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Analyzing the Chemical Parameters of an Studied Wooden Industry Wastewater Treatment with Advanced Ozonated System

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Abstract**—** *This research reports a study in which measured values before and after ozone addition for wastewaters collected from a wooden industry treatment process. It was found that ozone reduction of particle stability (i.e., increased alpha) depended on both the ozone dose and the water hardness, which is expressed in terms of the raw-water hardness to total organic carbon (TOC) ratio. Specifically, it found increases in alpha for ozone doses of 0.4 to 0.8 mg O_3/mg TOC and hardness-to-TOC ratios of at least 25 mg $CaCO_3$/mg TOC. In summary, the results showed the effect of ozone on alpha depends on ozone dose, calcium and hardness and algae type. With the advances in the technology used to generate ozone, ozone is becoming more affordable to install and cheap to operate. Typically an Ozone installation will pay for itself over 12 months in chlorine savings.*

Keywords**—** *Chemicals, Ozone, Treatment, Wastewater, Wood.*

I. INTRODUCTION

Wastewater of wooden industries which are by-products of cellulose causes a hazardous water vapor that is dangerous because of containing different combinations of chlorophenolic. The most hazardous part of these substances is monomers of chlorophenolic combinations [1]. These monomers and especially monomers with high molecular weights are seen in such wastewater treatment systems. All monomeric combinations of chlorophenolic are removed completely in both aerobic and anaerobic ways [2], [3]. Concentration of each one of these monomers among treated wastewaters is usually less than 100nm, and most of them are less than 50 nm. In a research it was revealed 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 [4].

Ozonated wastewater provides necessary substances for bio-treatment in both aerobic and anaerobic stages [5], [6]. For providing the essential substances for final biological treatment, sufficient solution which is ozonated wastewater is produced in some groups [7], [8]. 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 [9].

II. MATERIALS AND METHOD

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

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. 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 Amprometric electrode [10]. 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-ethil from the acidified sample. The standard temperature began in 70^0C for 2 minutes, and reached to 240^0C, and the final temperature of 240^0C continues 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 [11].

The effect of ozone below a certain critical concentration value is small or zero [12]. Above this level all pathogens are eventually destroyed. This effect is called all-or-none response and the critical level the "threshold value".

When wastewaters are ozonated, the particle volume concentration may not remain constant [13]. It may increase following ozonation due to production of particles through precipitation (e.g., oxidation of Fe or Mn producing $Fe(OH)_3$ or MnO_2 particles) or it may decrease due to break up or shrinkage of organic part such as algae [14]. In the controlled experiments with synthetic waters, precipitation from Fe or Mn would not occur; however shrinkage or break up of the algal cells can occur [15]. Alpha values indicate the stability of the particles, low values, e.g., 0.01, indicate stable particles that flocculate very slowly, whereas higher alpha values

approaching 1 indicate destabilized particles that flocculate rapidly.

The particle volume concentration may change upon ozonation affecting rates of particle flocculation [16]. Therefore, absolute alpha values cannot be determined accurately. What is more important is the relative effect of ozone on alpha. For these reasons, the relative effect of ozone on alpha, not absolute alpha values, is present. Relative alpha a_{rel} is defined as follows;

$a_{rel} = a_{(test)} / a_{(ref)}$
where $a_{(test)}$ = the alpha value for any test case
$a_{(ref)}$ = the alpha value for the reference condition of no preozone

Ozone increases the flocculation kinetics for all calcium cases as indicated by the increase in a_{rel}. When Ca is low (0 and 30 mg/L [$CaCO_3$]), the effect of ozone on the algae particles is about the same as that indicated by the approximately equal a_{rel} values. At the highest Ca concentration tested, ozone has a great effect at 1mg/l (a_{rel} of 10), while increasing ozone to 3 mg/l decreases a_{rel} to 5. This increase in a_{rel} at 1 mg/l and then decreases at higher ozone may be due to interacting effects between ozone and calcium.

