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Ozonation and Its Application in Wastewater Treatment

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ABSTRACT

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. Ozone is produced when oxygen (O2) molecules are dissociated by an energy source into oxygen atoms and subsequently collide with an oxygen molecule to form an unstable gas, ozone (O3), which is used to disinfect wastewater. Most wastewater treatment plants generate ozone by imposing a high voltage alternating current (6 to 20 kilovolts) across a dielectric discharge gap that contains an oxygen-bearing gas. Ozone is generated onsite because it is unstable and decomposes to elemental oxygen in a short amount of time after generation. When ozone decomposes in water, the free radicals hydrogen peroxy (HO2) 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. Ozonation process has been widely applied in water and wastewater treatment, such as for disinfection, for degradation of toxic organic pollutants. However, the utilization efficiency of ozone is low and the mineralization of organic pollutants by ozone oxidation is ineffective, and some toxic disinfection byproducts (DBPs) may be formed during ozonation process. Catalytic ozonation process can overcome these problems to some extent, which has received increasing attention in recent years. During catalytic ozonation, catalysts can promote O3 decomposition and generate active free radicals, which can enhance the degradation and mineralization of organic pollutants. Ozone removes iron, manganese and arsenic from water by oxidation to an insoluble form that is further separated by filtration. Both processes require ozone in molecular form, but the removal of organic pollutants that are refractory to other treatments can be possible only by exploiting the indirect radical reactions that take place during ozonation. Ozone decomposes in water, especially when hydrogen peroxide is present, to yield the hydroxyl radical, the strongest oxidizer available in water treatment.

Keywords: Protoplasmic oxidation, Catalytic ozonation, Free radicals

1. HISTORY

In 1886, several studies had shown that ozonized air could sterilize polluted water, which led the city of Oudtshoorn in the Netherlands to build the first-ever ozone treatment for drinking water production in 1893.This demonstration plant gained a lot of attention, especially from French scientist Marius Paul Otto,

who refined the concept to build and commission the ozone treatment plant of Nice in 1907.Marius Paul Otto conceived the longest operating plant in history: the ozone water treatment of Nice. One hundred fourteen years later, that plant – after of course several upgrades – is still running, making it the longest operating ozone water plant in the world.
The next decade would see about 50 ozone plants built in Europe, of which a good half in France.The first world war brutally stopped this rapid expansion. But not for the reasons you'd spontaneously expect. Indeed, a lot of chemical research occurred during this conflict, leading to a better understanding and mastering of chlorine, which happened to not only kill people, but also pretty well disinfect water.
Wastewater ozonation has achieved its widest application in the United States of America in the past ten years. Many U.S. facilities designed in the 1970s have manifested significant operational and maintenance problems with the first generation application of ozone technology to wastewater treatment. These problems are reviewed and solutions recommended. The secondgeneration facilities of the 1980s demonstrate higher levels of efficiency, reliability, and operability. The broad application of ozonation to wastewater treatment in the United States of America (U.S.) in the 1970s was carried out with little or no reference to the prior experience of the applications of ozone in the field of drinking water treatment attained in Europe.
Ozone used for wastewater disinfection became popular early on when the widespread use of ozone gained popularity in the 1970's and 1980's. Due to lack of equipment reliability and rising costs, the use of ozone almost completely disappeared from this application. In recent years however, ozone is getting another chance in many locations across the USA and Europe. This is partly due to improvement in equipment reliability and lower cost; however, the main reason for this revival is the secondary benefits that ozone offers along with the increased costs of chemicals creating an economic advantage.

1.1. INTRODUCTION TO OZONATION

Ozonation in wastewater treatment is a mature and efficient alternative to improving traditional methods. Historically, wastewater treatment uses chlorine for disinfection because of its effectiveness and low cost. However, a study in 1970 found that chlorine-free reacts with organics to create disinfection by-products (DBPs). These DBPs could adversely affect public health and aquatic life. There were also fish kills in water bodies receiving wastewater disinfected with chlorine. The US Environmental Protection Agency (US EPA) promoted research on alternative disinfection, such as Ozonation and UV light disinfection technology. One technology that has proven to be highly effective in treating wastewater is Ozonation. Ozonation is a process where ozone (a molecule containing three oxygen atoms) is generated in situ by an ozone generator. this ozone gas is dissolved in water to kill microorganisms and remove organic and inorganic pollutants. The ozone acts as a powerful oxidizing agent, breaking down organic compounds and neutralizing harmful bacteria and viruses by a safe chemical reaction. It is a widely used technique in both industrial and municipal wastewater treatment. Once the ozone is in the water, the ozone molecules attach to the pollutants or microorganisms and oxidize them, effectively destroying them. Ozone can be applied in various stages of the process, providing a high degree of flexibility for wastewater treatment plants. Also, Ozone can be combined with other oxidants like hydrogen peroxide to create Advanced Oxidation Processes (AOPs) in any water purification process.

Ozone is more effective than chlorine at killing viruses and bacteria. Also, the ozonation process required a short contact time (approximately 10 to 30 minutes). As ozone decomposes rapidly and completely, there are no harmful residues. Also, after ozonation, there is no regrowth of microorganisms, except for those protected by the particulates in the wastewater stream. Moreover, Ozone is produced onsite, and thus, there are fewer safety problems associated with shipping and handling.A wastewater treatment process typically includes several stages, including pretreatment, primary treatment, secondary treatment, tertiary treatment, and disinfection. Wastewater treatment aims to remove pollutants and contaminants from water so that they can be safely released into the environment. The industry uses bio and mechanical filtration for the bulk reduction of BOD/COD. By the filtration method, BOD/COD is reduced from 115,000 mg/L to 50-100 mg/L. Bio and mechanical filtration are becoming very expensive when it comes to reducing BOD/COD to a lower level. That is where hundreds of Water Treatment Plants (WTP) use ozonation. Ozone can be used as the final step in the wastewater process because it is very effective as a water polisher. For instance, ozonation economically reduces BOD/COD to safe levels before discharge into the receiving water Aside from decreased processing costs, ozone systems will also help eliminate the penalties associated with contaminated water disposal. Further benefits include the implementation of a clean, environmentally friendly technology, increasing oxygen demand, and an improvement in aesthetic characteristics due to a reduction in turbidity.

