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ADVANCED TECHNOLOGIES FOR WASTEWATER TREATMENT BY OZONATION – A REVIEW

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Abstract: Water pollution due to animals, human faeces or sewage systems is one of the most dangerous sources of contamination because they contain many pathogenic microorganisms. Disinfection is a necessary step to destroy or inactivate micro-organisms and prevent the spread of dangerous diseases. The properties of ozone, especially the ability to oxidize, have led to its use in water treatment. Ozone is an "ideal" reagent because it does not introduce, in water or in the atmosphere, reaction products with unfavorable effects. In this paper are presented the most representative studies on the use of ozone in wastewater treatment.
Keywords: wastewater, ozonation

1. INTRODUCTION

Water pollution due to animals, human faeces or sewage systems is one of the most dangerous sources of contamination because they contain many pathogenic microorganisms. Disinfection is a necessary step to destroy or inactivate micro-organisms and prevent the spread of dangerous diseases. The disinfecting process has been considered as one of the most important steps in wastewater treatment and improper attention to this process can caused a social disaster.

The application of the disinfection process is necessary in the case of industrial waters from slaughterhouses, breeding establishments, tanning, canning factories, food industry where fermentation processes take place. The disinfection mechanism comprises two phases: penetration of the disinfectant through the cell wall and denaturation of protoplasmic protein, including enzymes. Until now, different methods have been used for drinking water disinfection, such as using the ultra-violet light and adding ozone or chloride (Bidhendi et al, 2006).

Disinfection is considered to be the primary mechanism for the inactivation/destruction of pathogenic organisms to prevent the spread of waterborne diseases to downstream users and the environment. It is important that wastewater be adequately treated prior to disinfection in order for any disinfectant to be effective. Disinfection can be accomplished by physical or chemical procedures. The most used means of disinfection of water are: ozonisation (chemical disinfectant) and ultraviolet radiation (physical disinfectant) (Dokovska et al, 2014). The properties of ozone, especially the ability to oxidize, have led to its use in water treatment. Ozone is an "ideal" reagent because it does not introduce, in water or in the atmosphere, reaction products with unfavorable effects.

The first ozone decontaminating facilities were built at the end of the nineteenth century, when in 1898 in Berlin, Siemens and Halske had experienced the use of ozone in water treatment. The first treatment plant equipped with ozone was built in 1906 at Nissa by Marius Paul Otto. The use of ozone for disinfecting water increased after 1968, following studies by Coin and C. Gomella, which demonstrated its ability to inactivate viruses (Blăgoi and Puscaș E.L., 1997).

Ozone requires less contact time and lower concentrations than chlorine, chlorine dioxide and chloramines to achieve disinfection, but its instability and reactivity means that it is unable to provide an enduring disinfection residual in distribution. The stability of ozone decreases with increasing pH and temperature. At 15°C and a pH of 7.6 the lifetime of the residual is reported to be in the order of 40 minutes, but at higher temperatures it can be as low as 10 - 20 minutes. This occurs due to a decrease in the efficiency of transfer of ozone into water as temperature increases. Ozone disinfection is generally used at medium to large sized plants after at least secondary treatment. In addition to disinfection, another common use for ozone in wastewater treatment is odor control.

Ozone treatment has the ability to achieve higher levels of disinfection than either chlorine or UV, however, the capital costs as well as maintenance expenditures are not competitive with available alternatives. Ozone is therefore used only sparingly, primarily in special cases where alternatives are not effective. The cost of ozone disinfection systems is dependent on the manufacturer, the site, the capacity of the plant, and the characteristics of the wastewater to be disinfected. Ozonation costs are generally high in comparison with other disinfection techniques.

Ozone is the most powerful oxidant used to treat water for disinfection. According to this, numerous studies have been carried out, the most representative of these are presented in this paper.

2. MATERIAL AND METHOD

The microbicidal activity of ozone has been demonstrated since the late 1800. The first municipal water purification plant dates back to 1906 (Tordiglione et al, 2014). Ozone is the most powerful oxidizing agent, showing ten times the effectiveness of chlorine, and it's currently used to potabilize water (Boyce et al, 1981), disinfect swimming pool water

(Glauner et al, 2005) and decontaminate bioclean rooms (Masaoka et al, 1982). Ozone bactericidal activity seems to be primarily resulting from direct oxidative damage and the effects of ozone have been tested on different bacterial strains, including E. coli, Salmonella sp., S. aureus and Bacillus subtilis (Stoll et al, 2008).

