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Evaluation of NH_4^+ and PO_4^{3-} Removal in Treatment of an Industrial Wastewater Containing Chlorophenolic Contaminants with Ozonation

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ABSTRACT

In this research, treatment of an industrial wastewater was experimented in order to remove the value of NH_4^+ and PO_4^{3-} in two different methods. Such wastewaters contain specific poisonous chlorinated phenolic combinations, which in biological reactors in a liquid phase could be absorbed much easier and with a higher velocity. After the treatment, the concentrations of NH_4^+ and PO_4^{3-} 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 was dramatically different and proved the remarkable efficiency of the cyclic ozonation-biotreatment system. By bio-ozone-bio treatment the value of consumed ozone was considerably increased, but through this way the quality of treatment and the value of dissolvable substances and returnable to the environment were increased. In cyclic ozonation-biotreatment reactor 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 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.

Keywords: Chlorophenolic Contaminants, NH_4^+, Ozonation, PO_4^{3-}, Wastewater Treatment.

INTRODUCTION

In this research where 13 steps of measurement were done in order to achieve the expected result, all parameters which were measured proved the usefulness of the ozonation method for treating this industrial wastewater from resistant and poisonous pollutants that cause suitability of the wastewater after treatment to be used for different purposes such as in effluent depletion to surface water, effluent depletion to leaching pit and for agricultural or irrigational consumption. NH_4^+ and PO_4^{3-} are the most remarkable contaminants which were studied in this research and their removals were recorded after adding ozone from the fifth step. Because of high molecular weight of these poisonous combinations it was necessary to perform in a way that in a sequential process these combinations could be changed to smaller and dissolvable substances in the environment [1, 2]. For availability to a rate of impurity which is necessary for the ozone generator, the air which was used as the source of oxygen was treated and processed before

anything else in order to be cleaned out of any fat, moisture, hydro carbons, and dust. Ozonized air was blown in to the reactor where the magnetic mixer plate provided effective mixing conditions for the complete solubilisation of gas in the liquid phase [3]. At the end of ozonation phase the remaining ozone in the liquid phase was cleaned by about 5 h air blowing.

MATERIALS AND METHODS

In this study two main methods of bio-ozone-bio treatment and professional biological treatment were done continuously as one of the main purposes of this research was a comparison of artificial ozonation and biological natural ozonation for treating wastewater [4]. In continuous treatment at first wastewater producer source was considered biologically [5]. The time that the system needed to reach to a spesific fixed limit was about 90 h which was 3 times more than the total time or 4.5 times more than the total time in aerobic systems. The most error percent in the final stage was less than 0.5 %, and this value even became less in aerobic reactors.

The ozonation process in the wastewater treatment was done according to the following system. There are three components to the ozonation system: the ozone generator, the ozone contactor, an ozone destruction device. A schematic of this process is shown below in figure 1.

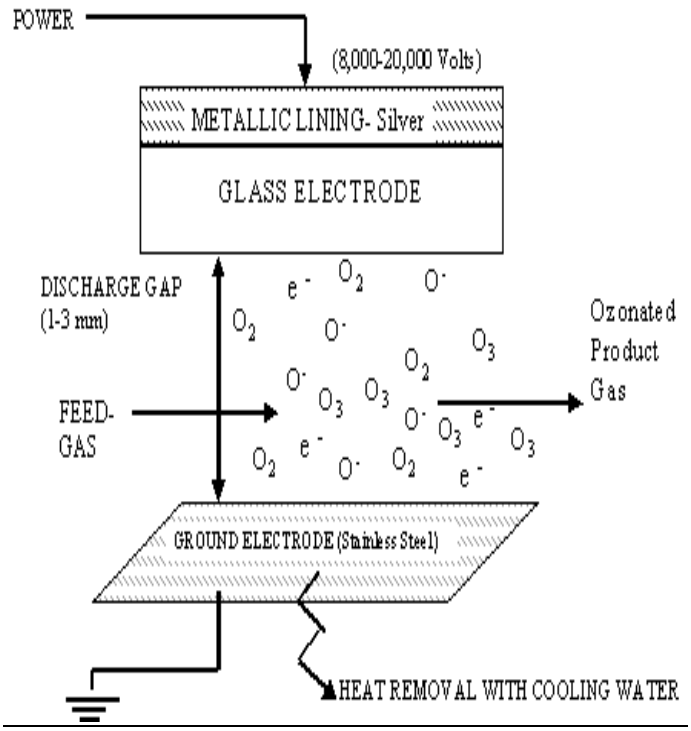

Figure 1: A schematic dielectric ozone generator [19]