1.2. INTRODUCTION TO CATALYTIC OZONATION

Refractory organic pollutants in water generally exhibit low biodegradability, high toxicity, and ease of being enriched in organisms, which threaten the safety of human health and the ecosystem. Industrial wastewaters usually contain various refractory organic pollutants(such as phenolic compounds, chloro-organics, PAHs,etc.). However, these compounds are difficult to be effectively removed by conventional biological wastewater treatment technologies. As one of the advanced oxidation processes(AOPs), heterogeneous catalytic ozonation is attracting a great deal of attention because of its high removal efficiency of refractory organic pollutants in water treatment. The catalyst is crucial in determining the efficiency of removing organic pollutants in heterogeneous catalytic ozonation.

Various catalysts have been constructed to enhance the conversion of O3 to produce reactive species and degrade organic contaminants. Compared with homogeneous catalysts, heterogeneous catalysts are easier to be recycled and can be used under a wide range of pH [4, 5]. Consequently, heterogeneous catalysts are more suitable for the actual water treatment processes.Up to present, the studied ozonation catalysts are mainly transition metal-based (such as Mn, Fe, Ce, Cu, etc.) materials. Among them, the catalysts based on Mn usually show good activity for catalytic ozonation. However, their stability during catalytic ozonation remains poor. The leaching of Mn ions could lead to the reduction of catalytic activity and cause secondary pollution of water, hindering the practical application of heterogeneous catalytic ozonation. Consequently, developing highly efficient and stable Mn-based catalysts is becoming a priority for catalytic ozonation of organic pollutants.It was deduced that the construction of Mn-X bimetallic oxide could generate a synergistic effect and improve the activity and stability of a Mn-based catalyst in catalytic ozonation. It is well-known that Ce-based catalysts possess excellent stability for catalytic ozonation. In this work, Mn-Ce bimetallic oxide was synthesized as the active component by a redox process between KMnO4 and Ce(NO3)3 · 6H2O. Moreover, From previous study confirmed that CNT can accelerate the reduction of Ce4+ to Ce3+ in the CeO2/CNTs/O3 system, and Ce3+ catalyzes the conversion of O3 to produce -OH to degrade organic pollutants .

Employing CNT as a support could facilitate electron transfer and increase the exposure of active sites, which thereby enhance the catalytic efficiency of Mn-Ce bimetallic oxide. In addition, considering magnetic materials are easily recycled, the magnetic CNT@Fe3C was prepared as the support for Mn-Ce bimetallic oxide. The synthesized Mn-Cebimetallic oxide loaded CNT@Fe3C(Mn0.7Ce0.3Ox/CNT@Fe3C)was employed for catalytic ozonation. It was speculated that the Mn0.7Ce0.3Ox/CNT@Fe3C could perform good performance towards catalytic ozonation because of the possibly synergetic function of Mn and Ce, and the promoted electron transfer and increased active sites by the utilization of CNT. The prepared catalyst was characterized by SEM, XRD, BET, and XPS. The activity of Mn0.7Ce0.3Ox/CNT@Fe3C towards catalytic ozonation was evaluated using phenol as a model pollutant. Furthermore, EPR measurements and radical quenching experiments were conducted to identify the main ROS for phenol mineralization in the Mn0.7Ce0.3Ox/CNT@Fe3C/O3 system.

1.3 Ozone Treatment

ADVANTAGES

- Ozone is more effective than chlorine in destroying viruses and bacteria.
- The ozonation process utilizes a short contact time (approximately 10 to 30 minutes).
- There are no harmful residuals that need to be removed after ozonation because ozone decomposes rapidly.
- After ozonation, there is no regrowth of microorganisms, except for those protected by the particulates in the wastewater stream.
- Ozone is generated onsite, and thus, there are fewer safety problems associated with shipping and handling.
- O3 is also highly efficient at killing bacteria, viruses, and protozoa and is always generated on-site. It does not require transportation or storage of dangerous materials.
- As it disinfects, it oxidises inorganic and organic impurities such as iron and manganese. It will also oxidize sulphides which can assist in filtration.
- As it is a 50 percent stronger oxidizer than chlorine, it requires significantly less contact time to remove inorganic/organic compounds than conventional methods.
- Ozone produces less THM disinfection by-products than result from chlorine disinfection (but bromate may be formed). Waste waters treated with this disinfection do not contain chlorine or chlorinated disinfection by-products, thereby making dechlorination unnecessary.

DISADVANTAGES

- Low dosage may not effectively inactivate some viruses, spores, and cysts.
- Ozonation is a more complex technology than is chlorine or UV disinfection, requiring complicated equipment and efficient contacting systems.
- Ozone is very reactive and corrosive, thus requiring corrosion-resistant material such as stainless steel.
- Ozone is extremely irritating and possibly toxic, so off-gases from the contactor must be destroyed to prevent worker exposure.
- Because of its toxicity, this chemical needs to be consistently monitored.
- Within the ozone system there are higher than fatal concentrations of ozone and the release of this gas would clearly be highly dangerous. Ozone detectors and other safety steps are essential.
- A related disadvantage is the need to ensure conformance with building regulations and fire codes concerning the storage of liquid, high-purity oxygen. Although it forms less THM's than chlorine

based disinfectants if bromine is present in the water bromate will be formed. This is equally as dangerous.

- Ozone has a half-life of 20 minutes in air and water depending therefore leaving no residual kill of pathogens in the water after this time and another disinfectant must be added.
- It is also the most expensive technology in this review, the systems need to be highly automated and very reliable and this comes at a cost.

1.4. APPLICATIONS OF OZONATION

1.4.1. Ozone applications

1.Ozone in drinking water treatment

Ozone is highly effective in the treatment of drinking water. Since 1906 the city of Nice, France has been ozonizing mountain stream water for potable purposes. Today more than 600 other French water treatment plants are using ozone for number of purposes. Throughout the world more than 1,300 drinking water treatment plants employs ozone for one or other purposes, 20 plants are being operated in U.S. using ozone technology. Most tastes and odor in water supplies come from naturally occurring or man made organic material contamination. Bacterial decomposition of humic material imparts taste to surface water, also the action of algae and actinomycetes give rise to objectionable tastes. Most of these odors are removed by treatment with ozone.

