International Research Journal of Advanced Engineering and Science
ISSN (Online): 2455-9024

Assessment of Total Organic Carbon (Soluble and Suspended) Removal in a Bio-Ozone-Treatment of an Industrial Wastewater with and without Sediments

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Abstract— *In this research, removal of soluble and suspended Total Organic Carbon (TOC) with and without sediment in treatment of an industrial wastewater system before and after ozonation was studied and compared. 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 and the most important purpose of this research was ozone usage in wastewater treatment system to remove such combinations as well as the total organic carbon. Since ozone is a highly oxidant agent, the pilots were made of materials resistant to ozone and the important parameters which should be considered well are ozonation time, and ozonation dose. After the treatment, the measured soluble and suspended TOC in the cyclic ozonation-biotreatment system compared to the soluble and suspended TOC in the treatment method without ozonation. Sedimentation was the other factor which was considered in this experiment and TOC was measured with and without sediments. The comparison revealed that the outstanding efficiency of the cyclic ozonation-biotreatment system in removing both soluble andd suspended TOC with and without sediments is extremely considerable.*

Keywords— *Ozonation, Sediment, TOC, Wastewater Treatment*

I. INTRODUCTION

The Total Organic Carbon is one of the most important composit parameters in the assessment of the organic pollution of water. Since it includes all carbon compounds as one mass, it is exactly defined as an absolute quantity [1], [2]. Therefore, it may be determined directly. In relation to the TOC also parameters like the organic and inorganic carbon in water including the elemental carbon (TC), the carbon contained in water; elemental carbon, total carbon dioxide (TIC), Volatile Organic Carbon (VOC), and Purgeable Organic Carbon (POC), are mentioned. The total organic carbon (TOC) is a measurement method for the content of carbon of dissolved and undissolved organic substances in water.

In general, the TOC is determined by oxidizing a water sample [3], [4]. The produced CO_2 is detected quantitatively. However, not all methods succeed in the complete oxidation of a sample. Often enough this may result only in SOC (Some Organic Carbon) instead of the TOC.

Decreasing or removing the value of suspended and soluble solids seems to be more complicated and difficult by using the simple biological methods of treatment [5]. The Ozonated wastewater provides necessary substances for bio-treatment in both aerobic and anaerobic stages [6], [7]. And as a result, a very significant improvement in removing solved and suspended solids could be achieved. To provide the essential substances for final biological treatment, sufficient solution -ozonated wastewater- was produced in some groups. Because of high number of groups and the number of adding ozone, calculation of final value and real value of added ozone to the solution was also very difficult ,but done successfully [8-10].

In cyclic ozonation-biotreatment reactors liquids are passed sequentially and according to bio-ozone-bio-treatment method, and it showed when ozone is consumed very quickly, no ozone can enter the reactor[11], [12].

II. MEASUREMENT APPROACH

For performing such a system, first studying and experimenting on different oxidation methods were considered.

A. Thermal Oxidation

With this oxidation method the sample was combusted in a reactor and a maximum temperature of about 1,000°C was reached, which however did not allow the complete oxidation of all carbon compounds. Therefore, a catalyst-platinum- was used at this temperatures. Normally, the catalytic combustion method could handle a TOC concentration of up to 4,000 mg/l (To reach higher ranges the sample usually needs to be diluted with demin water).

A unique and patented high temperature (HT) method at 1,200°C enabled the complete oxidation of all carbon compounds without any catalysts. It measured TOC concentrations up to 50,000 mg/l without dilution. In a special heat resistant ceramic reactor the water sample was evaporated and all carbons were completely oxidized to CO_2 gas. Afterwards, the CO_2 concentration was analyzed with a Non-Dispersive Infrared (NDIR) detector. Thus, the TC, TOC and TIC could be determined within only 3 minutes.

This ultrahigh temperature method also was used for both, the most challenging and highly contaminated waters and waters relatively free of solid maters. The analyzers used the batch injection method with the advantage that the analyzers can easily handle sticky, oily and hard to oxidize dissolved and suspended organics resulting in a fast, reliable and accurate analysis. Even with rapidly fluctuating TOC levels the correct TOC concentration could be measured, whereby

Amir Hajiali, "Assessment of Total Organic Carbon (Soluble and Suspended) Removal in a Bio-Ozone-Treatment of an Industrial Wastewater with and without Sediments," *International Research Journal of Advanced Engineering and Science*, Volume 3, Issue 1, pp. 220-223, 2018.

International Research Journal of Advanced Engineering and Science
ISSN (Online): 2455-9024

peaks throughout the course of the day were determined without any memory or adsorption effects [13].

