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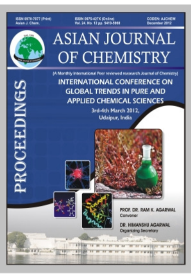

Treatment of Pulp Factories Wastewater Containing Chlorophenolic Compounds with Ozonation†

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In this research, a comparison between biological treatment and a combination of that with ozonation treatment is studied. Wastewater arising from pulp factories has toxic and poisonous materials, which make some serious environmental problems and that is for containing specific poisonous chlorophenolic compounds that in biological reactors in a liquid phase can be absorbed much easier and with a higher rate. Because of high molecular weight of these toxic compounds the treatment is performed in a sequential process to make these compounds smaller and change to dissolvable substances in the environment. Through this way the quality of treatment and the value of dissolvable substances, which can be returned to the environment are increased. A remarkable reduction of chemical oxygen demand, total organic carbon and adsorbable organically bound halogens in this treatment system in comparison with the most common biological treatment system is achieved.

Key Words: Wastewater treatment, Ozonation, Chlorophenolic compounds, Chemical oxygen demand, Total organic carbon, Adsorbable organically bound halogens.

INTRODUCTION

Wastewater of chlorine whiteners which are by-products of cellulose causes a hazardous water vapour that is dangerous because of containing different combinations of chlorophenol[1,2]. This is known as a pollutant factor in the environment which is even not possible to be solved by treating wastewater in traditional ways. The most hazardous part of these substances is monomers of chlorophenolic combinations[3]. These monomers and especially monomers with high molecular weights are seen in such wastewater treatment systems. All monomeric combinations of chlorophenol are removed completely in both aerobic and anaerobic ways. Concentration of each one of these monomers among treated wastewaters is usually less than 100 nm and most of them are less than 50 nm. By this research it became clear that the production of such substances is variable, but it never reaches to more than 30 %, it is necessary to mention that COD, TOC and AOX especially AOX of absorbable chlorine were possible to be calculated. It has been proved that left combinations of chlorine will remain in the environment for a long period of time. Ozonated wastewater provides necessary substances for bio-treatment in both aerobic and anaerobic stages[4]. For providing the essential substances for final biological treatment, sufficient solution, which is ozonated wastewater is produced in some groups. Because of that which is high number of groups and the number of adding ozone, calculation of final value and real value of added ozone to the solution is very difficult[5].

EXPERIMENTAL

Two main methods of bio-ozone-bio treatment and professional biological treatment were done continuously. In continuous treatment at first wastewater producer source should be considered biologically[6]. The main purpose of this research is a comparison of artificial ozonation and biological natural ozonation for treating wastewater.

First the wastewater enters the BFB system with a water vapour, which has been formed by biological dissolvable substances, then it enters a gas reservoir tank which includes ozone gas and extra air. Ozone has been dissolved by UV. The environment's pH is kept about 7 in the whole reaction time. The concentration of ozone in the BFB system cycle is measured and controlled by an electrode called amprometric electrode. Such a kind of system has been modeled from

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anaerobic reactors which were used in the 1990`s. This kind of system can be designed for pulp factories wastewater treatment for about 2 years. The treatment process begins by removing salts and other harmful combinations and increasing the concentration of dissolvable substances and it continues by extracting 200 mL of Di-ethyl from the acidified sample. The standard temperature begins in 70 ºC for 2 min and reaches to 240 ºC and the final temperature of 240 ºC continues for 3 min. The concentration of the liquid phase is also measured. The brown colour of wastewater, which is removed during ozonation is because of a medium existence[7]. Moreover the mentioned electrode is used for measurement that makes the ozone value to be limited to about 20 mg/L.