2. Ozone treatment of contaminated ground water

The use of ozone in cooling tower treatment has significantly increased in recent years. Several factors give this concept a great deal including Money savings due to lower operating costs over time

No on-site chemical inventory

No toxic discharge, chloramines

Water conservation due to no TDS buildup from disinfectants

Ozone is produced on-site and requires no storage of dangerous chemicals

Lower corrosion rates of the system

No regular disinfection system maintenance required

No special training for employees operating the system

Elimination of Legionella spread and hazard to human heal.

3.Removal of suspended solids

At chino basin, California a 5-mgd secondary treatment plant has been using ozone to micro flocculate and removes suspended solids without adding chemicals since 1978. Effluent from this plant is recharged to ground water. Ozonation reduces levels of suspended solids without adding any total dissolved solids to the effluent, provides effective virus removal and is cost effective, over alternative treatment processes. Dosages of ozone required in the process are 10 mg/L. In California a 5 mgd secondary treatment plant has been using ozone to micro flocculate and removes SS.

4. Ozone and swimming pool water treatment

The use of ozone for treatment of swimming pool water has been developed in Europe since 1950. There are 3,000 swimming pool using Ozonation processes. Since the pink eye reaction are caused by chloramines thereforeozone based treatment plantare getting more popularity.

In recent years German swimming pool technologists have developed an innovative water treatment process that takes advantage of the oxidative power of ozone and that substitutes bromine for chlorine. It has been shown that pink eye reactions are caused by chloramines and that bromamines do not produce this effect.

In the new treatment process bromide is added to the pool water, which then is ozonized. During ozonization bromide ion is oxidized to bromine, which is biocide/ disinfectant. The ozonized water is passed through GAC to destroy the ozone. Water containing bromine and no ozone enter the pool.

1.4.2. Industrial Applications of Ozonation

1. Ozone in dyeing industry effluent treatment

The wastewater produced by the dyeing industry contains many artificial colouring agents. We can classify the effluent based on different parameters. Physical properties includescolour, turbidity (dissolved and suspended impurities) etc. whereas chemical properties includes the constituents of acidic dyes, basic dyes, sulphides dyes, azo dyes, metallic complex dyes etc.

Generally speaking, biological treatments are only capable of bringing about, slight improvements in wastewater colour. This is because the molecules responsible for colouration are not biodegradable. Effluent colour can however be improved by aeration or oxygenation. One-way of decolourization might be through destruction of the double nitrogen-nitrogen bonds, this is confirmed by the appearance of NO and NOz radicals following ozone treatment.

2. Ozone in removal of colour

Surface water are generally coloured by natural organic materials such as humic, fulvic and tannic acids. These compounds results from the decay of vegetative materials and are generally related to condensation products of phenol like compounds, they have conjugated carbon/carbon double bond. Ozone rapidly break organic double bond. As more of this double bond is eliminated, the colour disappears. Surface water can usually be decolourized when treated with 2-4 ppm of ozone.

3. Ozone in treatment of toxic waste

The detoxification of industrial wastewater is an issue that has taken a marked importance in recent times. The chemical industry, in particular, discharges many substances of high immediate toxicity. For this type of waste, mere dilution is not a sufficient anti-pollution measure. The concentration levels are crucial factor when considering toxicity. Ozone is increasingly used in tertiary treatment for eliminating all traces of harmful substances. The advantage here is that ozone treatment does not require the use of additives, which may prove toxic than the compound removed.

In mixtures containing toxic compounds, ozone will not always react specifically with the compound that we wish to eliminate. For this reasons it is advisable, wherever possible to apply conventional purification techniques first and follow up with Ozonation as a second or third stage. Concentration levels are a crucial factor when considering toxicity.

Thusozone is increasingly used as final treatment stage for eliminating all traces of harmful substances.

4. Ozone in elimination of phenols

Many types of industrial plant discharge phenolated wastewater such as coking plant, oil refineries, petrochemical plant, mines, chemical and pharmaceutical process lines, foodstuff, canning plant, paint stripping shops, hi aeronautical industry etc.

A number of purification methods exist for eliminatingthese toxic compound from wastewater. One such method is oxidation of ozone. Several highly detailed studies have been conducted into the way ozone reacts with phenols. Basically, ozone breaks down phenols to form oxalic acids and oxygen. Studies into the kinetics of Ozonation reactions show that many factors can affect the efficiency of the purification process. Predominant among these factors are the temperature and above all the pH.Thus increasing the pH from 8.0-11.0 doubles the rate at which phenols are broken down. At the higher pH value, ozone attacks phenolated compounds in preference to the other oxidizable matter, and this substantially reduces reaction times. Generally five parts of ozone are required to break down one part of phenol in wastewater.

1.5. Efficient Water Quality Parameters

Table. 1.1 Parameters:

Parameters	Unit	Test methods
pH	—	pH meter
Conductivity	μs/cm	Conductivity meter
TDS	mg/L	Calibrated EC-TDS meter
Nitrate	mg/L	UV Vis spectrophotometer-304 nm
COD	mg/L	Titration using potassium dichromate
DO	mg/L	DO meter
Fecal coliform	CFU/100 mL	Membrane filtration method
Ferrous	mg/L	UV Vis spectrophotometer-515 nm
Chromium	mg/L	Atomic absorption spectrophotometer
Cadmium	mg/L	Atomic absorption spectrophotometer
Lead	mg/L	Atomic absorption spectrophotometer

Using ozone technology, we are mainly focusing on treatment of physiochemical and microbial parameters of water. ozone can be produced by various ways and in the current study a dielectric barrier discharge (dbd) technique was used. DBD has numerous applications such as ozone production, surface modification, material processing, biological decontamination, pollution control by oxidation of volatile organic compound or nitrogen monoxide, uv or vacuum ultraviolet (vuv) generation, aerosol charging, and electrofiltration, and one of its important application is the treatment of potable water and wastewater.