B. Photochemical Oxidation (UV-Persulphate Method)

Here the TOC was oxidized by means of UV light and a digesting reagent, sodium persulphate, and the produced CO_2 was measured with a NDIR detector. This method suits the determination of TOC in clean water (drinking water, condensate, boiler feed water), since particles are hard to oxidize completely. The Thermal Oxidation method combined this technique with the direct TOC method or Non-Purgable Organic Carbon (NPOC) method, whereby the continuously provided water samples could be treated in a multi stage process [14].

C. Wet Chemical Oxidation

With this method the water sample was oxidized by means of strong chemicals as oxidants such as ozone. The ozone oxidation acids and bases were used to adjust the pH value of the sample along the pH scale. However, the oxidation potential of such methods was relative, since particles and more complex carbon compounds could only be partially digested or not at all. With regards to the latest standards of occupational safety and environmental protection a combination of this method with the previous ones is recommended according to the achieved results [15], [16].

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.

Results of the experiments showed that ozone could be effective for solving most organic materials in activated sludge or for making them mineral. Furthermore bio dissolubility increase related to the solved materials was reported. In fact ozone usage for sludge caused a remarkable increase in existing of bio situation related to organic materials which is being bio analyzed smoothly [17], [18]. Both solubility effects and facility increase for maintenance caused increasing of an organic material to be mineral in biological treatment, and it could explain the effect of an ozonation treatment on reduction of sludge production too[19], [20].

III. Materilas and Method

After the experiments and measurement approaches accomplished, ozonation-an advanced oxidation technology-which is a kind of wet chemical oxidation was used for the soluble and suspended Total Organic Carbon removal. Advanced Oxidation Technologies are efficient choices in underground water treatment and wastewaters particularly the ones containing recalcitrant materials. Such processes are based on the formation of highly reactive OH radicals with a standard electrode potential of 1.5V which is twice that of chlorine (with a standard electrode potential of 0.75). These processes react with most organic compounds with constants of $K \approx 10^6$-10^9 $m^{-1}s^{-1}$ and start a large collection of reaction which ultimately leads in organization of organic pollutants.

First the wastewater entered the BFB (bio-fluidized bed) system with a water vapor which had been formed by biological dissolvable substances; in the next step it entered a gas reservoir tank which included ozone gas, and extra air [21], [22]. The environment`s PH was kept 6.1 to 8.8 in the reaction time. The concentration of ozone in the BFB system cycle was measured and controlled by an electrode called Amprometric electrode. Such a kind of system was modelled from anaerobic reactors which were used in the 1990`s [23], [24].

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 [25]. The standard temperature began in 85^0C for 2.5 minutes, and reached to 250^0C -255^0C, and the final temperature of 255^0C continued for 3 minutes. The concentration of the liquid phase was also measured. The brown colour of wastewater which was removed during ozonation was because of a medium existence [26-28]. Moreover the mentioned electrode was used for measurement that made the ozone value to be limited to about 20 mg/l.

IV. Results and Discussion

The experimental studies revealed that the total TOC without sediment was 39 mg/lit before the ozonation process while it decreased to 31 mg/lit after ozonation which shows an average 8 mg/lit more removal. This trend of reduction could be recorded when there were maximum sediments with maximum velocity of 2.18, 1.09 and 0.73 cm/min with the total TOC removal of 8, 12, and 13 mg/lit respectively (Table I).

The same removal efficiency was witnessed with soluble TOC with maximum sediment velocity of 2.18, 1.09 and 0.73 cm/min that revealed a removal efficiency of 2.8 %, 22.2% and 28 % respectively while the removing percentage without sediment was 0 after ozonation in comparison with its content before the ozonation (28 mg/lit to 28 mg/lit) (Table II).

In suspended TOC the increasing trend of removal was the result in all cases, in suspended TOC without sediment there was an 8 mg/lit removal (72.7 %) and with maximum sediment velocities of 2.18, 1.09 and 0.73 cm/min the removals efficiencies were 87.5, 46.1, and 85.7 mg/lit respectively (Table III).

TABLE I. Total TOC removal of wastewater before and after ozonation with and without sediment.

Wastewater`s TOC/ Maximum Sediment Velocity (cm/min)	Average TOC contents Before Ozonation (mg/lit)	Average TOC contents after Ozonation (mg/lit)	Removed TOC (mg/lit)	Removing Percentage (%)
Total TOC without Sediment	39	31	8	20.5
Maximum Sediment Velocity of 2.18	43	35	8	18.6
Maximum Sediment Velocity of 1.09	40	28	12	30
Maximum Sediment Velocity of 0.73	32	19	13	40.6

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International Research Journal of Advanced Engineering and Science
ISSN (Online): 2455-9024

TABLE II. Average soluble TOC removal of wastewater before and after ozonation with and without sediment.

