IJSES

International Journal of Scientific Engineering and Science
Volume 2, Issue 2, pp. 15-18, 2018. ISSN (Online): 2456-7361

Ozone Usage in Wastewater Treatment of a Paper Industry for Removing Soluble and Suspended Chemical Oxygen Demand

Amir Hajiali
Postdoctoral Fellow at Yerevan State University (Department of Ecological Chemistry), Lecturer at Islamic Azad University (North Tehran Branch), Tehran, Iran
Email address: a.hajiali.env@gmail.com

Abstract— *In this research, removal of Suspended and Soluble Chemical Oxygen Demand (COD) with and without sediment in treatment of an industrial wastewater system before and after ozonation was studied and compared. A case study of a paper industry wastewater treatment is reported to prove the suitability of ozonation for COD removal. The ozone application as an end treatment is used to provide a perfect oxidation yield of organic matter in a landfill leachate. The combination of ozonation and biological process appears quite effective for the post-treatment of biological effluents from paper industry. Wastewaters of pulp factories which are by-products of cellulose cause a hazardous water vapor that is dangerous because of containing different combinations of chlorophenol. After the treatment, the measured soluble and suspended COD contents in the cyclic ozonation-biotreatment system compared to the ones in the treatment method without ozonation. Sedimentation was also considered in this experiment. The average percent reduction in total COD due to ozone addition was 32.5, 34, 46.3 and 60 in without sediment, and with maximum sediment velocity of 2.18, 1.09 and 0.73 cm/min respectively. The comparison proved the remarkable efficiency of the cyclic ozonation-biotreatment system in removing COD both with and without sediments.*

Keywords— *COD Removal, Ozonation, Sediments, Wastewater Treatment.*

I. INTRODUCTION

In the new century, it is much more necessary to treat industrial wastewaters using environmentally friendly technics. Due to some limitations in different treatment systems, a complete study and comparison in order to achieve the most efficient method in treating wastewaters must be done before any industrial treatment performance [1]. Among primary manufacturing industries, paper manufacturing is the fourth largest user of energy and the largest generator of wastes, measured by weight. Water is the basic medium of pulp and paper manufacturing; it carries fibers through each treatment step and separates spent pulping chemicals and the complete mixture of organic residues from the pulp [2].

The paper industry is one of the biggest users of water and complex chemicals during dyeing and whitening processing at various processing stages. The unused materials from the whitening processes are discharged as wastewater that is high in biochemical oxygen demand (BOD), chemical oxygen demand (COD), temperature, pH, color and turbidity, and toxic chemicals.

The effluent from these industries contains different types of dyes and whiteners, and because of their high molecular weight and complex structures, they are resistant to biodegradation and oxidizing agents [3]. The direct discharge of this wastewater into the water bodies affects the flora and fauna. The treatment methods of such wastewaters include chemical coagulation/flocculation, activated carbon adsorption, oxidation, membrane techniques and electrochemical methods [4], [5].

These discharges are varied and insoluble dyes such as disperse, sulfur, and these dyes cannot be removed by some common methods such as simple biological treatment or carbon adsorption. Also Biochemical Oxygen Demand and Chemical Oxygen Demand are two different ways to measure how much oxygen the water will consume when it enters the recipient.

In both cases the oxygen-consuming substances are mostly of organic origin [6]. These substances should be reduced to a minimum content in the wastewater treatment plant [7]. Industries usually concentrate more on COD and municipalities more on BOD removal [8]. With chemical treatment, removal of COD is improved at all kinds of wastewater plants. The more particle-bound COD, the more efficient the removal rate.

Decreasing or removing the value of suspended and soluble COD seems to be more complicated and difficult by using the simple biological methods of treatment [9]. The Ozonated wastewater provides necessary substances for bio-treatment in both aerobic and anaerobic stages [10], [11]. And as a result, a very significant improvement in removing soluble and suspended COD could be achieved. To provide the essential substances for final biological treatment, sufficient solution -ozonated wastewater- can be produced in some groups [12].

II. MEASUREMENT APPROACH

The process of pulp and paper processing involves production of effluent water streams with high chemical oxygen demand loads [13]. COD is a measure of the oxygen requirement of the organic matter susceptible to oxidation by a strong chemical oxidant. It is used to define the organic strength of industrial wastes and polluted waters [14]. COD wastes usually are not readily biodegradable and often contain compounds that inhibit biological activity [15] in wastewater treatment facilities.

Previous studies have considered applications of ozone to water treatment, but primarily as a disinfectant, where ozone's effectiveness is well documented [1], [15]. Ozone is not only useful in removing COD in this wastewater, but also is used to reduce and control taste and odor problems in surface water treatment systems [16].