When ozone decomposes in water, the free radicals hydrogen peroxy (HO_2) and hydroxyl (OH) that are formed have great oxidizing capacity and play an active role in the disinfection process. It is generally believed that the bacteria are destroyed because of protoplasmic oxidation resulting in cell wall disintegration (cell lysis). The effectiveness of disinfection depends on the susceptibility of the target organisms, the contact time, and the concentration of the ozone.

A line diagram of the ozonation process is shown in Figure 1. The components of an ozone disinfection system include feed-gas preparation, ozone generation, ozone contacting, and ozone destruction.

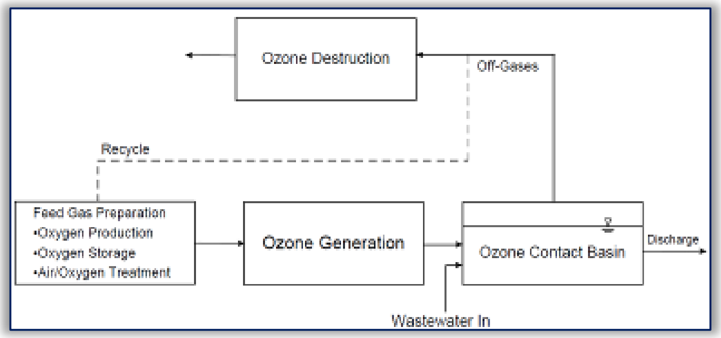

Figure 1 - Ozone process schematic diagram

Ozone disinfection has been proven to be one of the most effective methods and is widely used to inactivate pathogens in water, particularly in Europe, the US and Canada, since the first treatment plant in Nice was built in France.

3. RESULTS

Due to its high oxidation potential, bactericidal properties, ease of on-site generation from air or oxygen, and ease of destruction to form ordinary oxygen, ozone has become widely used in a large number of applications, the most representative being the wastewater treatment field. In the following, are presented the most representative studies in this area.

John W. Birks et al., (Birks et al, 2015) have studied uncontaminated measurement of ozone dissolved in wastewater using a new MicroSparge ™ technology. The authors describe a new approach to the measurement of dissolved ozone and provide an example of its use in ozone monitoring during waste water treatment in the tertiary stage. Figure 2 is a schematic diagram of the ozone monitor showing additional components.

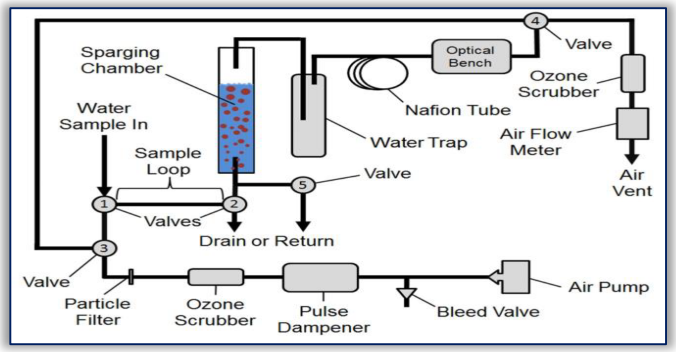

Figure 2 - Detailed schematic diagram of the MicroSparge™ ozone measurement instrument

The MicroSparge™ instrument was evaluated by continuously monitoring dissolved ozone concentration in a potable research demonstration project, specifically a project in which water of wastewater origin is treated to a point where it can ultimately be reused as drinking water.