Wastewater`s TOC/ Maximum Sediment Velocity (cm/min)	Average TOC contents Before Ozonation (mg/lit)	Average TOC contents after Ozonation (mg/lit)	Removed TOC (mg/lit)	Removing Percentage (%)
Soluble TOC without sediment	28	28	0	0
Maximum Sediment Velocity of 2.18	35	34	1	2.8
Maximum Sediment Velocity of 1.09	27	21	6	22.2
Maximum Sediment Velocity of 0.73	25	18	7	28

TABLE III. Average suspended TOC removal of wastewater before and after ozonation with and without sediment.

Wastewater`s TOC/ Maximum Sediment Velocity (cm/min)	Average TOC contents Before Ozonation (mg/lit)	Average TOC contents after Ozonation (mg/lit)	Removed BOD (mg/lit)	Removing Percentage (%)
Suspended TOC without Sediment	11	3	8	72.7
Maximum Sediment Velocity of 2.18	8	1	7	87.5
Maximum Sediment Velocity of 1.09	13	7	6	46.1
Maximum Sediment Velocity of 0.73	7	1	6	85.7

Also they revealed that the organic suspended solids are effectively oxidated to CO_2 or broken to gelatin sizes that are passed through a filter which is used for getting the samples of soluble TOC. Fig. 1 shows the average wastewater`s TOC removing before and after ozonation in all cases.

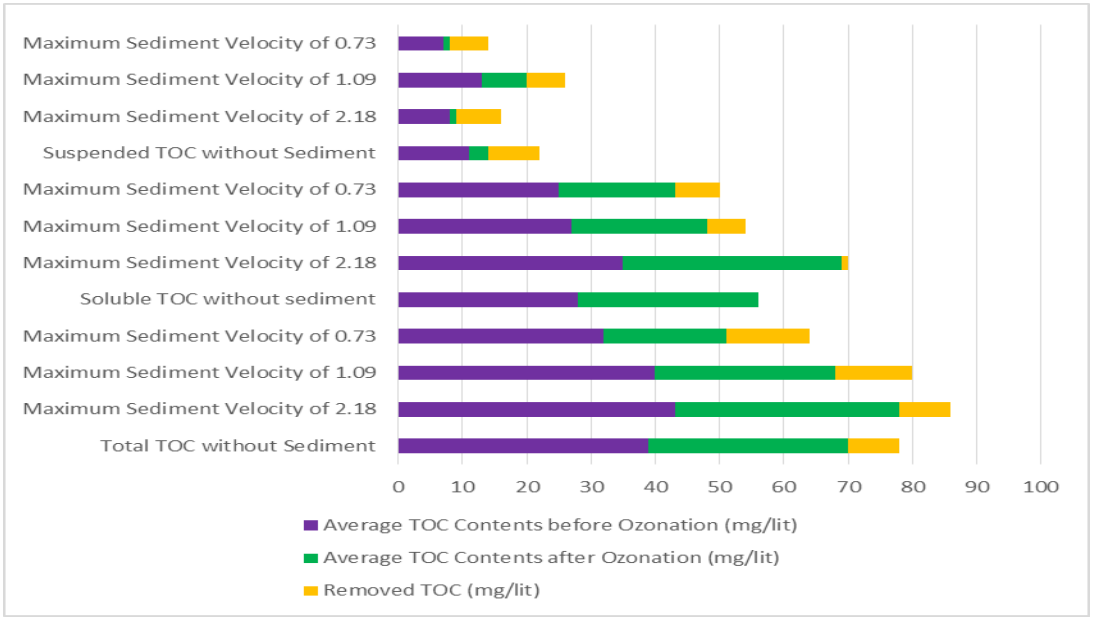

Fig. 1. Average wastewater`s TOC removing before and after ozonation.

V. Conclusion

The increase of priority pollutants through wastewaters has caused in affiliation towards oxidative decomposition processes for removing pollutants. Among some physical, chemical and biological processes for wastewater treatment, each has got functionality, effectiveness and expense limits. For instance physical processes such as combination, adsorption or volatility into air, and pollutants are transferred from the liquid phase to the second phase but they are not destructed. Since final removing of biological solid materials which contain hazardous pollutants is one of the most important problems in pulp factories wastewater treatment which has a lot of costs, ozonation process as an advanced oxidation technology was used for treating that and the experimental evaluations were carried out to determine the efficiency of such a system in removing TOC that the great removal efficiency proved its functionality.

Acknowledgment

It is my pleasure to thank Professor Gevorg P. Pirumyan (Head of chair of Ecological Chemistry Department at Yerevan State University in Armenia) and Dr. Luiza Cintra Campos (Director of Environmental Engineering program in the Department of Civil, Environmental & Geomatic Engineering at University College London) as well as Professor Mohammad Mehdi Maneshi (Professor at New York City College) for their great ideas, help and support.

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