

COD and TOC Removal Assessment in Effluent From Anaerobic Bioreactor and Effluent From Cyclic Ozonation-Biotreatment in a Pulp Factory Wastewater Treatment

Amir Hajjali*

Ph.D. of Engineering in Earth Science, Environmentalist & Researcher, Islamic Azad Uni., P.O.Box: 19395-1539, Tehran, Iran

Abstract

‘In this research, treatment of wastewater from a pulp factory was experimented in order to remove the value of COD and TOC in two different methods. Such wastewaters contain specific poisonous chlorinated phenolic combinations, which in biological reactors in a liquid phase can be absorbed much easier and with a higher velocity. After the treatment, the concentrations of COD and TOC were measured in the cyclic ozonation-biotreatment system and were compared with the same parameters` achieved measures in effluent from anaerobic bioreactor. The comparison revealed that the removal in both is dramatically different and proved the remarkable efficiency of the cyclic ozonation-biotreatment system. Because of high molecular weight of these poisonous combinations it is necessary to perform in a way that in a sequential process these combinations can be changed to smaller and dissolvable substances in the environment. By bio-ozone-bio treatment the value of consumed ozone is considerably increased, but through this way the quality of treatment and the value of dissolvable substances and returnable to the environment are increased. In cyclic ozonation-biotreatment reactor liquids are passed sequentially and according to bio-ozone-bio-treatment method, and it shows when ozone is consumed very quickly, no ozone can enter the reactor actually. Experiments showed that the ozone value never reaches the ozone value in the new comer wastewater to the system when wastewater of system is consumed again. It means that if new wastewater is entered, the ozone value is more than the previous one in the system.’

© 2016 ‘Amir Hajjali’ Selection and/or peer-review under responsibility of Energy and Environmental Engineering Research Group (EEERG), Mehran University of Engineering and Technology, Jamshoro, Pakistan.

Keywords: ‘Anaerobic Bioreactor; COD; Ozonation- Biotreatment; TOC; Wastewater ‘

1. Introduction

Wastewater of pulp factories which are by-products of cellulose causes a hazardous water vapor that is dangerous because of containing different combinations of chlorophenol [1]. This is known as a pollutant factor in the environment which is even not possible to be solved by treating wastewater in traditional ways. What was successfully done in this research was treating such a wastewater by a sequential method through which ozonation was combined with the biological treatment and proved a remarkable difference in the treated wastewater`s characteristics. The most hazardous part substances here were monomers of chlorophenolic combinations which caused increasing of the two important factors in wastewater treatment (Chemical Oxygen Demand and Total Organic Carbon). These monomers and especially monomers with high molecular weights were seen in such wastewater treatment systems. All monomeric combinations of chlorophenolic were removed completely in both aerobic and anaerobic ways. Concentration of each one of these monomers among treated wastewaters was usually less than 100nm, and most of them were less than 50 nm. This research revealed that the production of such substances was variable, but it never reached to more than 30%, and with a specific focus on the COD, and TOC which were considered to be experimented in this research, it has been proven

* Corresponding author. Tel.: +98-91-01868601; fax: +98-21-22631054.
E-mail address: a.hajjali.env@gmail.com

that there were dramatic removals in such parameters and that the reduction of them in effluent from anaerobic bioreactor and effluent from cyclic ozonation-biotreatment were considerably different.

Ozonated wastewater provided necessary substances for bio-treatment in both aerobic and anaerobic stages. For providing the essential substances for final biological treatment, sufficient solution which was ozonated wastewater was produced in some groups. Because of that which was high number of groups and the number of adding ozone, calculation of final value and real value of added ozone to the solution was very difficult, but it was done successfully [2].

2. Materials and Method

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.