Measurements were made during three multi-day periods for a total of 20 days, as shown in the three graphs of Figure 3. Grab samples were occasionally obtained and analyzed by the indigo method using a Hach colorimeter. The continuous ozone measurements show the high degree of variability of ozone during the treatment process despite application of a nearly constant ozone dose rate. The sharp positive excursions in ozone were found to be due to the chlorine in the feed water, thereby reducing the ozone demand and allowing higher ozone concentrations. The high variability in dissolved ozone concentration as function of time, despite constant applied ozone dose, demonstrates the possibility of reducing cost in ozone treatment by using a feedback from the dissolved ozone monitor to control the ozone generator. Note that occasionally the treatment process was shut down to allow back flushing of the activated carbon filters. As seen in Figure3, during those times, the ozone measurements decreased to zero, as expected, and with a very fast response time.

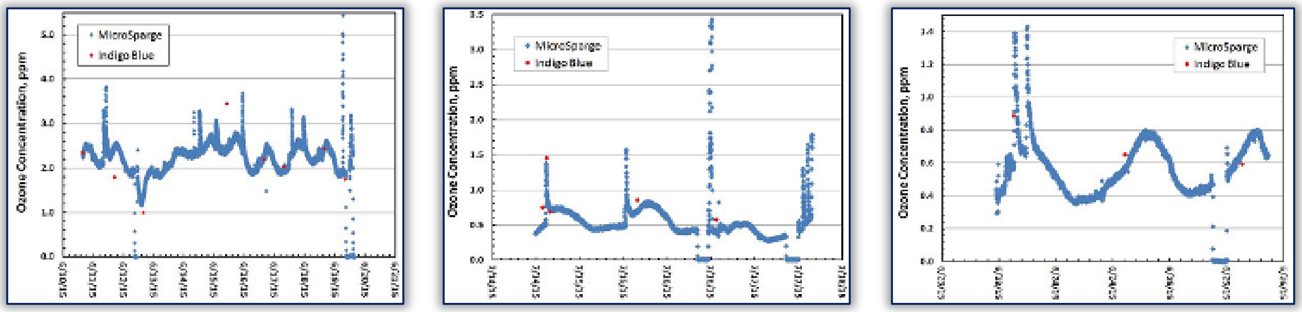

Figure 3 - Comparison of MicroSparge™ and indigo blue ozone measurements in treated wastewater

The method has a fast response time (20 s, the average of 2 independent 10-s measurements) and good precision of <0.05 ppm. This new method for measurement of dissolved ozone concentration currently is being applied to a wide range of waters to determine the limitations of the technique with respect of loadings of organic compounds and particulate matter.

In study [7], (Marcelino et al, 2016), the authors proposed a multistage treatment system to treat real pharmaceutical wastewater containing the antibiotic amoxicillin.

Ozonation (O_3), and ozonation combined with aerobic biodegradation, were performed. The real pharmaceutical wastewater presented a high concentration of organic matter (TOC: 803 mg $C*L^{-1}$ and COD: 2775 mg O_2*L^{-1}), significant amoxicillin content (50 mg L^{-1}) and acute ecotoxicity (Aliivibrio fischeri aTU: 48.22).

The ozonation experiments were performed in a 1000 mL borosilicate glass bubble column reactor for 180 min at semi-batch conditions, in which the ozone-containing gas was continuously sparged through a cylindrical porous-stone diffuser, at ambient temperature (25 °C ± 6). The reactor was connected to an O_3 generator and an O_2 concentrator from air (Figure4).

For the conditions tested, the surface response of TOC removal by ozonation (regarding pH and the oxygen flow rate), show that increase in the oxygen flow increased the level of TOC removal. The mass balance results showed that the reaction system was not able to utilize all the produced ozone. The largest part of the supplied ozone (>50%) was lost in the outlet gas stream, as shown in Figure 5.

Ozonation alone at the optimum condition could achieve 46% of TOC removal; however, the combination of aerobic biodegradation and ozonation was able to improve the degradation of the practically all of the organic matter present. More than 98% of the original wastewater COD and TOC were removed, and removal of more than 99% of colour and amoxicillin was achieved. Moreover, the ecotoxicity of the final wastewater had also decreased in comparison with the ozonation treatment alone. The ozonation process reduced approximately 62% of the original toxicity, whereas the combined treatment removed 90%. A summary of these comparisons is presented in Figure 6.

In the effort to improve the efficiency and cost effectiveness of wastewater treatment, combining aerobic biodegradation with ozonation in a multistage treatment system has emerged as a feasible option.