III. Materials and Methods

A pilot study was performed on the effluent from a pulp factory to determine to what extent COD reduction could be achieved through addition of high pressure oxygen and ozone. The study included reduction of during oxygen/ozone injection.

To determine the project's success, COD was monitored in the effluent before and after oxygen/ozone injection as well as pH, temperature and dissolved oxygen (DO). Experiments showed that the ozone value never reached the ozone value in the new comer wastewater to the system when wastewater of the system was consumed again. It means that if new wastewater is entered, the ozone value is more than the previous one in the system.

In addition, one of the challenges faced by wastewater treatment facilities is the contact time between injected ozone and wastewater stream that was considerably less than optimal.

Experiments were performed to model the kinetics of the oxygen COD degradation reaction and estimated the overall potential of the process for a longer contact time that would be included in a permanent system.

In this study, for the solved and suspended soluble COD removal horizontal roughing filters were selected as the pretreatment filters. Horizontal roughing filters perform better than other treatment filters [17],[18].

Adaptive Ozone Solutions designed and installed in the ozone system that was used in all pilot studies and experiments. Their patented technology uses electrochemical cells to generate ozone and supplies concentrated oxygen and ozone feed streams to wastewaters via aerosol diffusers.

All tests were performed in triplicate with averages presented. Dissolved ozone concentration was measured with a portable dissolved ozone analyzer. The analyzer had capability to measure dissolved ozone in the low range of 0–200 ppb and also the range of 0–2 ppm, typical of water bottling or municipal water treatment applications.

Wastewater flow through the system was 76 liters/minute. Ozone measurements taken at the first sample port, 1.5 meters from injection, showed no residual ozone. Tests were performed multiple times to verify the zero reading. A final experiment was performed to quantify the effect of increasing the ozone injection rate on effluent COD.

A side stream of the effluent stream was diverted and dosed with increasing quantities of ozone under the same water flow velocity and contact time as tests performed on the total effluent stream.

Ozone was generated and injected with oxygen as aerosol bubbles using an AO_3 system. Initially just oxygen was added, after which both oxygen and ozone were added with the oxygen amount approximately constant at 0.53 grams/min/liter water. At each ozone level, samples were drawn and analyzed for DO and COD.

The average percent reduction in COD due to ozone addition was remarkable, but increasing ozone above a loading rate of water did not improve COD reduction. Addition of both oxygen and ozone did improve COD removal compared to just oxygen addition.

For eight weeks during June through September, an AO_3 installed ozone generator injected 5 grams/minute of ozone, in addition to high pressure oxygen, into the approximately 85 liters/min effluent water stream of a pulp factory.

The ozone loading rate was 0.050 grams/min/liter water and that for oxygen was 0.5 grams/min/liter water. During this time, Bioxide addition was reduced incrementally from its peak application rate of 1450 liters per day to 1225 liters per day, 890 liters per day.

COD, Dissolved oxygen, temperature and pH were measured both at a sample point upstream of the injection point and one downstream of the injection point, but prior to entering the sewage lines.

Process limitations required that the post ozone injection sampling point be located within the plant, such that the contact time of the oxygen/ozone stream in the system prior to the second sample point was limited to approximately under two minutes [19]. Because of the limitations associated with the existing piping system at the site, the previous COD and DO measurements were taken after a contact time of only approximately two minutes.

Given the achieved reduction in COD for such a short reaction time, experiments were performed to estimate the kinetics of the reaction of oxygen with COD waste and, hence, estimate the effectiveness of oxygen and ozone to continue to reduce COD in the effluent.

Dissolved oxygen was measured as a function of time in post injection samples to estimate how rapidly oxygen is consumed by COD waste. 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.

IV. Results and Discussion

The experimental studies revealed that the total COD without sediment was 126 mg/lit before the ozonation process while it decreased to 85 mg/lit after ozonation which shows an average 41 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 COD removal of 48, 56, and 64 mg/lit respectively (Table I).

The same removal efficiency was witnessed with soluble COD with maximum sediment velocity of 2.18, 1.09 and 0.73 cm/min that revealed a removal efficiency of 17%, 33.3% and 55% respectively while the removing percentage without sediment was 8.6% after ozonation in comparison with its content before the ozonation (81 mg/lit to 74 mg/lit) (Table II).

In suspended COD the increasing trend of removal was the result in all cases, in suspended COD without sediment there was a 34 mg/lit removal (75.5 %) and with maximum sediment velocities of 2.18, 1.09 and 0.73 cm/min the removals efficiencies were 67, 82.3, and 80 mg/lit respectively (Table III).

