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Ozonation of secondary industrial effluent for beneficial reuse

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ABSTRACT

One of the most important pollutants in industrial towns is wastewater, which, with the right amount of purification, may be utilized to replace water shortages in the agricultural sector. The purpose of this study was to study the effectiveness of ozonation in removing contaminants from industrial effluent. The effluent from the industrial town's wastewater treatment facility was the subject of studies to determine whether it might be used in the town's green areas. Investigated was the efficacy of ozone in lowering chemical oxygen demand (COD), dye, digestive coliform, and total coliform in the effluent. The experiment was conducted with ozone dosages of 0.5, 1.5, 2.5, 4.5, 10, 15, and 25 mg/L·min and retention times of 2, 5, 10, 15, 30, 45, and 60 min. The optimal ozonation time and dose were found to be 25 mg/L·min and 60 min, respectively, which significantly decreased COD (18.6%), dye (82.1%), total coliform, and digestive coliform (100%), respectively. According to the findings, ozonation can be a good alternative to the chlorination approach since it greatly decreased the quantity of dye and coliforms in the effluent. ozone dosages of more than 25 mg/L·min or the utilization of an ozone generator with a higher power were required in order to further reduce the COD of wastewater. Finally, by comparing the effluent requirements to the Environmental Protection Organization Standards, it was concluded that the effluent is of appropriate quality for irrigation and agriculture.

Keywords: Ozonation; Industrial wastewater; Chemical oxygen demand; Dye; Microbial load

1. Introduction

One of the main environmental problems on a worldwide scale has been defined as water shortage. The problems with water demand and supply have been spreading around the world as a result of climate change, desertification, population increase, and urbanization [1,2]. The United Nations (UN) estimates that losses account for 17.3% of all renewable freshwater resources. The fact that this number varies throughout the various global areas reveals that water stress rates are above 25% in 5 out of 11 regions. Southern, Central, and Northern Africa have water stress ratings of 78%, which are considered to be severe and excessive [3,4]. Reusing treated wastewater (TWW) has been viewed as a viable solution for agriculture as well as for obtaining water security and management as a result of these growing issues [5,6].

Sewage production will increase as water demand increases. Raw sewage discharge into the environment diminishes surface and groundwater streams' quality and

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contaminates the ecosystem [7–9]. Each cubic meter of sewage has the potential to contaminate 40 to 60 m^3 of freshwater resources. To comply with environmental regulations, it is therefore required to eliminate or decrease these contaminants. Environmental contamination and disruptions to aquatic ecosystems and the food chain will result from the release of these wastewater into the environment if the treatment is not executed properly [10–12].

Reusing wastewater, as well as purification and recycling of used water, protect the environment. The presence of diverse combinations of rare elements, heavy metals, and microbes in wastewater has restricted their usage in a variety of industries [13,14]. Nevertheless, wastewater may be utilized in a variety of industries based on the kind and composition of the wastewater. Wastewater must be managed carefully such that biological problems do not endanger human health or the environment while yet allowing it to be a valuable resource for use in agriculture [15,16].

Freshwater discharge from urban and industrial sources can be easily used in agriculture with the right amount of treatment. Aquaculture and irrigation are two uses for treated wastewater in various nations across the world [17,18]. In many situations, the goal of industrial wastewater treatment is not only to save the ecosystem and water resources but also to recycle and repurpose treated wastewater in industrial operations. The majority of the time, industrial towns have a centralized treatment facility where industrial wastewater can be disposed of and treated, and if the required industry is situated there, it is feasible for the factories and industries to discharge wastewater to this facility [19–21].

In accordance with the design considerations of the town's treatment plant and present related regulations, manufacturers should in this situation discharge their wastewater to this treatment plant [22]. The standard for industrial towns' wastewater discharge to industrial treatment facilities, which is often used in Iran, is known as the "Effluent Standard for Industrial Wastewater Discharge to the Wastewater Collection System of Industrial Towns" [23]. After completing all purification procedures following the "Standard of the Environmental Organization Concerning Sewage Effluent", the purified wastewater may be used to irrigate green space or released into the environment [24]. Since water is used in so many different ways throughout industrial operations, it is possible to focus on the treatment of industrial wastewater to reuse water in the sector.