First the wastewater entered the BFB (bio-fluidized bed) system with a water vapour 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 [6]. The environment`s pH was kept 6.7 to 8.9 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 modeled from anaerobic reactors which were used in the 1990`s [7], [8]. This kind of system could be designed for dyeing industries` wastewater treatment for about 2 years as well. The treatment process began by removing salts and other harmful combinations [9], [10], [11] and increasing the concentration of dissolvable substances [12], and it continued by extracting

200mL of Di-ethyl from the acidified sample [13]. The standard temperature began in 70^0C for 2 min, and reached to 240^0C, and the final temperature of 240^0C continued for 3 min. The concentration of the liquid phase was also measured [14]. The brown colour of wastewater which was removed during ozonation was because of a medium existence [15]. Moreover the mentioned electrode was used for measurement that made the ozone value to be limited to about 20 mg L^{-1}.

Ozone was produced in an ozone generator. The feed gas could be either air or pure oxygen. A high voltage was applied to two electrodes and the high voltage produced an arc. In the arc part, the O_2 was converted into O_3. Ozone is very unstable and reverts back into O_2 in min. That is why ozone must be generated on-site and cannot be shipped to the water treatment plant. About 1/10 percent of the oxygen flowing past the electrodes was converted into ozone. When air was the feed gas ozone concentrations between 1 and 4 percent were generated. When the feed gas was pure oxygen, the ozone concentrations would be between 4 and 12 percent by weight. About 80 to 95 percent of the energy was converted to heat, and had to be removed at the ground electrode, usually through cooling water. The operational variables consisted of the applied power, the efficiency and design of the generator, the flow of feed gas, and the temperature [16], [17], [18].

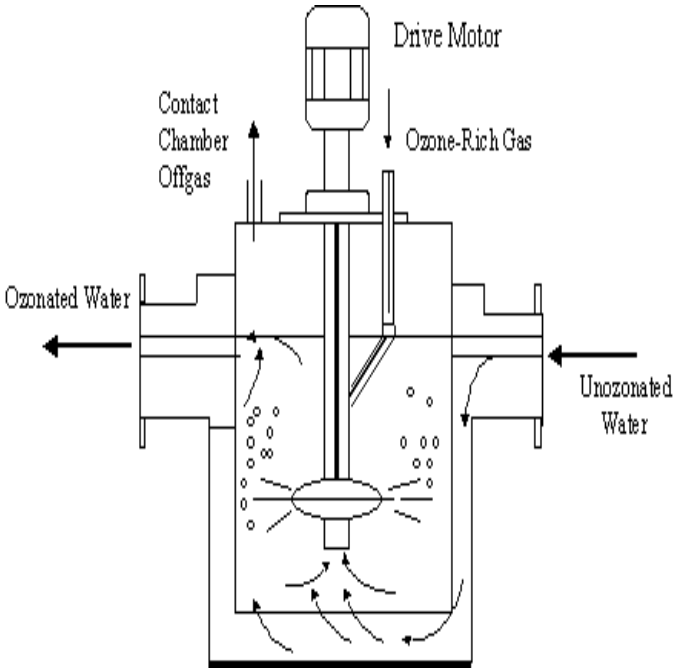

Figure 2: A schematic turbine diffuser contactor [19]

Air feed systems had to remove dust and moisture from the air. This was done using filters, driers and compressors. A lot of machinery and supervision was necessary. A pure oxygen system used liquid oxygen (LOX) and was much simpler. Only a vaporizer was needed in this case. For the ozone to do its work of disinfection and oxidation it had to be brought into the water and dispersed as finely as possible [20]. This was accomplished generally through fine bubble diffusers located in baffle chambers, or in a turbine type contactor. A typical ozone contactor usually has several compartments in series with bubble diffusers at the bottom. In the first compartment the water flew downward against the rising bubbles, and in the second compartment the water flew upward. The chambers were covered to prevent the escape of ozone and to increase the partial pressure of the ozone in the contactor. Additional chambers followed to guarantee a contact time between the ozone and the water. Each of the chambers had sampling ports so that the ozone concentration in each chamber could be determined. This was needed to calculate the product of concentration and detention time to get the required contact time value. The last chamber ought to still

have an ozone concentration of 0.1 ppm. Figure 2 shows a schematic turbine diffuser contactor, which mixes the ozone with the water.

