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STUDY ON OXIDATION MECHANISM OF OZONATED WASTEWATER TREATMENT: COLOR REMOVAL AND ALGAE ELIMINATION

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With the advances in the technology used to generate ozone, it is becoming more affordable to install and cheap to operate in water and wastewater treatment processes. Typically an ozone installation will pay for itself over 12 months in chlorine savings. In this paper the oxidation process of industrial wastewater treatment is studied and the effects of such a system on color removal and algae elimination are discussed in details. Ozone is highly unstable and must be generated on site. Its oxidation potential (2.07 *V*) is greater than that of hypochlous acid (1.49 *V*) or chlorine (1.36 *V*), and therefore it leads to much more efficient results in color removal as well as algae elimination in comparison with other alternatives in specific wastewater treatment systems.

Keywords: algae, color, oxidation, treatment, wastewater.

Introduction. Using ozone coupled with biological treatment has been known to be a very efficient form of wastewater treatment that is cost effective as well. In such wastewater treatment plants there are four distinct stages: holding, pre-treatment with ozone, biological digestion through aeration, and the final polishing stage using oxidation by ozone.

In the holding stage the wastewater is macerated with a grinder pump. In this maceration larger solids are broken down so that larger areas are available for reactions with the ozone. Large pieces of organic material are removed as sludge and separately treated as listed above. The tanks in this stage are also used to balance the quantities of wastewater for further stages so that the process proceeds with continuous batches. The pre-treatment with ozone is then carried out in the primary ozone treatment tank. Ozone is generated by an ozone generator using oxygen enriched air. The fluid in this tank is continuously circulated through an ozone diffusion system. Tools for measurement of ozone levels are used to monitor activity. The wastewater is then transferred to the aeration tank, where the water is treated with air to encourage aerobic biological treatment. Biomass is accumulated with microbes that utilize the organic matter in the wastewater to produce additional biomass and carbon dioxide and water. Only a certain portion of the tank's content is transferred to the subsequent proceed, thus allowing the biomass

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helping aerobic digestion to accumulate to proper proportions. The polishing or final process of wastewater ozone treatment is meant to reduce the biochemical oxygen demand to its lowest level. Ozone is added at predetermined hydraulic rates depending on the condition of the water flowing into this tank. Through continuous circulation dissolved ozone levels are maintained at pre-designated levels. After the designed detention time the treated water is released through surface drains into the environment or to any other usage desired. Each tank is connected to the other and the filling and discharge from the tanks are determined by the high level float in the initial tank [1–3].

Materials and Methods.

Oxidation Mechanism. The free radicals (HO_2 and HO) react with a variety of impurities such as metal salts, organic matter including microorganisms, hydrogen and hydroxide ions. They are more potent germicides than hypochlous acid by factors of 10 to 100 fold and disinfect 3125 times faster than chlorine. Oxidation potential does not indicate the relative speed of oxidation nor how complete the oxidation reactions will be. Complete oxidation converts a specific organic compound to carbon dioxide and water [4]. Oxidation reactions that take place during wastewater treatment are rarely complete, due to the large amount of contaminants and relatively short durations of time during which the wastewater pollutants are oxidized. Therefore, partially oxidized organic compounds such as aldehydes, carboxylic acids are produced during the relatively short reaction periods. These aldehydes and carboxylic acids can be removed by other means prior to complete mineralization to reduce the amount of ozone needed for complete oxidation of these chemicals.

There are three fundamental mechanisms, which apply to the oxidation of organic compounds reacting with an oxidizer. Each mechanism is unique as in how organic compounds react with an oxidizer. But, in some cases, oxidants will react with organic compounds by all three mechanisms, although in sequential steps [5, 6].

The first is the addition mechanism, which occurs with organic compounds, containing aliphatic unsaturates such as olefin. Ozone can be added across a double bond to form an ozonide. This reaction occurs readily in nonaqueous solvents, but as soon as water is added, the ozone hydrolyzes to other products with cleavage of the former double bond.

The second is the substitution mechanism which involves replacement of one atom or functional group with another. The specific reaction also can be viewed as an insertion reaction, whereby oxygen is inserted between the ring carbon and hydrogen to form the hydrogen group on the ring. Oxidation also can involve cleavage of carbon-carbon bonds to produce fragmented organic compounds.

Effect of Temperature and pH. It is clear that other parameters affect the reaction mechanism and rates as found by various studies. The effectiveness of ozone to oxidize organic and inorganic compounds is a function of the temperature of water and pH levels. In wastewater applications there are many variables such as: water temperature, pH, COD, BOD, TSS, heavy metals and so on, which need to be considered.

Ozone at low pH levels (less than 7) reacts primarily as the O_3 molecule by selective and sometimes relatively slow reactions. Ozone at elevated pH (above 8) rapidly decomposes into hydroxyl free radicals, which react very quickly. Many compounds that are slowly oxidized will oxidize rapidly when the pH is adjusted to the alkaline side. It was found that pH 8–10 is most suitable for the oxidation of organic molecules [7, 8].