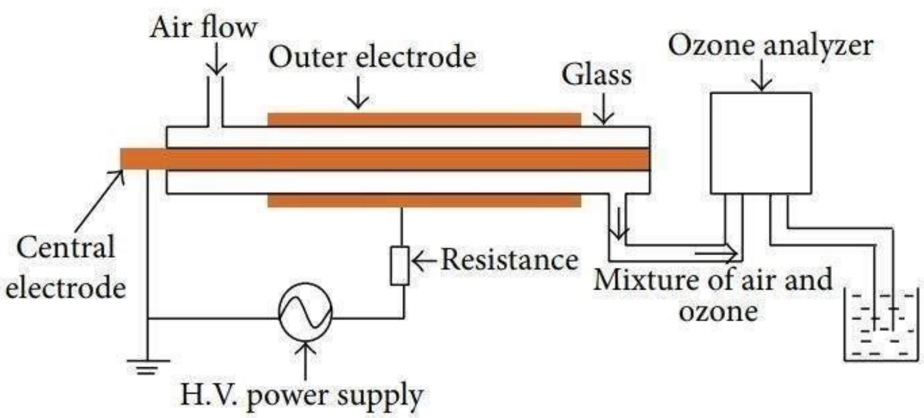

Fig 1.1. EXPERIMENTAL SETUP OF DBD SYSTEM FOR OZONE GENERATION

Different physicochemical and microbial parameters of inlet and outlet samples from guheshwori wwtp were analyzed before and after treatment by ozone for two seasons (premonsoon and postmonsoon). in premonsoon season, the amount of water is low by which pollutants are more concentrated in the samples whereas in postmonsoon season washing off of solid might take place and thus there will be dilution of organic and inorganic pollutants. the following parameters were tested.

1. pH

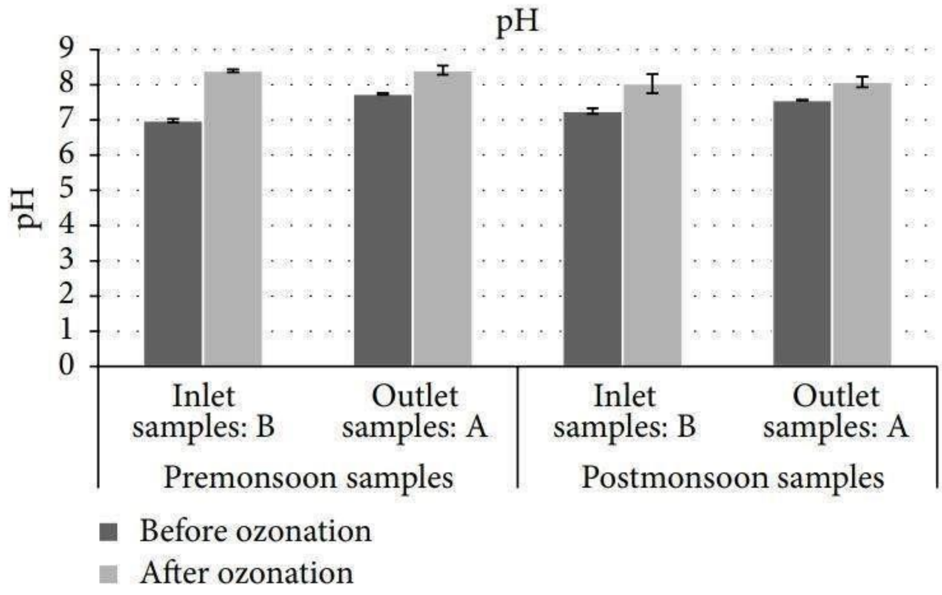

Fig. 1.2 pH

The mean value of ph of inlet samples (b) and outlet samples (a) from system s1 is found to be 6.97 and 7.74, respectively, for premonsoon season and 7.25 and 7.56, respectively, for post monsoon season. after ozonation the mean value of ph is 8.39 and 8.41, respectively, for inlet and outlet samples for premonsoon season and 8.03 and 8.08, respectively, for postmonsoon samples which indicates slight increase in ph after ozonation.subedi et al has also reported no significant change to marginal increment of ph after ozonation.

2. Dissolved Oxygen (DO)

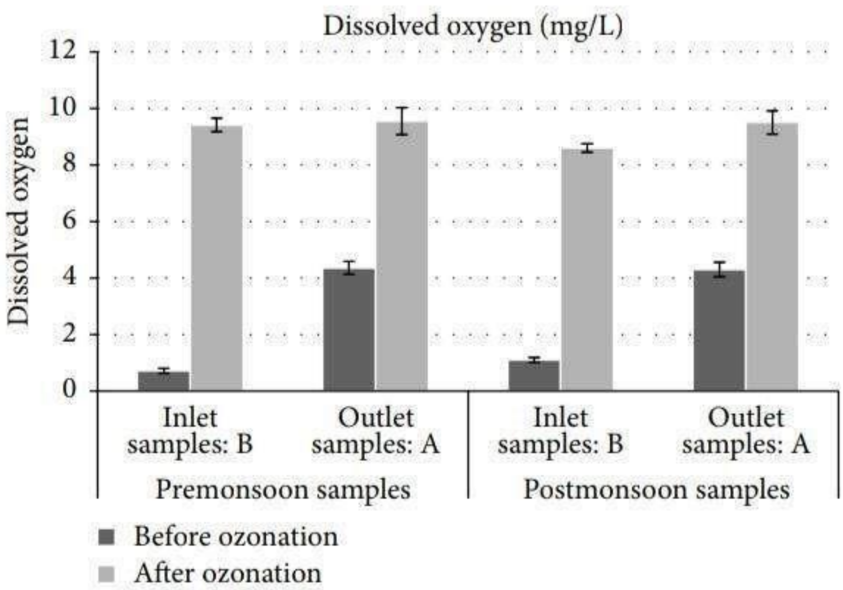

Fig. 1.3 Dissolved Oxygen

For premonsoon sampling, the mean value of dissolved oxygen for five replicates of inlet samples (b) and outlet samples (a) from system s1 is found to be 0.72 and 4.36, respectively. after treatment by ozone, the mean do values are 9.41 and 9.55, respectively, for b and a samples. Similarly, for postmonsoon sampling, the mean value of dissolved oxygen for five replicates of inlet samples (b) and outlet samples (a) from system s1 is found to be 1.1 and 4.3, respectively. after treatment by ozone the mean do values are 8.6 and 9.5, respectively, for b and a samples. from the above data it is clear that the value of do increased after treatment by system s1 but this do value is not enough to sustain aquatic life. minimum do level required for protection of aquatic life is 5.8 to 6.8 mg/l. importantly, as shown in figure 4, after treatment by ozone (system s2) the do level increased significantly and reached up to 9.55.