Industrial wastewater treatment often involves a combination of subsequent treatment techniques and equipment that may produce an output of the appropriate quality. The chemical precipitation method, advanced oxidation processes, and filtration are some of the most important physio-chemical and oxidation techniques in industrial wastewater treatment [25–27]. Ozonation is a cutting-edge technology that can replace wastewater chlorination since it is effective at decreasing viruses and parasites while still being environmentally benign. The oxidation–reduction potential of ozone is 2.07 V, making it a particularly effective oxidant [28]. Ozone (O_3) is the most effective choice for oxidation and disinfection due to its strong oxidizing capacity and the presence of oxygen molecules as a by-product. Higher concentrations of ozone lead to the oxidation and destruction of the virus's exterior protein coat. Additionally, the microorganism's DNA or RNA structure is impacted [29,30].

Approximately 1,000 ozone disinfection systems exist today, virtually all of which are employed to treat water sources (mostly in Europe). Ozone is frequently used in these facilities to manage taste, odor, and dye production. Ozone has previously been largely utilized for water disinfection, however, new developments in ozone generation and dissolving technology have enabled the utilization of ozone in wastewater disinfection more efficiently and economically with alternative agents [31,32]. In addition to controlling smells, ozone may be utilized in advanced wastewater treatment to separate soluble refractory organic compounds instead of surface adsorption with carbon [33].

The active industrial units in the industrial towns are very different, and as a result, the wastewater entering the town's treatment plant now contains a wide variety of contaminants from agriculture, the manufacturing of jams and pickles, sanitary wastes, etc. In order to properly treat the incoming wastewater, utilize the right treatment technology, and use the treated effluent for irrigation and agriculture, this volume demands consideration of the many types of wastewater that enter the treatment plant. To safeguard public health, avoid water source contamination, conserve the environment, repurpose treated wastewater, and treat the city's wastewater, various forms of wastewater must be collected, treated, and disposed of quickly in the modern day due to the increased environmental threats they provide. The government needs to actively consider and monitor the effective management of industrial wastewater. The purification of Ab Barik Industrial Town effluent, which is mainly utilized to irrigate green spaces and agricultural areas, as well as the need to reduce the allowed level of contaminants closer to environmental requirements, become viable alternatives to compensate for the shortage of water. Since there hasn't been any action done regarding the use of ozone to reduce pollutants in the water treatment plant of Ab Barik Industrial Town, the goal of this study has been to achieve the highest level of efficiency while taking into account the effectiveness of the ozonation process in treating the industrial town's wastewater as well as the necessity of paying attention to, utilizing, and returning water.

2. Materials and methods

2.1. Chemicals and instruments

The effluent from the water treatment plant in the industrial town was the subject of this applied experimental study, which was carried out on a lab scale in Shiraz's Parham Gostar Laboratory complex (Shiraz, Iran). All sampling and testing were carried out following the Hach technique [34] as well as the procedures detailed in the 23rd edition of the Standard Methods for the Examination of Water and Wastewater [35]. Sigma-Aldrich Company (USA) provided the required chemicals, including sulfuric acid (H_2SO_4), mercury sulfate ($HgSO_4$), silver sulfate (Ag_2SO_4), potassium dichromate (K_2CrO_4), lauryl sulfate broth culture medium, and EC broth culture medium. In this investigation, a Compact Ozone Generator (OZONEUF, Model No. 6-5-11015, FRANCE CO. LIMITED) was employed to produce ozone.

2.2. Sample collection

The wastewater from an industrial town treatment facility was investigated for this study. The raw sample was analyzed for chemical oxygen demand (COD), dye, and coliform in the Parham Gostar Laboratory after being sampled twice in a 4-L HDPE (high-density polyethylene) and sterilized glass container for microbiological analysis. To determine the optimum dose of ozone, the sample was exposed to a range of ozone exposures (0–25 mg/L·min), with the investigated parameters being measured for each dose. Fig. 1 depicts the steps of wastewater treatment in the industrial town, together with sampling and analyzing procedures.

The formulas below were used to calculate the elimination effectiveness [Eq. (1)]:

$$\text{Removal efficiency}(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

The parameter concentrations C_0 and C_t (mg/L) are indicated before and after contact time, respectively.