The time that the system needs to reach to a specific fixed limit is about 90 h, which is 3 times more than the total time or 4.5 times more than the total time in aerobic systems. The most error per cent in the final stage is less than 0.5 % and this value even becomes less in aerobic reactors. After the first considerable COD reduction in primary(A-B) biological treatment (about 20 to 30 %), in the next stage of biological aerobic to anaerobic traetment (C-D-E) decrease after ozonation treatment shows itself in a very large scale and more than the two previous stages. Of course in this stage if ozonation process is omitted, COD reduction will definitely shows itself very much less than this amount.

Table-1 showed that the TOC might have been increased in samples. This meaningful difference may exist because of errors in measurement tools or methods, so for that we can consider the error factor of 2 to 5 and explain the increase in TOC. In others such differences will not be seen. The most considerable treatment is seen in AOX volume, which is because of gradual ozone adding to the system. To explain the relation between AOX reduction and biological treatment without ozonation existance is very hard and to some how impossible. A comparison between previous observations and the reached information in this study shows that a separate biological treatment can have a very important role in reduction of AOX value. The ratio of separated AOX on separated COD (ΔAOX/ΔCOD) in the ozonation period (B-C) is about 0.11 in sample number 2 and 0.22 in sample number 3. This ratio for the total bio-ozone-bio treatment was 0.15 for sample number 2 and 0.14 for sample number 3 at the beginning. This more ratio in sample number 3 may exist because of more concentration of ozone in this sample.

RESULTS AND DISCUSSION

In this reactor liquids are passed sequentially and according to bio-ozone-bio-treatment method and it shows that when ozone is consumed very fast, no ozone can enter the reactor actually. Experiments showed that the ozone value never reaches the ozone value in the new wastewater to the system when wastewater of the system is consumed again[8]. It means that if new wastewater is entered, the ozone value is more than the previous one in the system.

The removal of chemical oxygen demand removal in the anaerobic system (30 to 180 g/m^3) is very remarkable. Total organic carbon removal value in a similar reactor in samples 3 and 4 was not high (85 and 90 g/m^3), AOX removal value in anaerobic reactors is usually high about 25 g/m^3, which is rarely seen. It is essential to mention that reducing the ΔAOX/ΔCOD ratio could be caused by improved biological COD removal or by reduced AOX removal efficiency by ozone (Figs. 1-3).

TABLE-1
GENERAL VARIABLES DURING BIO-OZONE-BIOTREATMENT

Measured Global Variables	Sample	Ozone consumption (ΔO) (gm^{-3})		
		Case 1	Case 2	Case 3
COD	A	593	594	1880
	B	436	472	1390
	C	436	346	1178
	D	432	328	1085
	E	406	264	1009
TOC	A	224.5	224.5	632.6
	B	183.4	189.1	619
	C	183.4	207.8	537
	D	182.7	136.8	517
	E	177.9	140.5	508.9
AOX	A	47.6	49	121
	B	36.6	36.6	90.2
	C	36.6	22	43
	D	27.4	17.2	41
	E	24	15.1	38.1