The initial step of the decomposition of ozone is the reaction between ozone and hydroxide ion to form ozone ion and hydroxyl radical $(\dot{O}N)$, the hydroxyl radical then reacts further. This process would explain the increased dissociation of ozone with increasing alkalinity. Recently, the studies have shown experimentally that with increasing pH, the kinetics of ozonation of organic compounds changes. As was concluded hydroxyl radicals may be the important active species in ozonation. Therefore, the alkalinity of water is a key parameter in advanced oxidation processes. Ozone decomposes rapidly in water with a half-life of a few minutes at about 20 *min* at room temperature, but can be much faster in less than 10 *min* in the presence of bicarbonate and carbonate ions, which are excellent scavengers for free radicals [9].

In addition, carbonate ions are 20 to 30 times more effective in scavenging for hydroxyl free radicals than bicarbonate ions. For this reason we stated that the pH of 8.0 to 10.0 is most appropriate for ozonation since it was found that at pH 10 the bicarbonate ions are converted to carbonate ions.

Effect of Catalysts. There are several catalysts used in combination with ozone such as semi-precious and precious metals, ultrasonic agitation, H_2O_2, electro coagulation. But the most commonly used and well documented are the ultraviolet rays at wave length of 254 *nm*.

Ultraviolet has been found in the past 10 to 15 years that when this treatment is combined with ozone, there is a rather explosive reaction as the two in a sense destroy each other creating a highly reactive hydroxyl ion. The end result of this is that many compounds that neither UV nor ozone independently can remove, however with the combination of UV and ozone can be removed and the rate of removal is extremely rapid, sometimes in as little as two seconds [10].

The produced free radicals by this reaction contain at least four radicals: (O) Excited Atomic Oxygen species, (HO) Hydroxyl radicals, (HOU) Hydroperoxy radicals and Excited Carbon containing species. Compounds, usually refractory or slowly reacting with ozone or UV alone, but reacting to the combination of such organo metallic complexes, Cyanides, Phosphorous and Nitrogen compounds. Ultrasounds have not been fully exploited in relation to wastewater treatment and have not been fully understood and documented at present. It is known that in many cases it works with the ozonation treatment in ways quite similar to UV. Principally it excites the ionic structure of both water and the contaminants in waste stream and as a result the ozonation process is expedited (either in speed of reaction or it actually causes a reaction, where the contaminant was refractory to the ozone treatment) [11, 12].

Wastewaters, which are slightly reactive to ozone, show excellent reaction with the electrochemical methods such as for domestic and textile wastewaters. Precious and semi-precious metals catalysts studies show that the presence of such metals speed up the reaction rates, which in some cases can double or triple. One hundred percent mineralization occurs when these types of catalysts are combined with ultraviolet at 254 *nm*.

Results and Discussion. Water is shown colored when visible radiation is absorbed by dissolved materials, or when light is reflected from suspended solids. These two sources of color are the basis for the distinction between pseudo and true color. Pseudo color is due to absorption as well as light reflection. The true color depends solely on the type and amount of the dissolved substances. Particles with a size of 400–800 *nm* that means within the wavelength of visible light are responsible for light reflection. It is possible with filtering (membrane 0.45 μm) the phenomenon of reflection to be eliminated. It should also be noted that the difference between pseudo and true color is related to the turbidity of water [13]. The units Pt–Co are defined as color measurement units. These units are considered equivalent. The acceptable limits of color values for the disposal of treated wastewater range from 50–100 units Pt–Co, depending on the nature of the receiver (river, sea, lake, etc) [14].

True color is created by the presence of compounds that absorbs visible light in wavelengths of 400–800 *nm* or from compounds that fluoresce in the 200–400 *nm* spectrum. These are compounds of poly-aromatic structure, substituted aromatic structure, polyenia, concentrated hetero-circular molecules or perplex ions. It should be noted that π bonds absorb in the UV (200 *nm*) spectrum and the existence of conjugated bonds (polyenia) is necessary for the absorption in visible light spectrum. Most compounds responsible for color creation contain one or more aromatic rings and start to absorb color at 250 *nm* [15, 16].

The synthetic color carriers come mainly from industrial plants as dye-houses, clothing industries with washing-machines, food and beverage industries, slaughterhouses, and etc. When wastewater is treated with ozone after its exit from the chemical or/and biological treatment plant, according to the wastewater origin, its temperature, the degree of its previous process, and the usual dosage, a great color removal can be seen in the treatment system. The quality of the ozone treatment effluent in terms of color removal depends on the following aspects: the color values of the feed; ozone dosage; the wastewater type (typically color values do not decrease below 200 Pt–Co units, even if an especially high ozone dosage is applied); the wastewater temperature (best results with effluent from the existing treatment the temperature of which is much lower than the temperature of wastewater from the equalization tank); values of other characteristics of wastewater which are also affected by ozone (best results if BOD, COD and SS have already been decreased in a previous treatment level) [17].