2.3. Chemical oxygen demand measurement

According to the Hach technique, COD was measured. To carry out the test, thoroughly homogenize the sample, transfer 2 cc of the sample into the specific COD vial, shake it, then place the vials in an oven set to 150°C for 2 h. A spectrophotometer (DR 5000) at a wavelength of 620 nm was used to measure the vials after they reached room temperature [34].

2.4. Microbial load count

For demonstrating fecal contamination in water samples, coliforms (CFU) are a suitable microbiological indicator. Since they only come from feces and not from other environments, a subset of coliforms is therefore identified and is known as fecal coliforms. Total coliforms (TC) are another name for coliforms in general, encompassing fecal coliforms (FC) and non-fecal coliforms. According to the Standard Methods for the Examination of Water and Wastewater, this test (searching and counting coliforms in water by multi-tube method) was conducted [35].

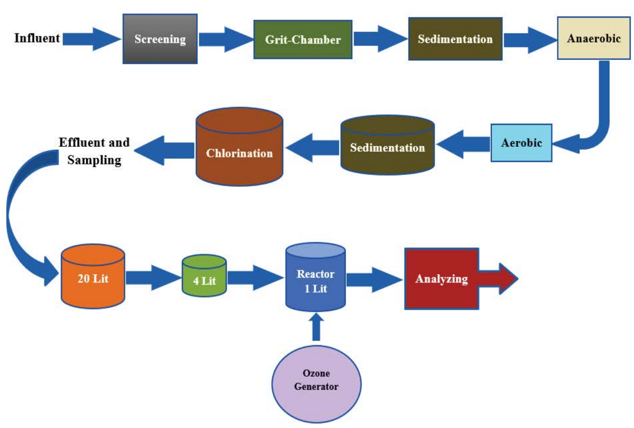

Fig. 1. Steps of wastewater treatment, sampling, and analyzing.

2.5. Dye measurement

The preferred technique for determining dye in municipal and industrial wastewater is the platinum-cobalt method. At a wavelength of 465 nm, this test was carried out using the Hach technique (Method 8025-color 465) [34]. In order to complete the test, the sample was filtered with Whatman Filter paper mm 47 and then poured into the glass tube of the spectrophotometer (DR 5000). The quantity of dye was then read in terms of Pt-Co units since even a tiny amount of turbidity generates apparent dye and mistakes and causes the true dye to be presented more than its value.

3. Results and discussion

3.1. Effect of ozone dosage

Ozone concentration is one of the most crucial factors in the amount of purification, disinfection, and pollution removal, as shown in Fig. 2. The elimination of total bacteria coliform and fecal coliform reduced from 1,100 to 0 CFU with the rise in ozone concentration from 0.5 to 25 mg/L·min, COD removal rate from 118 to 96 mg/L, and dye removal from 335 to 60 Pt-Co unit, which explains how ozone has excellent antibacterial and colorimetric properties, but as it turned out, the concentration of ozone did not considerably lower the concentration of COD. The low COD reduction might be caused by the ozonation of organic matter molecules, which produces tiny organic molecular components including acetic acid, aldehydes, and ketones that are not fully oxidized under the specified oxidative conditions and assist in the low COD reduction with ozonation concentration. The COD is strongly influenced by these tiny compounds, which ozonation cannot eliminate. Nevertheless, activated sludge technologies make it simple to biodegradation the substances that contribute to COD [36]. Ozone, which has one poor single bond and one powerful double bond, is an extremely potent oxidant. Molecular ozone can react as an electrophile or a nucleophile as a result of the interconvertible two-resonance structure of ozone. Ozone is a reactive gas that interacts with the components of wastewater in one of two ways: either as molecular ozone in a

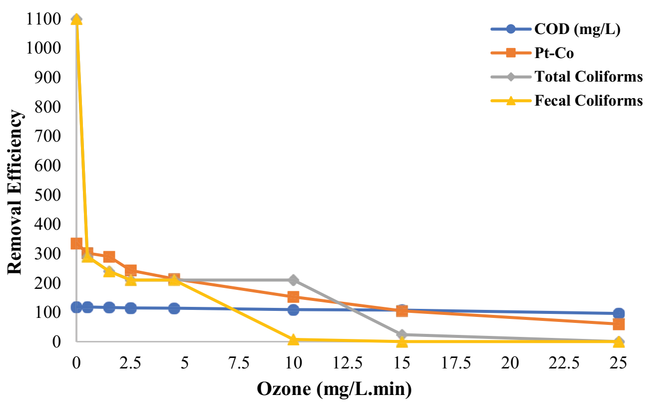

Fig. 2. Effect of ozone dosage on removal efficiency.