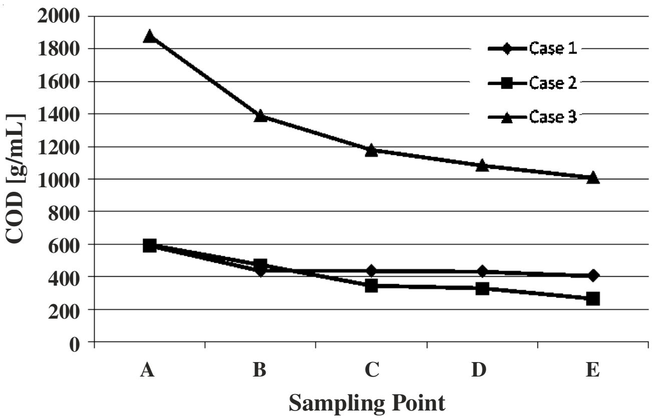

Fig. 1. Chemical oxygen demand removal in the sequential bio-ozone-biotreatmnet

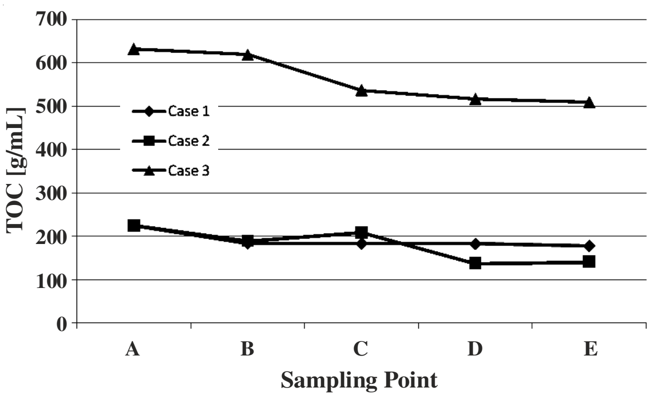

Fig. 2. Total organic carbon removal in the sequential bio-ozone-biotreatment

Table-2 shows that the measured variables (COD, TOC, AOX) in original wastewater, effluent from anaerobic bioreactor and effluent from cycle ozonation-bio treatment during bio-ozone-bio treatment, which is a good result of the comparison.

As it can be seen in the following figures a very remarkable decrease occurs in COD in all four samples and its value in effluent from cyclic ozonation-biotreatment reactor is 400 g/m^3 or less. The value of TOC also falls down dramatically to 200 g/m^3 and less in the samples in effluent from cyclic ozonation-biotreatment reactor and the value of AOX in all four samples goes down to less than 30 g/m^3 in effluent from cyclic ozonation-biotreatment reactor.

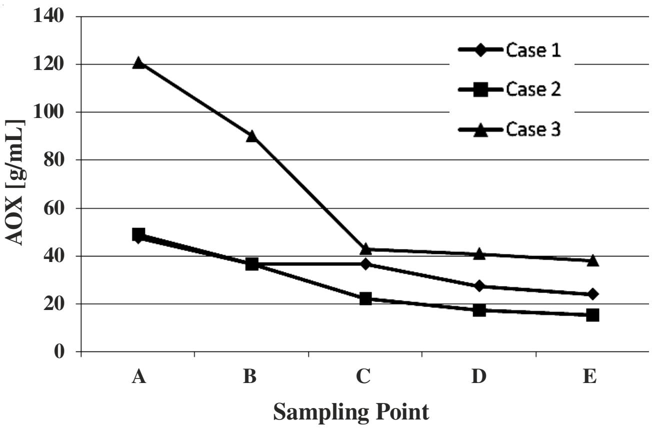

Fig. 3. AOX removal in the sequential bio-ozone-biotreatment

TABLE-2
MEASURED VARIABLES DURING OZONATION AND BIOLOGICAL TREATMENT

Measured Variables	Samples Origins	Sample 1	Sample 2	Sample 3	Sample 4
COD	A = original wastewater	504	528	1073	926
	G = effluent from anaerobic bioreactor	446	491	912	749
	H = effluent from cycle ozonation-biotreatment	348	308	421	336
TOC	A = original wastewater	212	229	388	370
	G = effluent from anaerobic bioreactor	192	192	298	287
	H = effluent from cycle ozonation-biotreatment	185	139	198	153
AOX	A = original wastewater	40	36.5	64.4	64.2
	G = effluent from anaerobic bioreactor	37.7	30.7	38.8	55.2
	H = effluent from cycle ozonation-biotreatment	27.8	14.2	18.9	15.3

With an accurate comparison between the value of COD, TOC and AOX in effluent from anaerobic bioreactor and effluent from cyclic ozonation-biotreatment reactor, it is proved that the difference is analytically vary considerable and the efficiency of the system in comparison with the common biological treatment system is remarkable. Of course the amount of all the three measured parameters in the effluent from anaerobic bioreactor with the consideration of their values in original wastewater has been decreased, but what is measured in the effluent from cyclic ozonation-biotreatment reactor is close to the standard values of the mentioned parameters and the treated wastewater is safer to be used in some other industries after treatment (Figs. 4-7).