To begin the treatment process, first the wastewater entered the BFB system with a water vapor which had been formed by biological dissolvable substances, then it entered a gas reservoir tank which included ozone gas, and extra air [3]. Ozone had been dissolved by UV. The environment's PH was kept about 7 in the whole reaction time. The concentration of ozone in the BFB system cycle was measured and controlled by an electrode called Amperometric electrode. Such a kind of system had been modeled from anaerobic reactors which were used in the 1990's. The treatment process began by removing salts and other harmful combinations, and increasing the concentration of dissolvable substances, and it continued by extracting 200ml of Di-ethyl from the acidified sample. The standard temperature began in 70^oC for 2 minutes, and reached to 240^oC, and the final temperature of 240^oC continued for 3 minutes. The concentration of the liquid phase was also measured. The brown color of wastewater which was removed during ozonation was because of a medium existence [4]. Moreover the mentioned electrode was used for measurement that made the ozone value to be limited to about 20 mg/l.

For the ozonation process, ozone was produced in an ozone generator. Feed gas could be either air or pure oxygen. A high voltage was applied to two electrodes and the high voltage caused the O₂ to be converted into O₃. Ozone is very unstable and reverts back into O₂ in minutes. That is the reason ozone must be generated on-site and cannot be shipped to the treatment plant [5]. So it was produced on site according to the mentioned method. The ozonated air was blown in to the reactor that here the magnetic mixer plate provided effective mixing conditions for the complete solubilization of gas in the liquid phase. At the end of ozonation phase the remaining ozone in the liquid phase was cleaned by about 5 hour air blowing [6]. Separator parts of ozonation system were like a reversible cycle. The whole reactor system was filled with 250 to 500 ml reactor's liquid. Gas flow among the columns of the system was 140 ml min⁻¹, and the rotation stream velocity of the liquid in the system was 50 to 80 ml min⁻¹. Pure oxygen was flowing through an ozone generator and the concentration value of the flowing ozone in the system was regulated by an electrical connection, and it was being controlled. The mentioned liquid was flowing through an absorber column sequentially with a specific velocity, and enters the liquid reservoir container which had 1 liter volume. The absorber column has a height of 0.4 m and a diameter of 4×4 mm. Also the apparatus's PH is calculated and regulated by a regulator. Furthermore there was an ozone demolisher in the final part of the reactor's system.

A cylinder reactor with a rising flow at the fixed temperature of 20^oC with an external ring for the wastewater flow with the help of a pump was also used. The flow caused micro-organisms and the under layer became mixed in the reactor's depth and increased the ability of the process for overcoming the over load in comparison with the continuous flow during bio-filtration. During filling, the slope of concentration increased along the reactor that this slope became fixed when the flow continued again, and the contents were mixed. Because of the high flow (100 l/h), and the linear velocity, the increase of concentration's slope was limited to the filling time and the beginning of the reactor's phase. At the beginning of each cycle the certain primary volume of wastewater was pumped in to the system, and then it flew along the whole reactor and finally left. For removing the excess biological mass the bottom of the reactor had to be repeatedly cleaned by an air compressor and cleaners [7]. Parameters such as insoluble DO (dissolved Oxygen), temperature, and PH were successively regulated.

3. TOC Calculations and COD Measurement

3.1. TOC Removal

Total organic carbon (TOC) is a non-specific test, which means TOC will not determine which particular compounds are present (most samples are complex mixtures which contain thousands of different organic carbon compounds). Instead, TOC will inform the user of the sum of all organic carbon within those compounds. The reasons for measuring TOC vary across industries, but generally and also in this experiment fall into two categories: process control, or regulatory compulsion.

3.1.1. TOC Detection Methods

Several methods exist for measuring TOC, however each method has two common objectives:

- 1) Oxidize organic carbon to carbon dioxide, and 2) measure the carbon dioxide generated.

Common oxidation methods include chemical agents (such as persulfate), combustion (usually aided by a catalyst), exposure to ionizing radiation (such as ultra violet light), exposure to heat, or some combination of these methods. There are fewer options for detecting carbon dioxide, two common methods are conductivity (in this experiment) and non-dispersive infra-red (NDIR). Conductivity based detection methods work by sensing an increase in ion concentration which is attributed to the increased presence of bicarbonate and carbonate ions created from the oxidation of organic compounds. Non-dispersive Infra-red detectors measure carbon dioxide by determining the amount of infra-red light absorbed across a known distance [8].