RESULTS AND DISCUSSION

The first measured contaminant was NH_4^+, and its removal trend proved the advantages of treatment after ozonation, It decreased from 69 (mg L^{-1}) without ozonation in the fifth step (where the ozonation started) to 8 (mg L^{-1}) with ozone treatment and indicated a sixty one (mg L^{-1}) more removal. This trend of decreasing continued in all other steps to the final one as it is revealed in fig.3. PO_4^{3-} was the other measured contaminant. As it can be seen and compared in the following graphs this parameter decreased from 27 (mg L^{-1}) in the fifth step by ozone injection to 4 (mg L^{-1}) in the same step while in treatment without ozonation it just decreased to 22 (mg L^{-1}), and this removal trend continued in the next steps too.

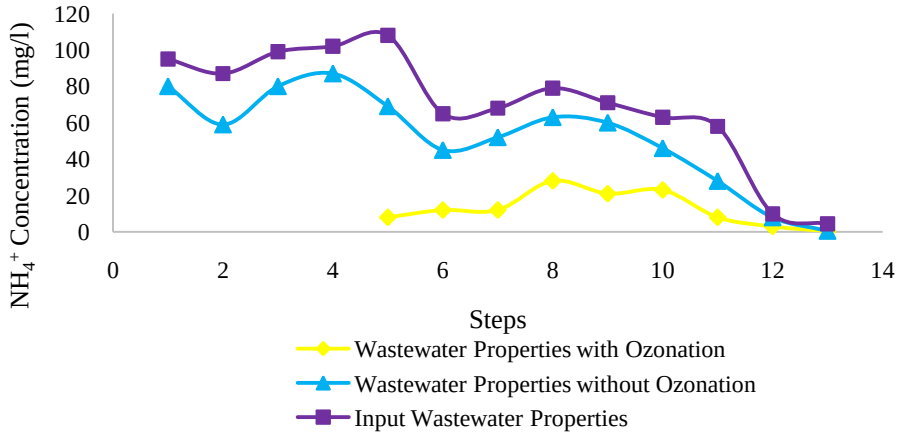

Figure 3: Concentration of NH_4^+in the input wastewater and output wastewater with / without ozonation

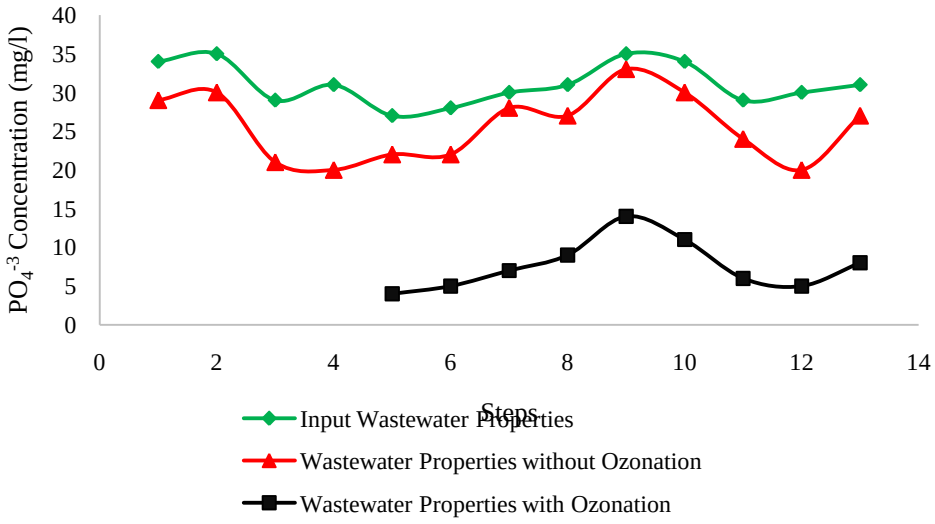

Figure 4. Concentration of PO_4^{3-} in the input wastewater and output wastewater with / without ozonation

NH_4^+ was the first contaminants that was studied and recorded and its removal trend proved the benefit of treating with ozonation where after ozonation started, NH_4^+ was decreased from 69 (mg L^{-1}) in the fifth step to 8 (mg L^{-1}) and indicated a sixty one (mg L^{-1}) more removal that emphasized the better efficiency of such a treatment system in comparison with the normal biological treatment method. This trend of

decreasing continued in all other steps to the final one. 45 (mg L^{-1}) to 12 (mg L^{-1}), 52 (mg L^{-1}) to 12(mg L^{-1}), 63 (mg L^{-1}) to 28(mg L^{-1}), 60 (mg L^{-1}) to 21(mg L^{-1}), 46 (mg L^{-1}) to 23(mg L^{-1}), 28 (mg L^{-1}) to 8 (mg L^{-1}), 8 (mg L^{-1}) to 3 (mg L^{-1}), 0.6 (mg L^{-1}) to 0.4 (mg L^{-1}) were the following decreases from the treatment without ozonation in comparison with treatment with ozonation.