Ozone Oxidation Capabilities in Wastewater Treatment

Discovered in 19th century Ozone a natural form of activated oxygen generally produced during lightening storms and continuously occurring in the stratosphere due to the action of ultraviolet is being rediscovered in 21st century [17]. Ozone is highly unstable and must be generated on site. Its oxidation potential (-2.07 V) is greater than that of hypochlorite acid (-1.49 V) or Chlorine (-1.36 V), Ozone is thought to decompose accordingly:

$O_3+H_2O \rightarrow HO_3+OH$
$HO_3+OH \rightarrow 2\ HO_2$
$O_3+ HO_2 \rightarrow HO+2O_2$
$HO+HO_2 \rightarrow H_2O+O_2$

This unstable form of oxygen breaks down to oxygen molecules and oxygen atoms which have high oxidation potential [18]. If we examine the oxidation power of Ozone will find out that O_3 is about five times more oxidizing than oxygen and about twice as much as chlorine [19]. These high potentials increase its reactivity with other elements and compounds. This reactivity is about 20 to 50 times more reactive than chlorine and Permanganates as it is well documented in the case of the high kill rate of micro-organisms (Funguses, Bacteria, and Viruses) [20]. This high kill rate means smaller retention times, storage tanks, are required to do the same disinfecting as other oxidants [21]. In other words the capital cost for building these tanks and treatment plants are reduced considerably.

In fig.1 the transformation of oxygen to ozone by electrical charge, and the process of disinfection by ozone can be seen.

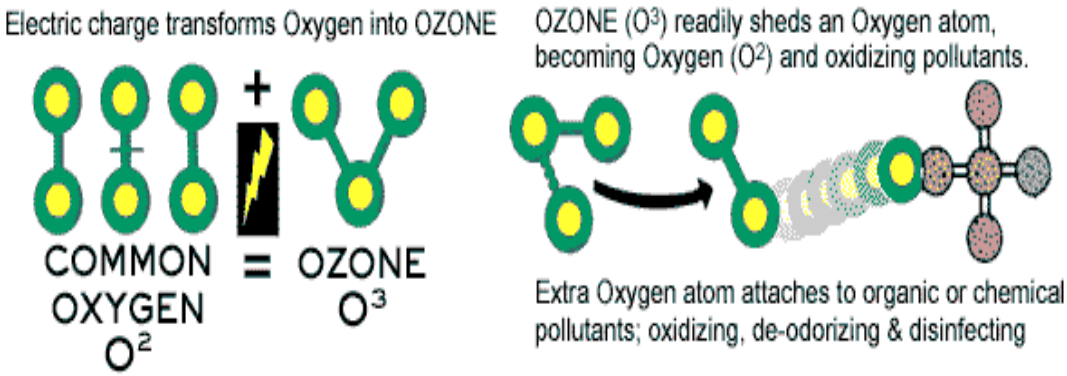

Fig. 1. Transformation of oxygen to ozone through electrical charge and the process of disinfection by ozone

Ozone generators are typically classified by:
- The control mechanism (either a voltage or frequency unit)
- The cooling mechanism either water, air or water plus oil)
- The physical arrangement of the dielectrics (either vertical or horizontal)
- The name of the inventor

However, generators manufactured by different companies have unique characteristics but also have some common configurations.

The off-gas from the contact chamber must be treated to destroy any remaining ozone before release into the atmosphere [22]. Therefore, it is essential to maintain an optimal ozone dosage for better efficiency. When pure oxygen is used as the feed-gas, the off-gases from the contact chamber can be recycled to generate ozone or for reuse in the aeration tank [23]. The ozone off-gases that are not used are sent to the ozone destruction unit or are recycled.