The best results concerning color removal are achieved, if the wastewater has been previously treated in order to lower the values of other characteristics so that the ozone oxidizing effect is "consumed" only or at least at a maximum proportion in color removal. Additionally the temperature must be below 30°*C* in order to achieve the best physical conditions for its solubility. The above remark certainly concerns the practical usage of ozone technology in wastewater treatment, as it indicates that increasing the ozone dosage can give good results even in treated wastewater as long as it is efficiently cooled.

Wastewater color removal requires an ozone dosage, which in most cases fluctuates from 50 to 100 *mg*/*L* to reduce the color to 85–92%. The ozone treatment installation represents a significant construction and purchase cost. On the other hand, the conventional treatment scheme using chemical coagulants for color removal has high operating costs (the cost of the coagulants themselves and the cost for the produced sludge management requirements). In general and for the same effluent quality, the investment of an ozone installation can be paid off in 3–5 years, depending on the size and other specific details of each case [18, 19].

Moreover, people involved in water treatment generally task about an "algae" problem. In fact, it is more accurate to use the term "plankton". This term includes all micro algae which under favorable conditions (the presence of ideal amounts of nutrients, heat and sunlight in the environment) can undergo periods of explosive growth. It also includes animal plankton (zooplankton), which belongs to a higher level in the food chain, as well as actinomycetes. All of these organisms range in size from of a few microns to a few millimeters. Tab. 1 presents a list of plankton species generally predominant in water and the effects that they produce.

Table 1

Algae species generally predominant in water and the effects they produce

Algae	Type				Dimension	Interference in water and wastewater treatment	
						bio-chemical	morpho-logical
Name	circular/oval	filamentous	rectangular	irregular	average	taste and odor problems	effect indefinite
Cyanophyceae							
Aphanizomenon	0	1	0	0	5	1	1
Microcystis	1	0	0	0	5	1	1
Oscillatoria	0	1	0	0	10	1	0
Chorophyceae							
Chlamydomona	1	0	0	0	20	1	0
Chlorella	1	0	0	0	8	1	0
Coelastrum	1	0	0	0	20	0	1
Mougeotia	0	1	0	0	35	0	0
Pandorina	1	0	0	0	10 (30)	1	1
Pediastrum	0	0	0	1	30	1	0
Scenedesmus	1	0	0	0	15	1	1
Ulothrix	0	1	0	0	10	0	0
Volvox	1	0	0	0	5 (500)	1	1
Cryptomonas	1	0	0	0	20 (40)	0	1
Bacilariophycea							
Asterionella	0	0	0	1	80	1	0
Coscinodiscus	1	0	0	0	200	0	1
Cyclotella	1	0	0	0	30	1	0
Diatoma sp.	0	0	0	1	60	0	0
Melosira	0	1	0	0	25	1	0
Nitzschia	0	0	1	0	40	0	0
Synedra	0	0	1	0	200	1	0

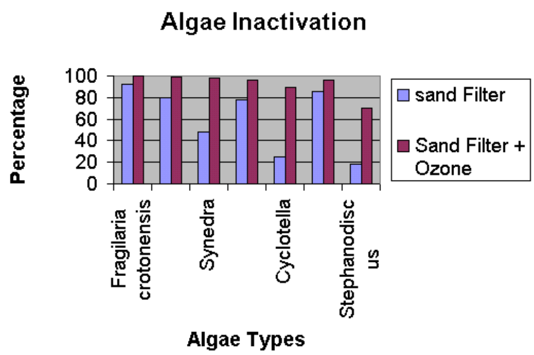
Ozone has been used for algae elimination with very good results. In the following table ozone with some other very strong oxidants can be compared, and it is seen that ozone gives very good results in short amounts of time.

Table 2

Algae elimination using ozone in comparison with other oxidants

Oxidant used	Oxidation conditions		Inactivation
Name	dose, *mg/L*	reaction time, *min*	%
Potassium permanganate	1	30	9.5
	2	30	68
	3	30	89
	1	60	68
	2	60	98
	3	60	100
Hydrogen peroxide	100	30	50
	100	60	75
Ozone	1	1	14
	2	1	64
	3	1	70
	1	5	26
	2	5	72
	3	5	76

The graph below shows a comparison of a system, which has only filtration with a system, which added ozone to do the algae control. For almost all types of algae, ozone can reduce them by more than 95%. As it can be seen, the correct installation is crucial for getting the best results for any system. If the ozone system is not well designed and installed, the desired benefits will not be achieved.



Comparison of Algae control with only filtration system versus a combination of ozonation and filtration systems.

Conclusion. Found out, the ozonation process can be used for treatment of industrial wastewater in different industries including oil industry, petroleum industry, food industry, pulp factories, tanneries, and so on. In this research the oxidation process of such a system was considered and investigated. And it showed that ozonation helps different industrial wastewater to be easily treated with better efficiency. Two main reasons can be mentioned for the above achievement; reduction of the chlorination activity, and the existence of an oxidation reaction in bio-ozone–biotreatment system. Therefore, bio-ozone–biotreatment process can be suggested as a very useful method for treatment of the mentioned wastewaters.

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