PO_4^{3-} was the other contaminant which was measured and the results showed the great effect of treatment with ozone. As it can be seen and compared in the three tables below this parameter decreased from 27 (mg L^{-1}) in the fifth step by ozone injection to 4 (mg L^{-1}) in the same step while in treatment without ozonation it just decreased to 22 (mg L^{-1}), and this removal trend continued in the following steps where, for instance in the ninth step although the flow rate was increased, but PO_4^{3-} was decreased from 35 (mg L^{-1}) in the input to 14 (mg L^{-1}) after bio-ozone-bio treatment, while after biological treatment it is 33 (mg L^{-1}). Also 8 (mg L^{-1}) in the final treatment step with ozonation in comparison with 27 (mg L^{-1}) without ozonation treatment while the input value was 33 (mg L^{-1}) can also be mentioned as a very considerable decrease.

In this experiment where 13 steps (ozonation was done from the 5th step) of measurement were done in order to achieve the expected result, all parameters measured proved the usefulness of the ozonation method for treating this industrial wastewater from the poisonous pollutants. The concentrations of studied parameters were in the input and output wastewater with and without ozonation as well as the pH, Temperature and Flow Rates in each step are presented in tables 1-3.

Table 1: Concentration of studied Parameters in the input wastewater

Steps	1	2	3	4	5	6	7	8	9	10	11	12	13
Flow Rate (l/h)	50.5	50.5	50.5	50.5	68.2	68.2	69	132	132	50.5	68.2	172	172
Temperature(°C)	19	19.6	21.7	22.4	22	22.1	21	21.4	26	23.1	22.8	25.1	22.9
pH	7.70	7.32	7.20	7.09	7.90	7.89	7.60	6.70	8.21	7.93	7.15	7.97	7.82
NH_4^+(mg L^{-1})	95	87	99	102	108	65	68	79	71	63	58	10	4.5
PO_4^{3-}(mg L^{-1})	34	35	29	31	27	28	30	31	35	34	29	30	31

Table 2: Concentration of studied Parameters in the output wastewater without Ozonation

Steps	1	2	3	4	5	6	7	8	9	10	11	12	13
Flow Rate (l/h)	50.5	50.5	50.5	50.5	68.2	68.2	69	132	132	50.5	68.2	172	172
Temperature(°C)	21	21.3	21.9	23	22.1	24.1	23	22.8	21.6	23.6	24.7	25.6	21.5
pH	7.91	8.2	7.05	7.05	8.8	8.9	8.21	7.8	8.4	8.3	8.43	8.36	7.99
NH_4^+(mg L^{-1})	80	59	80	87	69	45	52	63	60	46	28	8	0.6
PO_4^{3-}(mg L^{-1})	29	30	21	20	22	22	28	27	33	30	24	20	27

Table 3: Concentration of studied Parameters in the output wastewater with Ozonation

Steps	1	2	3	4	5	6	7	8	9	10	11	12	13
Flow Rate (l/h)	-	-	-	-	68.2	68.2	69	132	132	50.5	68.2	172	172
Temperature(°C)	-	-	-	-	22.4	24.1	24	24	26	22.2	25.3	22.5	20.5
pH	-	-	-	-	8.91	8.90	8.38	8.09	8.50	8.40	8.61	8.50	8.30
NH_4^+(mg L^{-1})	-	-	-	-	8	12	12	28	21	23	8	3	0.40
PO_4^{3-}(mg L^{-1})	-	-	-	-	4	5	7	9	14	11	6	5	8

APPLICATIONS

The results showed the great efficiency of such a treatment system that causes suitability of the wastewater after treatment to be used for different purposes such as in effluent depletion to surface water, effluent depletion to leaching pit and for agricultural or irrigational consumption.