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

Wastewater`s COD/ Maximum Sediment Velocity (Cm/Min)	Average COD Contents Before Ozonation (Mg/Lit)	Average COD Contents After Ozonation (Mg/Lit)	Removed COD (Mg/Lit)	Removing Percentage (%)
Total COD without Sediment	126	85	41	32.5
Maximum Sediment Velocity of 2.18	143	95	48	34
Maximum Sediment Velocity of 1.09	12	64	56	46.3
Maximum Sediment Velocity of 0.73	107	43	64	60

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

Wastewater`s COD/ Maximum Sediment Velocity (Cm/Min)	Average COD Contents Before Ozonation (Mg/Lit)	Average COD Contents After Ozonation (Mg/Lit)	Removed COD (Mg/Lit)	Removing Percentage (%)
Soluble COD without sediment	81	74	7	8.6
Maximum Sediment Velocity of 2.18	95	79	16	17
Maximum Sediment Velocity of 1.09	87	58	29	33.3
Maximum Sediment Velocity of 0.73	87	39	48	55

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

Wastewater`s COD/ Maximum Sediment Velocity (Cm/Min)	Average COD Contents Before Ozonation (Mg/Lit)	Average COD Contents After Ozonation (Mg/Lit)	Removed COD (Mg/Lit)	Removing Percentage (%)
Suspended COD without Sediment	45	11	34	75.5
Maximum Sediment Velocity of 2.18	48	16	32	67
Maximum Sediment Velocity of 1.09	34	6	28	82.3
Maximum Sediment Velocity of 0.73	20	4	16	80

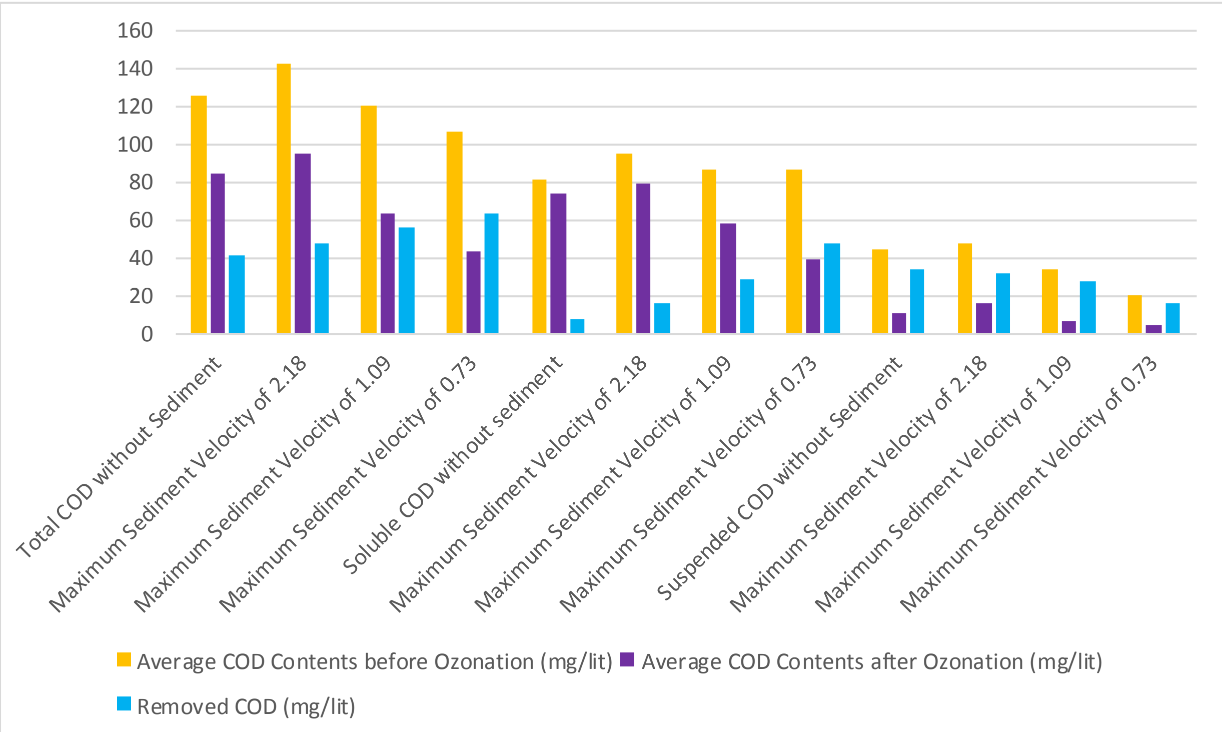

Fig. 1. Average wastewater`s COD removing before and after ozonation.

Average COD content before and after ozonation as well as the removal contents can be seen in Fig.1. It shows that the less the maximum sediment velocity was, the more total COD removal and Soluble COD removal contents were. Also the more the maximum sediment velocity was, the more the Suspended COD removal content was.