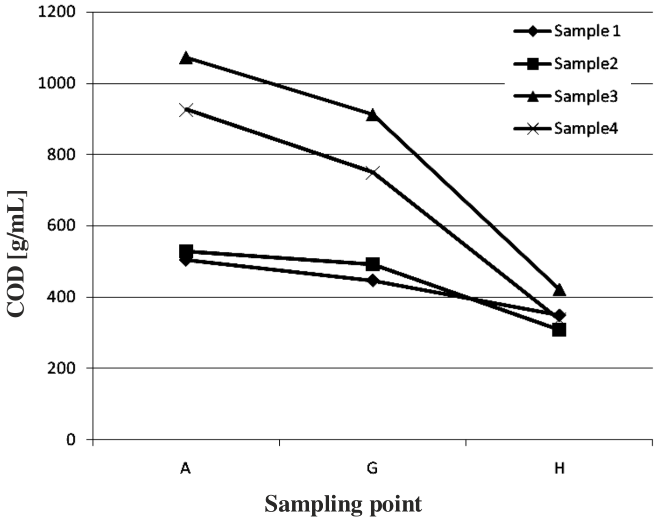

Fig. 4. COD concentration in cyclic ozonation-biotreatment system. A = original wastewater; G = effluent from anaerobic bioreactor; H = effluent from cyclic ozonation-biotreatment reactor

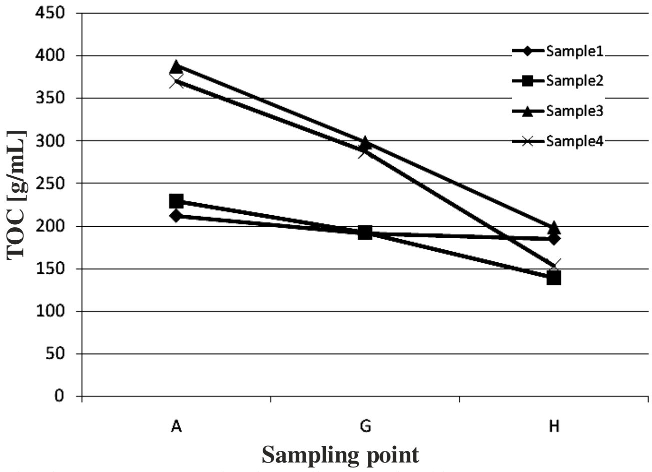

Fig. 5. TOC concentration in cyclic ozonation-biotreatment system. A = original wastewater; G = effluent from anaerobic bioreactor; H = effluent from cyclic ozonation-biotreatment reactor

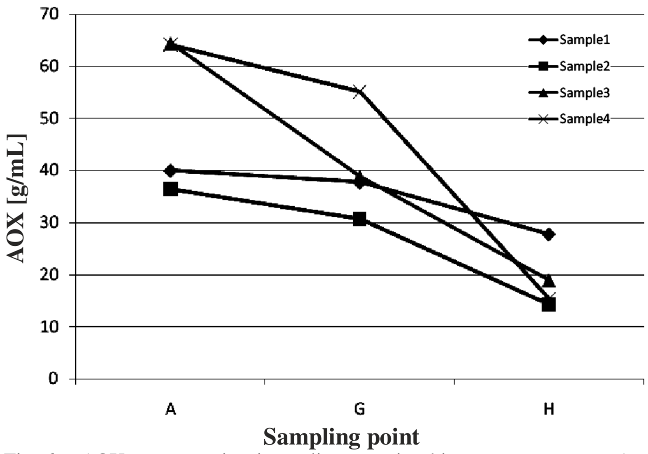

Fig. 6. AOX concentration in cyclic ozonation-biotreatment system. A = original wastewater; G = effluent from anaerobic bioreactor; H = effluent from cyclic ozonation-biotreatment reactor

Usually error factor in AOX experiments is high, because for analyzing AOX very high value of that is necessary and this value can't be completely returned to the cycle after recycling. When ozone value is provided sufficiently to the system, AOX value is low until the volume of input AOX to the system becomes 65 g/m^3.

