	78
Cl^-	516	514	510
Pb^{++}	0.076	0.072	0.070

ml/l). This was done to assess clarification and sedimentation by precipitation of complex ions that can be formed as a result of cation exchange reaction especially Cu, and Zn. Each of the three volumes (chemical and water) was mixed slowly for 30 min to create good effluent-chemical contact. These were later individually filtered through a bed of activated clay and sodium ion exchange. The activated clay was prepared from clay using phosphuric acid of 35% concentration and 20% hydrochloric acid, and latter drying the clay in an oven at a temperature of 100 ± 5 °C for 2 h. The clarified effluents were collected and the parameters pH, Cl^-, Pb, TSS and COD were analysed for. The method of analysis was consistent with the standard methods (APHA 1979). Average results obtained is as shown in Table II.

The second experiment on the effluent was caried out by treating the effluent with alum at a concentration of 40 mg/l with an addition of 20 ml of 0.2% urea solution. The mixture was agitated for 30 min with a machine (mechanical device) for effective effluent – chemical contact. The content was then filtered through a bed of activated clay as earlier reported. The clarified effluents were collected and analysed for parameters as in treatment A above. Average result of the analysis is as shown in Table III.

Similar procedure was carried out for the third portion of the water using 50 ml of standard volume of hydrogen peroxide solution of 30% concentrations. Each of the three portions of the water was treated with the hydrogen peroxide (0.5%, 1.0%, and 1.5%) volume of the effluent. The liquid content of effluent-hydrogen peroxide was agitated for 30 min with a mechanical device after the agitation, the content was filtered through a bed of activated clay as in treatment A. Clarified effluents were collected and analysed as in treatment A. The average result of the analysis is shown in Table IV.

The fourth portion of the effluent was divided into three equal volumes. Each of the volumes was treated with 50 ml alum solution of 40 mg/l and (0.5%, 1.0% and 1.5%) volumes of 30% concentrated hydrogen peroxide. The mixture was agitated

TABLE III

Quality of effluents obtained from alum clarification (40 mg/l) and urea (0.2%) solution passed over a bed of activated clay and sodium-ion exchange resin

Parameter	Value mg/l
pH	8.7
TSS	10
COD	64
Cl^-	510
Pb^{++}	0.070

TABLE IV

Quality of efluent obtained from Hydrogen peroxide passed through a bed of activated clay and sodium-ion exchange resin

Parameter	H_2O_2 solution (%)		
	0.5	1.0	1.5
pH	6.5	6.1	5.7
TSS	10	10	10
COD	53	43	40
Cl^-	510	510	510
Pb^{++}	0.07	0.07	0.07

for 20 min for effective effluent – chemical contact. After this, the content was filtered as in treatment A. Result of the clarified effluent analyses is shown in Table V.

4. Discussion

Effluent treatmen was carried out using alum at the clarification unit while hydrogen peroxide was used as treatment reagent. In all the treatment cases A, B, C and D, multiple treatments were carried out and average values reported for each Table. Treatment A (Table II) was obtained from alum clarification, the water was later passed through a bed of activated clay and sodium-ion exchange resin. In all the analyses sodium ion exchange resin was used to track the alum traces that may be dissolved in the effluent during clarification, as well as to remove other ions that

TABLE V

Quality of effluents obtained from Alum clarification (40 mg/l) and standard solution of Hydrogen peroxide (0.5%) passed through a bed of activated clay and sodium-ion exchange resin

Parameter	Value (mg/l)
pH	6.8
TSS	10
COD	52
CL^{-1}	510
Pb++	0.07

may cause impurities in the water. Analyses of the effluent showed a good reduction of TSS from 48 mg/l level to 10 mg/l. This shows a 79.2% of TSS removal while COD was reduced from 96 mg/l to 78 mg/l giving a 18.75% reduction. Lead was reduced from 2.0 mg/l to 0.07 mg/l (96.5% reduction). Reduction of chlorine from 798.75 mg/l to 510/l (36%) indicated possible chemical reaction of chlorine with cations in the effluent. Although, a pH of 7.2 was obtained, such pH reduction can be accounted for as presence of chlorine ions in the effluent. This is because all chloride salts present in the effluent are water soluble.

Analysis of treatment B where 40 mg/l of alum was used with 0.2% urea solution showed that urea activated alum synergetically leading to COD reduction from 98 mg/l to 64 mg/l (33.33%) while TSS reduction was from 48 mg/l to 10 mg/l (79.2%), lead ion reduction was from 2 mg/l to 0.07 mg/l (96.5) and chloride ion reduction was from 798.75 mg/l to 510 mg/l (36%). In both treatment cases A and B reduction of lead and chloride ions was constant, these showed that alum and urea have little effect on chloride reduction. Although the effluent have a pH 8.6 after treatment which is relatively alkaline, this may be due to the effect of urea since other treatment without urea did not exercise this pH value.