V. CONCLUSION

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

ACKNOWLEDGMENT

It is my pleasure 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) and Professor Mohammad Mehdi Maneshi (Professor at New York City College) for their great ideas, help and support.

REFERENCES

[1] C. Ishida, A. Salveson, K. Robinson, R. Bowman, and S. Snyder, "Ozone disinfection with the HiPOX reactor: streamlining an old technology for wastewater reuse," Carollo Engineers, Applied Process Technology and Southern Nevada Water Authority, 2007.

[2] Paper Task Force: Duke University, Environmental Defense Fund, Johnson and Johnson, McDonalds, Prudential Insurance Company of America, Time Inc., Pulp and Paper Manufacturing, pp. 170–176, December 1995.

[3] Prat C., Vicente M., Esplugas S., "Ozonization of bleaching waters of the paper industry," *Water Res.*, 23, pp. 51-55, 1989.

[4] Hewes, "Renovation of secondary wastewater effluents by ozonation of dissolved organic compounds", Ph.D. Dissertation, Texas A. M. Uni., December 1971.

[5] Di Iaconi, A. Lopez, R. Ramadori, G. Ricco, M.C. Tomei, Ozonation of "secondary effluents of tannery industry: kinetics and effect on biodegradability and toxicity," in *Proc. The International Conference on Wastewater Treatment, Standards and Technologies to Meet the Challenges of the 21st Century*, No. 2, Leeds, UK, pp. 625-639, April 2000.

[6] Amir Hajiali,"Total and suspended solids removal evaluation in effluent from anaerobic bioreactor and effluent from cyclic ozonation biotreatment in dyeing industry wastewater treatment,'' *Proceedings of the International Conference on Energy and Environment (CIEM) - IEEE*, p.115-119, 2017.

[7] H. Baldees, J. Becker, "Ozone treatment of textile and dye-house wastes, in ozone in water and wastewater treatment," *11th Ozone World Congress, San Francisco, CA. (Stamford, CT: Ozone Assoc., Pan American Group)*, vol. 2, pp. S-10-76 to S-10-83, 1993.

[8] Amir Hajiali, Pirumyan G., "Evaluation of soluble BOD and suspended particles BOD removal without and with sediment in different velocities before and after ozonation in an industrial wastewater treatment," *International Research Journal of Advanced Engineering and Science*, vol. 3, issue 1, pp. 7-10, 2017.

[9] Amir Hajiali, "Evaluation of NH4+and PO43 - Removal in treatment of an industrial wastewater containing chlorophenolic contaminants with ozonation", *Journal of Applicable Chemistry,* vol. 6, issue 5, pp. 934-940, 2017.

[10] T. George, L. Frakin, S. David, *Waste water engineering: treatment and reuse*, fourth Edition, Metcalf 8 Eddy, McGraw Hill, pp. 1288-1295, 2003.

[11] Amir Hajiali, Pirumyan G., Sharif Vaghefi H.R., Shahmiri M., "Treatment of pulp factories wastewater containing chorophenolic compounds with ozonation," *Asian Journal of Chemistry*, India, vol. 24, no. 12, pp. 5609-5612, 2012.

[12] H.Beffadhel, A. Ratel, "Removal of color and organic matters in industrial phosphoric acid by ozone: Effect on activated carbon treatment ozone," *Science Engineering*, vol. 17, issue 6, pp. 637-645, 1995.

[13] A. Hajiali, *Principles of Wastewater Treatment*, Yerevan, Armenia, pp. 143-150, 2012.

[14] E. E. Richardson, A. Hanson, and J. Hernandez, "Ozonation of continuous-flow activated sludge for reduction of waste solids," *Ozone Science and Engineering*, vol. 31, no. 3, pp. 247–256, 2009.

[15] W. Viessman, J. Hammer, E. Perez, and Chadik P., *Water Supply and Pollution Control, Pearson Publishing*, 8th edition, 2009.

[16] D. E. Phares, D. M. Rokjer, I. A. Crossley, and J. J. Franko, "Modeling and validating the effective hydraulic detention time for a 10 mgd ozone contactor at the lake Washington surface water treatment plant, Melbourne, Florida," *Ozone Science and Engineering*, vol. 31, no. 3, pp. 262–276, 2009.*:*

[17] N. Takahashi and T. Kumagai, "Application of ozonation to dyeing wastewater treatment—Case study in Nishiwaki treatment plant," *Ozone Science and Engineering*, vol. 30, no. 6, pp. 439–446, 2008.

[18] R. G. Rice, M. DeBrum, D. Cardis, and C. Tapp, "The ozone laundry handbook: a comprehensive guide for the proper application of ozone in the commercial laundry industry," *Ozone Science and Engineering*, vol. 31, no. 5, pp. 339–347, 2009.

[19] http://www.wef.org.