3.1.2. Preventing Damage to the Instrument

Two common pitfalls that can damage TOC measurement instruments or produce erroneous measurement results include sample overload (running a sample which far exceeds the maximum analyte specification), and carryover (contamination from a previous sample). Overload conditions are common when running unknown samples. Depending on the measurement technology used this condition can cause costly damage to an instrument. For example, a combustion-type instrument which uses platinum catalysts can very easily ruin the catalysts and require expensive replacements. Membrane-based TOC measurement instruments can also coat the surface of the membrane with organic carbon compounds from a high-concentration unknown sample. Such an event will leave the instrument out of operation while awaiting service. And what was done was to prevent such an event in our case. Carryover results from residual sample left from a previous measurement. It is most often observed when multiple replicates of a sample are measured, and a high concentration sample is followed by a low concentration sample. And hopefully it was not observed. The following equation calculates carryover as a percentage of the difference between the two sample concentrations:

3.1.3. Methods of Calculating TOC

Inorganic carbon is bound only to oxygen, as in carbon dioxide, bicarbonate, or carbonate (for example: limestone is calcium carbonate which is a form of inorganic carbon). Organic carbon can be bound to a variety of other elements such as hydrogen, nitrogen, or other carbon atoms. Other forms of carbon include purgeable versus non-purgeable carbon. Volatile organic compounds have a low boiling point, and can be purged from a solution by bubbling gas through a sample [9]. The following abbreviations are commonly used to describe various forms of carbon when measuring TOC:

TC: Total Carbon

TOC: Total Organic Carbon

TIC: Total Inorganic Carbon

POC: Purgeable Organic Carbon (also called VOC or Volatile Organic Carbon)

NPOC: Non-purgeable Organic Carbon

Calculating TOC can be done by subtracting the TIC from the TC. This method is described by the equation:

$$TC - TIC = TOC$$

This method works well when there is a large difference between TC and TIC (our case); however when TIC values are high the difference method can produce very erratic results because the margin of error for both the TC measurement and the TIC measurement must be added together [10]. In many TOC measurement applications it is reasonable to assume that the contribution of POC to the overall TOC value is negligible, and therefore the following approximation is used : $NPOC \approx TOC$

3.1. COD Removal

COD is a measurement of the oxygen required to oxidize soluble and particulate organic matter in water. Chemical Oxygen Demand is an important water quality parameter because, similar to BOD, it provides an index to assess the effect discharged wastewater will have on the receiving environment. Higher COD levels mean a greater amount of oxidizable organic material in the sample, which will reduce dissolved oxygen (DO) levels. A reduction in DO can lead to anaerobic conditions, which is deleterious to higher aquatic life forms. The COD test is often used as an alternate to BOD due to shorter length of testing time. It is necessary to mention where the COD is measured:

- Influent wastewater streams for process control
- Effluent wastewater streams to sewer or environment for regulatory compliance

3.1.1. Methods of COD Measurement

The used method for Chemical Oxygen Demand analysis was Method 410.4. The method involved using a strong oxidizing chemical, potassium dichromate $Cr_2O_7^{2-}$, to oxidize the organic matter in solution to carbon dioxide and water under acidic conditions. Often, the test also involved a silver compound to encourage oxidation of certain organic compounds and mercury to reduce the interference from oxidation of chloride ions [11]. The sample was then digested for approximately 2 hours at 150°C. The amount of oxygen required was calculated from the quantity of chemical oxidant consumed.

4. Results and Discussion

As it can be seen in table 1, COD and TOC were calculated in the original wastewater (A), in the effluent from anaerobic bioreactor (G), and in the effluent from cycle ozonation-biotreatment (H). This was done in 4 different samples in order to minimize the error percentage and reach to a reliable efficiency. The achieved data can be reached in two different following graphs for the measured and calculated COD and TOC in Fig.1. and Fig.2.