In another study, (Zhang et al, 2018), was analyzed the performance of catalytic microbubble (MB) ozonation using a commercial granular activated carbon (AC) as catalyst in synthetic acid red 3R wastewater treatment. The performance of catalytic MB ozonation treatment was investigated and compared with MB ozonation alone and coarse bubble (CB) ozonation under the same conditions, including ozone mass transfer, decolorization, TOC removal, ozone reaction efficiency and ozone utilization efficiency.

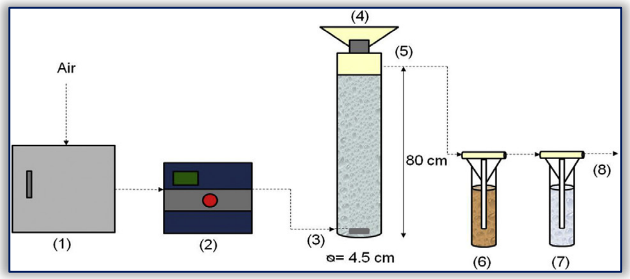

Figure 4 - Ozonation experimental setup: (1) O_2 concentrator, (2) O_3 generator, (3) O_3 inlet, (4) wastewater load, (5) O_3 outlet, (6) KI solution, (7) KI solution (security trap), (8) off-gas

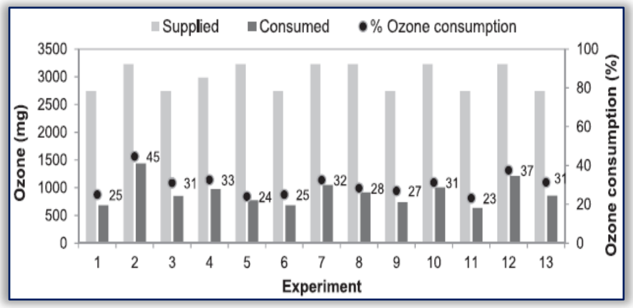

Figure 5 - Ozone consumption for each ozonation experiment performed: Total O_3 supplied (mg O_3 e light grey bars), total O_3 consumed (mg O_3 e dark grey bars), and percentage of O_3 consumption (percentage O_3 e black dots)

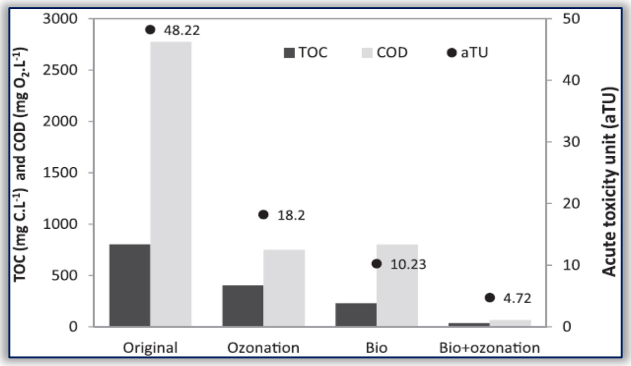

Figure 6 - Comparison of TOC (mg C*L-1), COD (mg O2*L-1) and the Aliivibrio fischeri acute toxicity unit (aTU) of the original wastewater, relevant to treatment by ozonation alone, biodegradation alone and by the multistage system

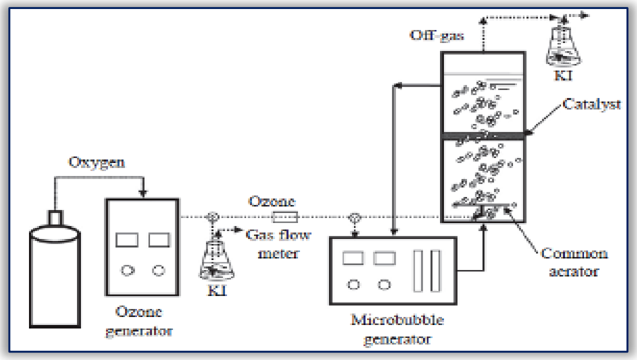

Figure 7 - Experimental apparatus

The experimental apparatus is shown in Figure 7. A sealed reactor with a diameter of 200mm and a height of 500mm was used and its work volume was 10 L with a water height of 318 mm. An ozone generator (Guanyu, China) was used to produce ozone from oxygen.