3. Total Dissolved Solids (TDS) (mg/L)

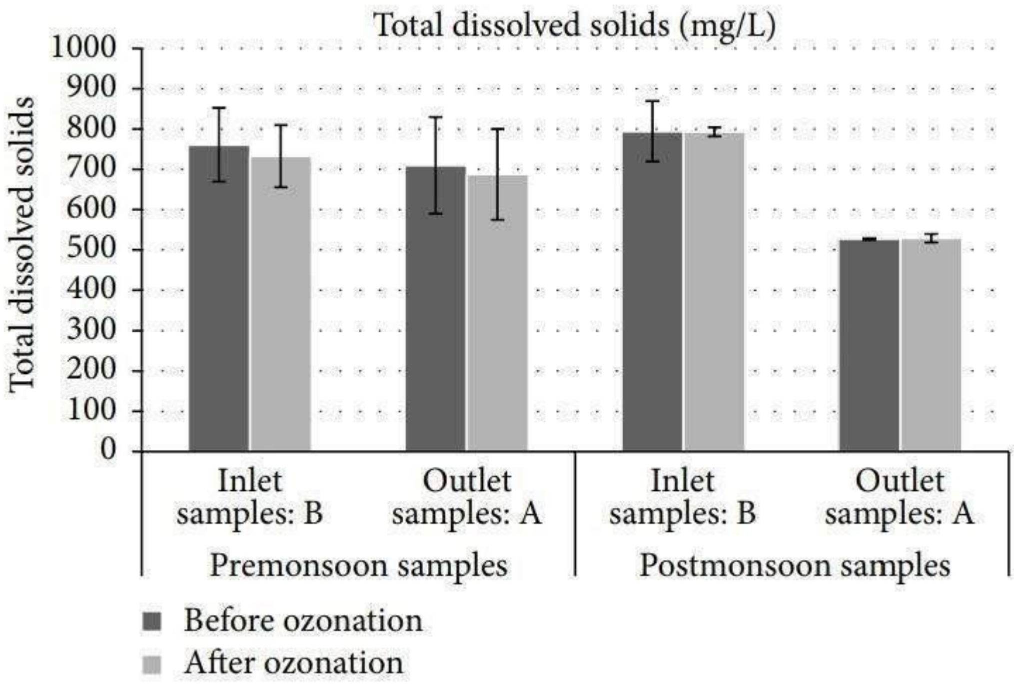

Fig. 1.4 Total Dissolved Solids

The mean value of tds of inlet samples (b) and outlet samples (a) from system s1 is found to be 760.50 and 709.25, respectively, for premonsoon season and 794.00 (b) and 527.20 (a) for postmonsoon season. after treatment by ozone, the mean tds values are 732.25 and 687.50, respectively, for b and a samples of premonsoon season and 792.80 and 529.25, respectively, for postmonsoon season. there was not any significant difference in total dissolved solids after ozonation ($p > 0.05$).

4. Chemical Oxygen Demand

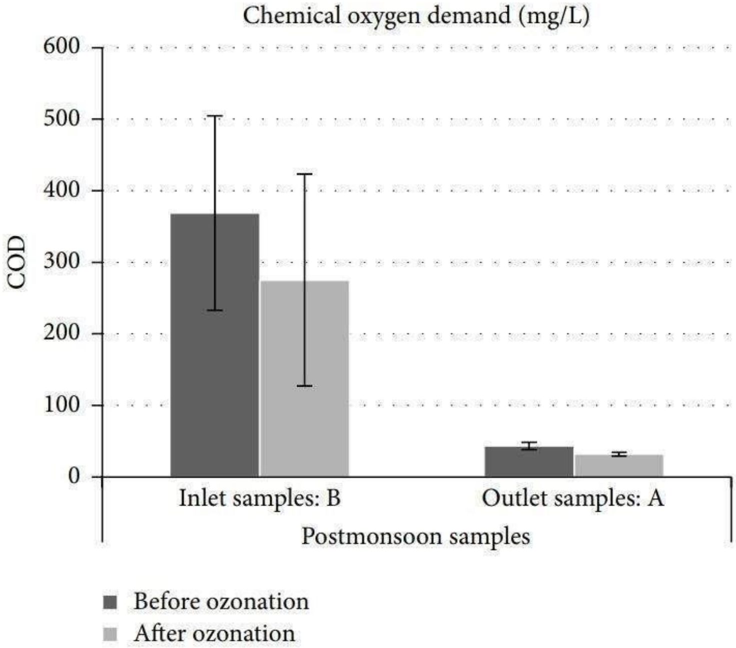

Fig. 1.5 Chemical Oxygen Demand

The mean value of cod of inlet and outlet samples from system s1 was found to be 368.8 and 43.6, respectively. after ozonation these values decreased significantly to 275.2 and 31.9, respectively. this result indicates the presence of series of chain reactions initiated by ozone dissolved in water which in turn fragmentize large organic molecules in water and thus decrease cod.

2. Study of Research Paper on Waste-water Treatment by Ozonation (Literature Review).

1. Catalytic ozonation for imazapic degradation over kelp-derived biochar: Promotional role of N- and S-based active sites (Da Wang, Shiwen Dong, Siqi Fu, Yi Shen - Feb 2023) **:**

In this work we studied Catalytic ozonation for imazapic degradation over kelp-derived biochar: Promotional role of N- and S-based active sites. The key point is Biochar rich in N and S derived from kelp biomass (KB) has been synthesized. Acid or base activation of KB enhanced its HCO performance. Rate constants k O3, IMZC ; kOH, IMZC, and k 1O2, IMZC have been determined. Graphitic N and thiophene S played critical roles in enhancing HCO performance.

2. Remediation of pesticides in commercial farm soils by solarization and ozonation techniques (C.M. Martínez-Escudero, I. Garrido, C. Ros) **:**

In this paper we researched Remediation of pesticides in commercial
farm soils by solarization and ozonation. It was deduced that the combination of solarization and ozonation treatment was efficient for all the studied pesticides both in freshly and in aged contaminated soils, being the lower degradation values found for the second type. This low removal suggests that the increase of pesticides & adsorption on soil resulting from ageing decreases their availability.