When hydrogen peroxide was used in both treatments C and D there was a considerable reduction of COD and chlorine ion. In treatment C (0.5% hydrogen peroxide conc) effluent analysis after the sodium resin exchange unit showed a considerably reduction of COD level from 96 mg/l to 53 mg/l (44.8%) while TSS was reduced from 48 mg/l to 10 mg/l (79.2%). Lead ions and chloride reduction followed the same pattern as in treatments A and B but the final effluent has a pH of 6.5. Comparism of treatments B and C showed that COD reduction was equal and was better than that of treatment A in the ratio of 1:1.2:2.4. Also reduction of both TSS, lead and chloride ions showed a similar pattern. This led us to investigate further increased concentration of hydrogen peroxide at 0.5% with an alum clari-

TABLE VI
Water characteristics affecting acceptability of water (WHO and FEPA)

		WHO standard	FEPA standard	
Parameter	Result	Desirable level	Max. A. L. allowable level	Limits for dischage in surface water
pH	6.8	7–8.9	6.5–9.5	6–9
Cl^{-}	510	200	600	600
Pb^{++}	0.07	Nil	<1	<1
COD	52	60	80	80
TSS	10	5	25	30

fication (40 mg/l). This treatment D, showed higher effectiveness relative to other treatments formulated for the effluent treatment. Such improved treatment showed a TSS reduction from 48 mg/l to 10 mg/l (70.2%), COD reduction from 96 mg/l to 53 mg/l (45.85%). Lead ion and chloride remained as in other treatments.

In all the treatments carried out, total reduction of both lead and chloride were constant at 0.07 mg/l lead and 510 mg/l chloride. This may be due to the fact that at such concentration, lead ion in the effluent exists in bonded form or as free ion which have no potential for chemical reaction. Also presence of 510 mg/l of chloride ion was attributed to the fact that hydrochloric acid was used in activating the clay used at the filtration unit. Also most of the chloride ions retained in the effluent even in the presence of hydrogen peroxide suggested that such chlorides are internally bonded which prevented its reduction in the presence of hydrogen peroxide. Comparison of results in treatment D showed a good compliance with both Federal Environmental Protection Agency (FEPA) and the World Health Organisation (WHO). Table VI shows the comparism of data from this research work with those of FEPA and WHO requirements.

From this table, final treated water from this unit can be recycled for plant use or discharged into the environment without negatively affecting the environment. From the analysis of the four treatments carried out, improved water quality in the last treatment where 0.5% of hydrogen peroxide (of 30% conc) was used showed higher oxidative ability. Thus giving free oxygen and pure water (Adeyinka *et al.*, 1997). The result obtained in this treatment agreed with an earlier report that alum clarification in the presence of peroxyl group has an advantage of chloride reduction (Adeyinka, 1991).

Although sodium ion exchange resin was used, its overall effect became evident only with clarification upon which floculation effect and cation exchange reaction served as purification processes leading to TSS and lead ion reduction.

5. Conclusion

Results obtained in this study showed that industrially polluted waste water can be treated using hydrogen peroxide as oxygen source for oxidation of impurities as well as for COD. Such waste water subjected to alum and hydrogen peroxide was found to be environmentally safe, cost effctive and easy to operate. It can be concluded that this process has both economic and technological advantage over high technology processes. Although, a limited understanding of the behaviour of the reaction and the factors influencing cation exchange is required, a model can be formulated for this process upon which a scale up process plant can be designed for industrial and municipal use.

References

Adeyinka, J. S.: 1996, Underground water pollution: the effect of peroxyl group in cation reduction, *J. Water Res. Vol.* **4**, 36–40.

Adeyinka, J. S.: 1996, Waste water treatment through reverse osmosis:A kinetic study, Proc. Intl. Con., Africa – U.S.A. on Manuf. Tech. (Accra, Ghana August 12–15, 1996).

Adeyinka, J. S. and Mamedov, B. B.: 1997, Effect of H_2O_2 as catalyst on product distribution of Ar-H Oxychlorination at low temperature, GJPAS/97/073 (in press).

Ademoroti, C. M. A. and Sridhar, M. K. C.: 1979, Fluidized bed technique in physico-chemical treatment, *EWT, Vol.* **19**, pp. 291–297.

American Public Health Association: 1979, Standard methods for examination of water and waste water, 14th Ed., New York.

Chem, W., Tan, S. K. and Tay, J. K.: 1996, Distribution, fractional composition and release of sediment-bound heavy metals in tropical reservoirs, *WASP, Vol.* **92**, Nos 3/4. 472.

Eckenfelders, W. W. and Cecil, L.: 1973, Application of new concept physico-chemical method of waste water treatment, *Prog. in Water Tech. Vol.* **1**. (Pergamon).

Gold, W. L.: 1971, Mercury in environment, *Sci. Amer.* **224**(5), 1521.

Hodges, L.: 1973, Environmental pollution: a survey emphasising physical and chemical principles, Holt Rinehart and Winston Inc.

Muganlinskii, F. F. and Adeyinka, J. S.: 1987, Low temperature oxidation of hydrochloric acid in industrial waste water using hydrogen peroxide, Sci. rept. AZINEFT KHIMIE (BAKU 1987).

Rebhurm, M. and Striets: 1974, Physico-chemical treatment of strong municipal waste water, *Water Res.* **8**, pp. 195–201.

Water Quality Criteria – Report of the National Technical Advisory Committee to the secretary of Interior, Washington, D. C. US Dept. of Interior (April 1968).

Water and Environment: 1993, *Inst. of Water Res. Symp.*, Series. II.