The decolorization efficiencies of acid red 3R wastewater over time during CB ozonation and MB ozonation with and without AC are shown in Figure 8. The completed decolorization with the decolorization efficiency of more than 99% was realized after 15 min and 25 min in MB ozonation with and without AC, respectively.

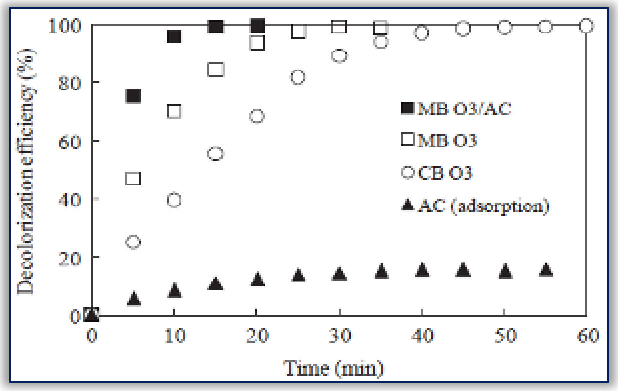

Figure 8 - Decolorization efficiency of acid red 3R wastewater

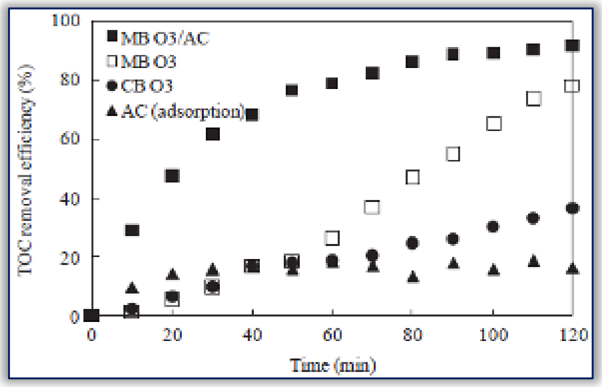

Figure 9 - TOC removal efficiency of acid red 3R wastewater

The TOC removal efficiencies over time in CB ozonation and MB ozonation with and without AC are shown in Figure 9. As expected, the TOC removal was efficient during the initial treatment period in catalytic MB ozonation with AC. Its TOC removal efficiency reached 78.2% after 60 min treatment and finally 91.2% after 120 min treatment, which was 18.6% higher than that in MB ozonation alone.

The comparison of these performances indicated that catalytic MB ozonation was considerably more efficient than CB ozonation and MB ozonation alone. The performance of catalytic microbubble (MB) ozonation using a commercial granular activated carbon (AC) as catalyst in synthetic acid red 3R wastewater treatment was more efficient than that of coarse bubble (CB) and MB ozonation alone. Therefore, the catalytic MB ozonation with commercial granular AC was a promising solution for wastewater treatment by ozonation process.

4. CONCLUSION

Disinfection is considered to be the primary mechanism for the inactivation/destruction of pathogenic organisms to prevent the spread of waterborne diseases to downstream users and the environment.

Ozone treatment has the ability to achieve higher levels of disinfection than either chlorine or UV, however, the capital costs as well as maintenance expenditures are not competitive with available alternatives.

Due to its high oxidation potential, bactericidal properties, ease of on-site generation from air or oxygen, and ease of destruction to form ordinary oxygen, ozone has become widely used in a large number of applications, the most representative being the wastewater treatment field.

The MicroSparge ™ technology for measurement of dissolved ozone concentration currently is being applied to a wide range of waters to determine the limitations of the technique with respect of loadings of organic compounds and particulate matter.

In the effort to improve the efficiency and cost effectiveness of wastewater treatment, combining aerobic biodegradation with ozonation in a multistage treatment system has emerged as a feasible option.

The comparison of these performances indicated that catalytic microbubble ozonation was considerably more efficient than coarse bubble ozonation and microbubble ozonation alone. Therefore, the catalytic microbubble ozonation with commercial granular activated carbon was a promising solution for wastewater treatment by ozonation process.

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