3. Catalytic ozonation of toluene and dichloromethane mixture at low temperatures over modified MnOx-based catalyst (Xiaoxiang Wang , Tong Wei , Yuce Wen , Chunya Yang **) :**

The research paper is about Catalytic ozonation of toluene and dichloromethane mixture at low temperatures over modified Mn-ox-based catalyst. Herein, toluene and dichloromethane were selected as the research objects to simulate the industrial exhaust VOCs gas, which were degraded over MnOx-based catalysts by catalytic ozonation in this work. The effects of carriers and K modification on the catalytic performance were systematically studied and then the preferable formula was optimized. Meanwhile, the relationship between structure and activity was established according to a series of characterization experiments. Ultimately, the degradation mechanisms of toluene and dichloromethane were tried to illustrate.

4. Fe-Mn-Cu-Ce/Al2O3 as an efficient catalyst for catalytic ozonation of bio-treated coking wastewater: Characteristics, efficiency, and mechanism (Run Yuan , Yihe Qin, Can He , Zichen Wang - Nov 2022)**:**

In this study, a Fe-Mn-Cu-Ce/Al2O3 catalyst was prepared, characterised, and used for the catalytic ozonation of bio-treated coking wastewater. To this end, the effects of different parameters on the catalytic performance of the Fe-Mn-Cu-Ce/Al2O3 catalyst (a) were analysed, and the catalytic mechanism for the degradation of organic pollutants in bio-treated coking wastewater (b) was elucidated. Furthermore, (c) a pilot-scale test of the catalytic ozonation of bio-treated coking wastewater was conducted, (d) the reusability of the catalyst alongside the operation cost of the pilot scale test were both evaluated, while the degradation kinetics and removal behaviour of organic pollutants in bio-treated coking wastewater were elucidated.

5. Activated sodium percarbonate-ozone (SPC/O3) hybrid hydrodynamic cavitation system for advanced oxidation processes (AOPs) of 1,4-dioxane in water (Kirill Fedorov, Manoj P. Rayaroth , Noor S. Shah – Dec 2022**) :**

This study was performed with the following objectives: i). to investigate the degradation of 1,4-dioxane in SPC/O3 process under hydrodynamic cavitation (HC); ii). to understand the synergy in HC/SPC/O3 the degradation kinetics of 1,4-dioxane in sole and coupled processes; iii). to identify the reactive species in HC/SPC/O3 by quenching experiments using specific radical scavengers; iv).to perform the degradation under environmental relevant conditions varying pH and in the presence of inorganic anions; and finally, v).to identify the transformation products and elucidate the mechanism of 1,4-dioxane degradation in HC/SPC/O3.

6. Synergistic effects of simultaneous coupling ozonation and biodegradation for coking wastewater treatment: Advances in COD removal, toxic elimination, and microbial regulation (Bin Cui, Shaozhu Fu , Xin Hao – 2020**)**:

This study aims to explore the feasibility of the SCOB for treating real coking wastewater, especially COD removal, toxicity elimination, and microbial regulations. To investigate the degradation characteristics of refractory organics in the SCOB system, individual biodegradation and ozonation systems were also established. The performance of COD removal and toxicity elimination for different systems were compared, and the long-term stability of the SCOB system was studied. Furthermore, the microbial community and metabolism regulations were elaborated, and the contribution of ozonation to coking wastewater treatment was analyzed. Finally, the synthesis mechanism of ozonation and biodegradation was revealed. This study confirmed the promising
potential of the SCOB process for treating highly polluted industrial wastewater.

7. Techniques for remediation of pharmaceutical pollutants using metal organic framework - Review on toxicology, applications, and mechanism (Baskaran Sivaprakash, Natarajan Rajamohan, Dhanapriya Singaram Ohan – Dec 2022) : In this research paper of an experiment, it is described that metal organic frameworks (MOF) have been proved to be promising materials used as stand-alone or combined technique. Special focus is given on the abatement of norfloxacin and ofloxacin contaminated wastewater using MOFs by adsorption, ozonation, photocatalytic degradation, electro-fenton methods, etc. Metal organic framework materials exhibit excellent adsorptive and photocatalytic properties due to the unique capability of forming ions and radicals for the treatment of organic pollutants and more particularly, the pharmaceutical contaminants.

8. Ozonation of Selected Pharmaceutical and Personal Care Products in Secondary Effluent—Degradation Kinetics and Environmental Assessment (Fátima Jesus, Eva Domingues, Carla Bernardo, Joana L. Pereira –Dec 2022)**:** In this study showed that ozonation is, indeed, an efficient process to remove contaminants from the water, highlighting that the time required to achieve a complete removal will increase as the complexity of the water matrix increases being higher in a Muncipal Wastewater than in ultrapure water.

9. Catalytic ozonation mechanisms of Norfloxacin using Cu–CuFe2O4 (Lanhe Zhang, Yiran Li , Jingbo Guo – Jan 2023) **:** This study talks about a new strategy for the modification of CuFe2O4 catalysts and provides new insights into the catalytic ozonation mechanisms for NOR removal. A novel CuFe2O4 catalyst with Cu 0 doping to improve electron transfer efficiency and CTAB doping has been developed to optimize the performance of CuFe 2 O 4 as a catalyst in the NOR removal process. Here, CCFO-2 catalyst was prepared and used to catalyze the ozonation of NOR. Optimal NOR removal efficiency was 81.58% and k obs was 0.03967 min -1 with 0.1 g•L -1 CCFO-2 dosage and 2.72 mg•L -1 O3 concentration at an initial pH of 7.

10. Calcium-based catalyst for ozone catalytic oxidation for advanced treatment of high salt organic wastewater (Gaoyan Shao, Zhiyong Zhou, Yuming Tu, Jianjie Chen – Sept 2022)**:** In this work Al2O3-PDA-SA-CaxOy catalyst was prepared and it showed a higher treatment performance for salt organic wastewater, and the removal efficiency of COD was enhanced from 29.81 % to 66.39 % compared with single ozonation. The carboxyl group in SA was cross-linked with Ca2+ for loading more metal Ca, and the N-doped graphitic carbon layer was obtained by PDA carbonization. The surface morphologies of Al2O3 support and Al2O3-PDA-SA-CaxOycatalyst were characterized by SEM.BET technology was used to analyze the specific surface area, pore volume, and pore diameter of the Al2O3 and Al2O3-PDA-SA-CaxOy catalyst.