Table 1. Measured variables during ozonation and biological treatment

Measured Variables	Samples` Origins	Sample1	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

What is very magnificent on the first glance at the both graphs is the reducing trend of COD and TOC, and specifically a remarkable reduction which is so vivid in all the four samples.

In COD measurement, the 504 in the original wastewater in the first sample became 446 in the effluent from anaerobic bioreactor while this amount changed to 348 in the effluent from cycle ozonation-biotreatment. This trend was almost similar in the other three samples that showed a 182 difference between the COD in effluent from anaerobic bioreactor and effluent from cycle ozonation-biotreatment in the second sample, 912 to 421 which was 491 reduction in the third sample as well as a 413 difference in the fourth sample where a reduction of 177 from the original wastewater to the effluent from anaerobic bioreactor changed to a 590 reduction in the effluent from cycle ozonation-biotreatment.

This efficient outcome was more or less similar in TOC calculation where the TOC in samples 1 to 4 from 212, 229, 388 and 370 in original wastewater changed to 192, 192, 298 and 287 in the effluent from anaerobic bioreactor respectively and then to 185, 139, 198 and 153 in the effluent from cycle ozonation-biotreatment. The data showed 7, 53, 100 and 134 more effective reduction in the comparison of the two effluents.

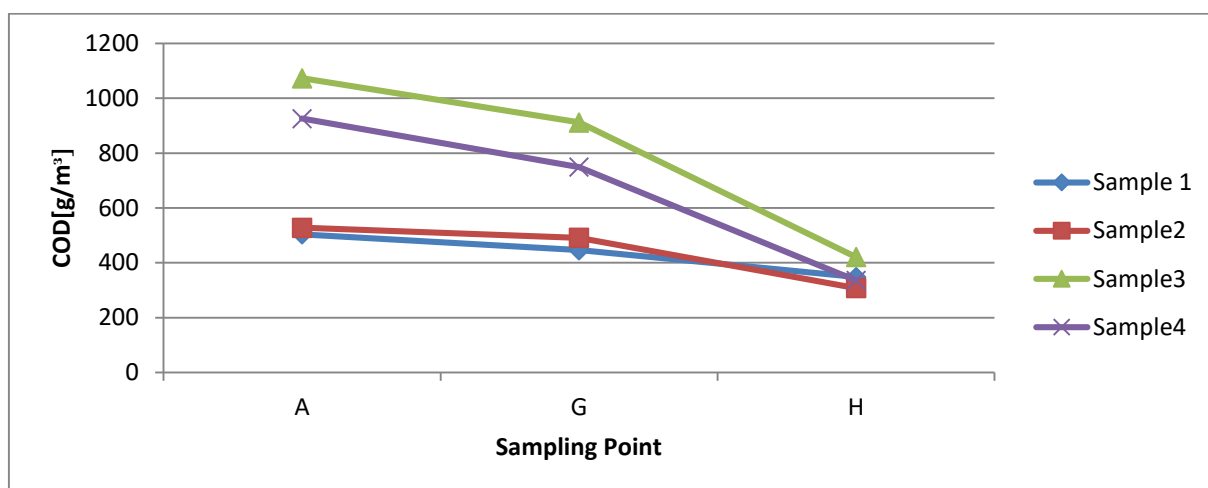


Fig.1. COD concentration in cyclic ozonation-biotreatment system.