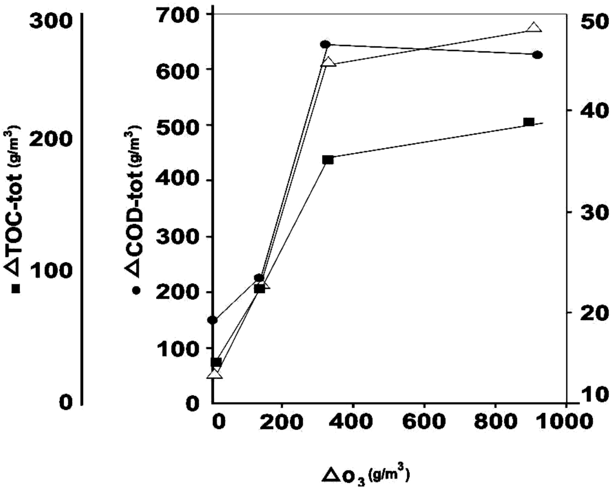

Fig. 7. Total removal of AOX, COD and TOC in the integrated cyclic ozonation-biotreatment system

ΔAOX/ΔCOD ratio was studied in 4 samples and were respectively 72, 10, 70 and 76 % for samples 1 to 4, which are all according to AOX (g) on Ozone (g). This value is considerably less than the volume that is achieved in sole ozonation and it means that biological treatment depends more on the COD removal value rather than reduction of ΔAOX/ΔCOD ratio. So according to that we can increase COD removal value or decrease AOX removal value by ozonation for improving biological treatment more.

Conclusion

In this research calculation and estimation of bio-ozone-bio treatment is possible to be done. And it shows that ozonation lets pulp factories wastewater to be treated easily with better efficiencies. For better treatment of poisonous substances and also simultaneous treatment of the combinations we can complete the system with excessive and other perfect systems[9]. ΔAOX/ΔCOD ratio is 0.14 when oznation is done only, where as if it is completed with bio-ozone- biotreatment, this ratio reduces to 0.08. Two main reasons can be mentioned for the above achievement; reduction of the chloration activity and existence of oxidation reaction in bio-ozone- bio treatment system. Therefore bio-ozone- biotreatment process can be suggested as a very useful method for treatment of such wastewaters.

REFERENCES

1. Metcalf and Eddy, Wastewater Engineering, Treatment and Reuse, edn. 4, Vol. 12, p. 1287 (2004).
2. H.-P. Kaballo, Y.G. Zhao and P.A. Wilderer, *Water Sci. Technol.*, **31**, 51 (1995).
3. C. Prat, M. Vicente and S. Esplugas, *Water Res.*, **23**, 51 (1989).
4. P.R. Gogate and A.B. Pandit, *Adv. Environ. Res.*, **8**, 553 (2003).
5. Z. Sozanska and M.M. Sozanski, in ed.: L.J. Bollyky, Eficiency of Ozonation as a unit process in the treatment of secondary effluents from pulp and paper industry. In Ozone in Wastewater Treatment 8z Industrial Appliciation; International Ozone Association: Vienna, VA; Vol. 2, pp. 203-220 (1989).
6. S.D. Lin and C.C. Lee, Water and Wastewater Calculations Manual, McGraw-Hill, edn. 2, **vol. 6,** p. 755 (2007).
7. S. Delerisand and T. Lebrun, Biolysis O:80 % of Sludge Reduction in Biological Treatment of Wastewater using ozone, Paris Nord/Villepinte, France, (2003).
8. J.L. Sotelo, F.J. Beltran, M. Gonzales and J.F. Garcia-Araya, *Ind. Eng. Chem. Res.*, **30**, 220 (1991).
9. R.H. Voss, *Enuiron. Sci. Technol.*, **17**, 530 (1983).