CONCLUSIONS

Results achieved from both of the treatment systems (with and without ozonation), and comparing the pros and cons of the treatment methods of the wastewater, also considering the components of the wastewater coming out of the pulp factory which contained chlorophenolic contaminants, and the significant removal of the two specific studied ones (PO_4^{3-} and NH_4^+) [21] in bio-ozone treatment revealed that the substitution of the new method (bio-ozone-bio treatment) instead of the biological treatment of such a wastewater saved both energy and time. Besides, the removal of the mentioned items which were the aim of the study indicated the efficiency of using ozone for treating this kind of industrial wastewater.

REFERENCES

[1] Amir, Hajiali, G.Pirumyan, H.R.Sharif Vaghefi, M.Shahmiri, Treatment of Pulp Factories Wastewater containing Chorophenolic Compounds with Ozonation, *Asian Journal of Chemistry*, **2012**, 24(12), 5609-5612.

[2] Muddegowda Harsha et al., Kinetic and Mechanistic Study of Chloramine-T Assisted Color Removal of Triphenyl Methylene Dyes Containing Waste Water: A spectrophometric Approach, *J. Applicable.Chem*, **2016**, 5 (5), 1175-1190.

[3] Metcalf, Eddy, Wastewater Engineering, Treatment and Reuse, fourth edition, **2004**, 12, 1287-1290.

[4] Amir Hajiali, Gevorg Pirumyan, Farideh Atabi, Mohd Fadhil Md. Din', As sessment of COD and AOX Removal in a Sequential Bio-ozone-Bio treatment of a Pulp Factory Wastewater Treatment System, *International Proceedings of Chemical, Biological and Environmental Engineering*, **2015**, 89, 83-86.

[5] Amir Hajiali, Gevorg P. Pirumyan., Evaluation of Turbidity and Color Removal in Treatment of Wastewater Containing Resistant Pollutants with Ooznatio, *IERI Procedia*, **2014**,9, 8-12.

[6] S.D. Razumovski, G.E. Zaikov, Ozone and its reactions with organic compounds, *Elsevier*, Amsterdam, **1984**.

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

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

[9] T. George, L. Frakin, S.David, Wastewater engineering: treatment and reuse, *fourth Edition, Metcalf & Eddy, McGraw Hill*, **2003**, 1288-1290.

[10] M. R. Khan, S. Zafar, Physico-Chemical Analysis of Kasur Land Soil Reclaimed After Pretreatment of Tannery Wastewater, *J.Applicable.Chem*, **2015**, 4 (2), 565-571.

[11] M. R. Khan, S.Ahad, Analysis of Kasur Tannery Pretreated Wastewater for Its Metal Toxicity, *J.Applicable.Chem*, **2015**, 4(2), 572-577.

[12] Kaza Somasekhara Rao, Kaza Kalyani Sekhar, Kaza Naga Krishna Vani, Kaza`s Carbons- Tools of Decolourisation of Aqueous Waste Effluent Water, *J.Applicable.Chem*, **2016**, 5(4), 708-713.

[13] R. Haberl, W.Urban, P.Gehringer, W.Szinovatz, Treatment of pulp-bleaching effluents by activated sludge precipitation, *Wat., Sci. Technol.*, **1991**, 29, 229-239.

[14] Shun Dar Lin, Water and Wastewater calculations manual, 2nd edition, **2007**, 6, 752-755.

[15] C. 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, *Proceedings of the*

International Conference on Wastewater Treatment, Standards and Technologies to Meet the Challenges of the 21st Century, No.2, Leeds, UK , **2000** ,625-639.

[16] M. Borghei, Principles of swage and industrial waste water treatment, *Sanati Sharif University, Tehran*, **2000**.

[17] 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, **1993**, S-10-76 to S-10-83.

[18] C.Chirat, D. Lachenal, C. Coste, J. Zumbrunn, zone Bleaching of Paper Pulp is ready for Implementation in Water and Wastewater Treatment, *Proceedings of the* 11th *Ozone in Word Congress. San Francisco, CA, (Stamford: Intl Ozone Assoc., Pan American Group),* Vol. 2, **1993**, S-10-66 to S-10-75.

[19] A. Hajiali, Principles of Wastewater Treatment with Ozonation, *Yerevan, Armenia*, **2012**, 224-226.

[20] H.Beffadhel, A. Ratel, Removal of color and Organic Matters in Industrial Phosphoric Acid by Ozone: Effect on Activated carbon Treatment Ozone, *Science Engineering*, **1995**, 17(6): 637-645.

[21] D. Snehal, N.N. Kale Bandela, Study of physico-chemical Parameters of Wastewater Effluents from Waluj Industrial Area, Aurangabad, *J.Applicable.Chem*, **2016**, 5(6),1307-1314.

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