11. Treatment of saline organic wastewater by heterogeneous catalytic ozonation with Al2O3-PEC-CaxOy as catalysts (Feng Liu, Yuming Tu, Jianjie Chen, Gaoyan Shao – Jan 2023) **:** In this study Al2O3-Pectin-CaxOy (Al2O3-PEC-CaxOy) was prepared as catalysts to improve the treatment of saline organic wastewater the removal rate of COD (62%) was significantly increased for Al2O3-PEC-CaxOy catalyst.Here the surface of Al2O3 carrier was coated with pectin, and calcium was loaded as the metal active substance. The carbonlayer formed after calcination increased the adsorption performance of Al2O3-PEC-CaxOy catalysts and contributed to the removal of organic pollutants. The result showed the Al2O3-PEC-CaxOy catalysts was good for long term use and economical.

12. Degradation of oxytetracycline and doxycycline by ozonation: Degradation pathways and toxicity assessment (Jeong-Ann Park, Marco Pineda, Marie-Line Peyot – Jan 2023) **:** In the study, a lower O3 inlet gas concentration supplied at a flow rate of 0.27 L/min, was shown to be more effective at removing OTC than the same dose of ozone applied at higher inlet gas .The DTC degradation was less efficient than for OTC and required twice amount of ozone. OTC inhibition ratio was increased to 37 % (5-min) and 46 % (15-min) within 1 min of ozonation.. Several TPs showed toxic effects .The aromatic ring hydroxylation and ring-opening pathways would cause less harm .

13. Catalytic ozonation of phenol by magnetic Mn0.7Ce0.3Ox/CNT@Fe3C (JingWang , Li Ma, Zhengwei Pan and Tingyun Li – Dec 2022): From the research paper we can understand the removal of refractory organic pollutants using ozonation with the help of Mn-Ce bimetallic oxide. Ozonation is a advanced oxidation process for the removal of refractory organic pollutants for water treatment. It was found that the reaction of bimetallic oxide will have a synergetic effect that the monometallic metal oxide. Apllying the use of carbonnanotubes can help accelerate the reduction of metal Ce and will also increase the rate of electron transfer. The magnetic property of bimetallic oxide Mn0.7Ce0.3Ox/CNT@Fe3C makes it easy to recycle and reuse, which is suitable for the treatment of wastewater.

14. Efficient catalytic ozonation over Co-ZFO@Mn-CN for oxalic acid degradation: Synergistic effect of oxygen vacancies and HOO-Mn-NX bonds (Menglu Xu, Yibing Zhang, Huaqin Yin, Jinnan Wang – Jan 2023) **:** Based on the above research we can understand that the catalyst Co-ZFO@Mn-CN with abundant of OVs and Mn-CN sites was synthesized for O3 activation, which could efficiently degrade organic pollutants. Doping of CO in ZnFe2O4 was used for activation of peroxymonosulphate(PMS) where , the OVs not only provided active site for PMS adsorption but also acted as a medium for the electrons transport from organics to PMS. In this process a large amount of O3 was generated due to which 70-100% of the organics could be mineralized with the help of ozonation.

15. Destruction and entrainment of microplastics in ozonation and wet oxidation processes (Carmen Solís-Balbín, Daniel Sol, Amanda Laca, Adriana Laca – Dec 2022) **:** The research explains the involvement of Ozonation and Oxidation to remove the MPs in water bodies which are constantly adding up in water pollution. MPs are found everywhere on our planet that there are not places free of this contaminant, which is even transported by the air and are harmful to our environment.Processesmainly photodegradation, photocatalysis, biodegradation, wet oxidation and ozonation are using in removing MPs from the water bodies.

3. CRITICAL ANALYSIS OF SELECTED RESEARCH PAPER

3.1 INTRODUCTION

Emerging micropollutants have been recently the target of interest for their potential harmful effects in the environment and their resistance to conventional water treatments. Catalytic ozonation is an advanced oxidation process consisting of the formation of highly reactive radicals from the decomposition of ozone promoted by a catalyst. The author has investigated the catalytic performance of bimetallic oxide ($CuFeO_2$) towards peroxymonosulfate activation. It has been found that the stability of bimetallic $CuFeO_2$ was significantly higher than the monometallic (Cu or Fe) oxide because of the synergistic effects. It was deduced that the construction of Mn-X bimetallic oxide could generate a synergistic effect and improve the activity and stability of a Mn-based catalyst in catalytic ozonation

1. **Did the author indicate why the study was undertaken?**
   Yes, the research aim to describe the purpose of the study. The author has investigated through experimental analysis and deduced appropriate results for carrying out the research.
2. **Was the background information provided adequate to understand the aims of the study?**
   Yes, it provided that the reader with critical information about the topic being studied such as, highlighting and expanding upon foundational studies conducted in the past, describing important existing literature that inform why and in what ways the research is conducted.

3.2 MATERIALS AND METHODS

1. **Were the methods described in sufficient detail for others to repeat or extend the study?**
   Yes, the methods described for preparation of catalyst and its use for ozonation is specified properly. However, they could have considered to study on other parameters such as BOD and COD which are also required to measure the degree of pollution.
2. **If standard methods were used, were adequate references given?**
   Yes, references given were adequate enough to understand the methods and preparation of compounds.
3. **If methods were modified, were the modifications described carefully?**
   No, the methods for modifications aren't mentioned in the paper. Eg- Instead of MnCeO as catalyst they could have used Cu-YO, Cu-AgO or other Bimetallic Oxides. However the paper did mention its purpose to use MnCeO as catalyst.
4. **Have the authors indicated the reasons why particular procedures were used?**
   Yes, the Authors have mentioned the purpose of all particular procedures. Eg- the reason to use Mn-X as catalyst instead Cu-X is because of its higher stability during chemical reactions
5. **Have the authors indicated clearly the potential problems with the methods used?**
   No, the authors have only provided the preparations and methods for ozonation, they haven't mentioned the potential problems faced by them.
6. **Have the authors indicated the limitations of the methods used?**
   Yes, the authors have indicated the limitations for various processes such duration, temperature and pH required for preparation of catalyst.
7. **Have the authors specified the statistical procedures used?**
   Yes, the authors have given statistical procedures using various line graph plots.
8. **Are the statistical methods used appropriate?**
   Yes, the statistical method seems to be appropriate as the authors have mentioned the data of parameters used in the experiment.