III. RESULTS AND DISCUSSION

The time that the system needed to reach to a spesific fixed limit was about 90 hours which is 3 times more than the total 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. After the first considerable COD reduction in primary(A-B) biological treatment (about 20 to 30 percent), in the next stage of biological aerobic to anaerobic traetment (C-D-E) this decrease after ozonation traetment showed itself in a very

large scale and more than the two previous stages. Of course in this stage if ozonation process was omitted, COD reduction would definitely show itself very much less than this amount. The general variables during Bio-ozone-biotreatment can be seen in table I.

The most considerable treatment is seen in AOX volume which was because of gradual ozone adding to the system. To explain the relation between magnificent AOX reduction and biological treatment without ozonation existance was very hard and to some how impossible. A comparison between previous observations and the reached information in this study showed 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) was 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.

In this reactor liquids were passed sequentially and according to bio-ozone-bio-treatment method, and it showed that when ozone is consumed very fast, 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.

TABLE I. General variables during Bio-ozone-biotreatment.

Measured Global Variables	Samples	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

Total removal of AOX, COD, and TOC in the integrated cyclic ozonation-biotreatment system can be seen in fig. 2.

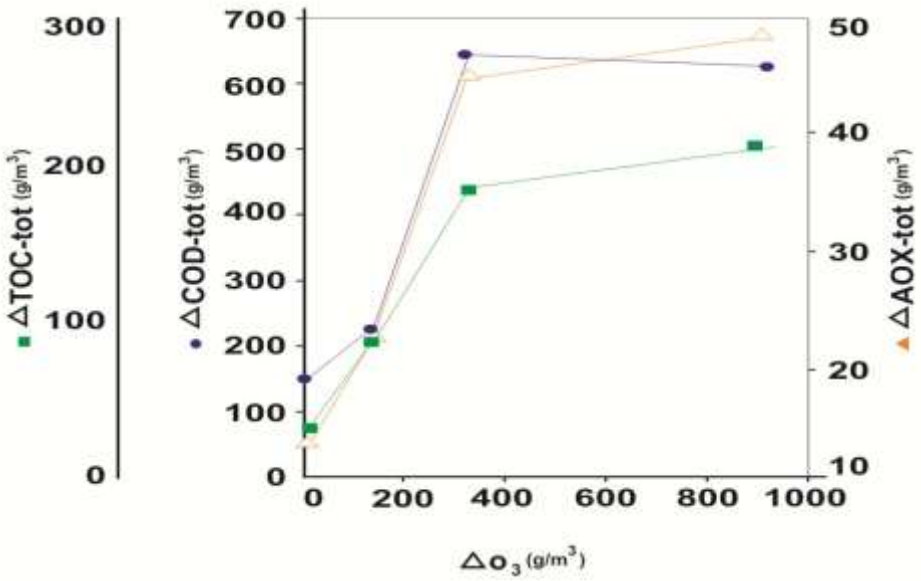

Fig. 2. Total removal of AOX, COD, and TOC in the integrated cyclic ozonation-biotreatment system.

COD removal in the anaerobic system(30 to 180g/m^3) was very remarkable. TOC removal value in a similar reactor against what was expected which was high value of TOC in samples 3 and 4 was not high (85 and 90 g/m^3), AOX removal value in anaerobic reactors was usually high about 25g/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.

Usually error factor in AOX experiments is high, because for analyzing AOX, very high value of that is necessary, and this value can not 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.

ΔAOX/ΔCOD ratio was studied in 4 samples and they were respectively 72%, 10%, 70%,and 76%for samples 1 to 4 which are all according to AOX (gr) on Ozone (gr). 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.

IV. CONCLUSION

In this research calculation and estimation of ozonated treatment was possible to be done. And it showed that ozonation lets wooden industries wastewater to be treated easily with better efficiencies. For better treatment of poisonous substances and also simultaneous treatment of the combinations, the system can be completed with excessive and other perfect systems. 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- biotreatment system. Therefore bio-ozone- biotreatment process can be suggested as a very useful method for treatment of such wastewaters.

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