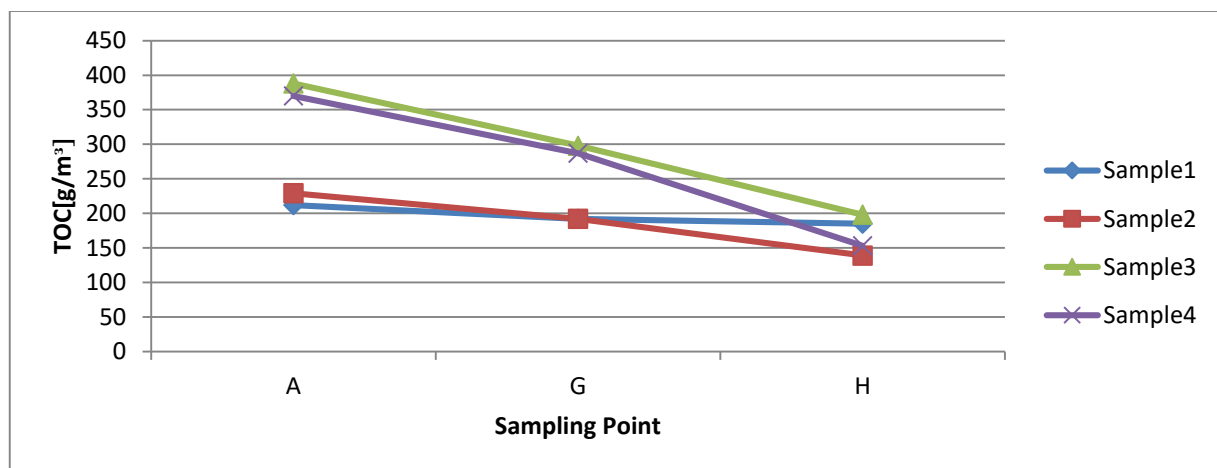


Fig.2. TOC concentration in cyclic ozonation-biotreatment system.

5. Conclusion

Two of the most important factors in this method were ozone dosage, and time. Since economical aspects are considered very important in wastewater treatment systems, and producing ozone because of its electrical costs seemed to be important, its low dosage and the limited time of ozonation that was spent in the treatment process proved the considerable efficiency of this method of treatment. Furthermore, in this reactor liquids were passed sequentially and according to bio-ozone-bio-treatment method, and it showed that when ozone was consumed very fast, no ozone could enter the reactor actually. Experiments showed that the ozone value never reached the ozone value in the new comer

wastewater to the system when wastewater of system was consumed again. It means that if new wastewater is entered, the ozone value is more than the previous one in the system.

Acknowledgements

I have to thank Professor Gevorg P. Pirumyan (Head of chair of Ecological Chemistry Department at Yerevan State University in Armenia) as well as Dr. Luiza Cintra Campos (Director of Environmental Engineering program in the Department of Civil, Environmental & Geomatic Engineering at University College London) for their great ideas, help and support.

References

- [1] Environmental Protection Organization. Environmental Standards. Air Pollutant investigation Office, Iran, 1987.
- [2] M. Sadegi, Investigation of ozone on biological decomposition of MTBE in buoyant systems, Tarbiat Modares University. Iran. 2004.
- [3] Advanced, New biofiltration of wastewater treatment with ozone, Advanced research company, Tehran. 2004.
- [4] A. Bowers, P. Gaddipatic , W, Eckenfelder and R, Monsen, 1989, Treatment of toxic or refractory wastewater with hydrogen peroxide, Wat, Sci, Technol.,21,47-486.
- [5] R, Parag, B, Aniruddha, 2003, A review of imperative technologies for wastewater treatment II: hybrid methods, Advances in Environ.Res.
- [6] A. Bowers, P. Gaddipatic , W, Eckenfelder and R, Monsen, 1989, Treatment of toxic or refractory wastewater with hydrogen peroxide, Wat, Sci, Technol.,21,47-486.
- [7] Bruno L., David AR., David RB., Ozone in waste treatment, application, and engineering, The United States of America, 1991, 90-117.
- [8] Metcalf and Eddy, Wastewater Engineering, Treatment and Reuse, fourth edition, 12, 1281-1390, (2004)
- [9]https://www.envirotechonline.com/articles/waterwastewater/9/mira_kovacheva/the_importance_of_measuring_total_organic_carbon/1907/#sthash.KO8qtBPf.dpuf
- [10]https://www.envirotechonline.com/articles/waterwastewater/9/mira_kovacheva/the_importance_of_measuring_total_organic_carbon/1907/#sthash.KO8qtBPf.dpuf
- [11] <http://realtechwater.com/chemical-oxygen-demand/>