3.3 DISSCUSSION

1. **Were the objectives of the study met?**
   The objective of this study was to find the catalytic performance of $Mn_{0.7}Ce_{0.3}O_x$/CNT@Fe_3C towards catalytic ozonation along with that the goal was also to find the effective mineralization and yes both of the goals were met.
2. **Do the authors discuss their results in relation to available information?**
   Yes the author discusses the results in relation to the available information as the paper has several reference to available information.
3. **Do the authors indulge in needless speculation?**
   No, the author was always on point and everything that was mentioned was relevant to the topic.
4. **If the results obtained were statistically significant, were they also biologically significant?**
   Yes, they were biologically significant and it is very clear from the mechanism and the observation which was given.
5. **If the objectives were not met, do the authors have any explanation?**
   All the objectives of the research were met.
6. **Do the authors adequately interpret their data?**

Yes, the author adequately interpreted their data, all the conclusions drawn from the experiment and observations were accurately interpreted.

7. **Do the authors discuss the limitations of the methods used?**
   No, the author does not talk about the limitations for this method. It only talks about how the method is effective without talking about the limitations.
8. **Do the authors discuss only data presented or do they refer consistently to unpublished work?**
   The authors majorly discussed about the present data and there were slight references to the previous research paper they had published.

3.4 RESULTS

1. **Were the experiments done appropriate with respect to objectives of the study?**
   Yes the experiments were successfully concluded on the basis of catalytic ozonation which was carried out based on the activity of the bimetallic oxide Mn0.7Ce0.3Ox/CNT@Fe3C
2. **Do the results obtained make sense?**
   Yes, the results obtained made a clear impact that the product is suitable to carry out waste water treatment analysis.
3. **Do the legends to the figures describe clearly the data obtained?**
   Yes, the data figures clearly describe the obtained product.
4. **Are the data presented in tabular form clear?**
   No, the data is not presented in a tabular form rather the amounts of chemical used are specified.
5. **Are the legends to the tables clear?**
   Yes, the legends are clear but are not provided in a clear table format.

3.5 OVERALL CONCLUSION

The conclusion arising from the paper is the use of bimetallic oxide Mn0.7Ce0.3Ox/CNT@Fe3C which can be used for waste water treatment by generating a synergistic effect and thus removing the haloacids concentration which is harmful for the health. Past studies and the mentioned experiments gave a clear idea on the topic and all the objectives of the research were met. The tabular data format and step wise procedures could have given some greater impact on the paper.

CONCLUSION

Ozone can be effectively used for the treatment of municipal and industrial waste water.Extensive research in application of ozone investigating the stoichiometry of reaction, reaction kinetics, reaction regime, mechanism of reaction has made possible to apply ozone safely in different fields of wastewater treatment. The application may be pre ozonation, post ozonation or solely Ozonation. Ozone is a powerful oxidant, leaves no residual harmful products, no sludge disposal problem and increases the DO content of wastewater which helps further in the degradation of residual pollutant. Therefore, ozone finds use in treatment of all types of waste such as municipal waste water, industrial waste water, contaminated ground water, treatment of swimming pool water, treatment of paper industry waste water, dye industry waste water, removal of colour, treatment of gaseous effluent, treatment of cyanide waste water, treatment of heavy metals, elimination of phenolic compounds etc. and specially as strong disinfectant. All these properties have made ozone as an ultimate treatment for all types of waste water treatment.

Most industrial wastewater and drinking water exhibit variable characteristics. It becomes difficult to treat them to acceptable limits. Often complex formation is found in waste water due to the use of different chemicals. All the conventional methods of treating the waste water results in partial removal of pollutants. Therefore the effluent is not safe for discharge in river stream or on land. Treatment with chlorine is an effective method but recent studies shows that it forms THM and chloramines that are carcinogenic in nature. Ozone is a good oxidant as seen from different studies. In the recent years the use of ozone has become more popular.

The oxidation potential and reactivity of ozone is exceeded only by fluorine. Ozone is capable of sterilizing all forms of bacteria and virus. The reaction with virus is so fast that it is difficult to study analytically. In the case of sewage treatment plant it causes destruction of filamentous bacterial growth and avoids bulking of sludge and foam formation. After treatment, the water can be used for gardening purposes. Ozone increases the life of biological activated carbon process. Ozone is quite effective in the removal of SS and turbidity. Application of ozone in treatment of swimming pool water eliminates the pink eye problem. Industrial applications include treatment of paper mill waste water, dye unit, toxic waste water, cyanide bearing wastewater, elimination of heavy metals, treatment of phenolic waste water etc. Ozone reacts with molecules responsible for colouration breaks the functional groups that have high electron density. Unfortunately, in India the practice of using ozone has not yet started. This may be due to high cost of treatment. In the near future India has to adopt the ozone technology as it is most effective method for eliminating the different water borne diseases.

FUTURE SCOPE OF WORK

In recent years, near surface ozone pollution, has attracted more and more attention, which necessitates the development of high efficient and low cost catalysts. In this work, CuO/Cu2O heterojunctioned catalyst is synthesized by heating Cu2O at high temperature, and is adopted as ozone decomposition catalyst. The results show that after Cu2O is heated at 180°C conversion of ozone increases from 75.2% to 89.3% at mass space velocity 1,920,000 cm3/(g·hr) in dry air with 1000 ppmV ozone, which indicates that this heterojunction catalyst is one of the most efficient catalysts reported at present. Catalysts are characterized by electron paramagnetic resonance spectroscopy and ultraviolet photoelectron spectroscopy, which confirmed that the heterojunction promotes the electron transfer in the catalytic process and creates more defects and oxygen vacancies in the CuO/Cu2O interfaces. This procedure of manufacturing heterostructures would also be applicable to other metal oxide catalysts, and it is expected to be more widely applied to the synthesis of high-efficiency heterostructured catalysts in the future.

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