direct way or through the production of secondary oxidants including hydroxyl radicals (•OH) in an indirect way. The production of two distinct oxidation products results from these two distinct reaction pathways, which are governed by two distinct kinetic regimes. In general, the following processes [Eqs. (2)–(6)] can occur in wastewater and eventually result in the degradation of organic compounds [37,38]:

$$O_3 + OH^- \rightarrow {}^{\bullet}O_2^- + HO_2^{\bullet} \quad (2)$$

$$HO_2^{\bullet} \leftrightarrow {}^{\bullet}O_2^- + H^+ \quad (3)$$

$$O_3 + {}^{\bullet}O_2^- \rightarrow {}^{\bullet}O_3^- + O_2 \quad (4)$$

$$HO_3^{\bullet} \rightarrow {}^{\bullet}O_3^- + H^+ \quad (5)$$

$$HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2 \quad (6)$$

When ozone exposure rises for disinfection, bacterial membrane permeability and protein leakage during oxidation processes also increase, leading to bacterial mortality [39]. In a study, Ibáñez et al. [40] investigated the removal of contaminants in urban wastewater under advanced oxidation with ozone. The investigation in this study looked at up to 30 contaminants. The findings indicated that the majority of the chemicals undergo full or partial transfer during the wastewater treatment process. Also, it is quite effective in removing and, more specifically, lowering the concentration of the majority of current pollutants. A study by Beniwal et al. [41] on taste and odor control and removal of microorganisms by the enhanced oxidation process of ozone/H_2O_2 was conducted. In this study, the effect of pre-decontamination was investigated using O_3 and H_2O_2/O_3 on a pilot scale, with and without a filter, from two different substrates (granular activated carbon and anthracite), as well as geosmin and 2-methylisoborneol (MIB). At 10°C, 80% to 81% of the geosmin is removed when ozone is applied before activated carbon and anthracite. At 16°C, this elimination rose to 89%–90%. Under ideal circumstances, 0.1 mg/mg (H_2O_2/O_3) in conjunction with biologically active carbon (BAC) at 16°C resulted in MIB removal (67%). Research on the effectiveness of antibiotic removal in secondary effluent was undertaken by Zheng et al. [42]. At baseline levels of 10.4, 1,360 and 300 mg/L, respectively, it seems that an ozone dose of 657 mg/L (120 min of reaction) was sufficient to accomplish an oxytetracycline reduction of 96% and COD and biochemical oxygen demand decreases of 29% and 33%, respectively [42]. According to the findings of the Wu et al. [43] investigation, the treatment would be effective with an ozone dosage of 3.15 g/h (concentration 52.5 mg/L). The color, COD, and total organic carbon removal efficiency of 1 L of raw wastewater after 25 min of ozonation were 95%, 56%, and 40%, respectively, with an influent COD content of 835 mg/L [43].

3.2. Effect of ozonation contact time

Another factor influencing the removal rate of contaminants, COD, and microorganisms is ozonation contact time. In accordance with the obtained data, it was discovered that the COD removal rate decreased from 118 to 66 mg/L as the contact time increased, indicating the poor performance and prolonged contact duration of ozone in the reaction medium (Fig. 3). For the other parameters, the removal rate of the parameters has significantly risen with the prolonging of the ozonation contact time, with bacteria showing the greatest removal rate. The exposure of contaminants to ozone-produced radicals rises with longer contact times, which likewise enhances the removal efficiency. On the other hand, the presence of disruptive and radical scavengers in wastewater might inhibit the activity of these radicals and result in a minor decrease in the removal of wastewater contaminants [40]. Similar outcomes were found in Ahangarnokolaei et al. [44] investigation of the ozonation process's use in the treatment of textile effluent. They also discovered that the longer the contact period, the more effectively contaminants are removed by the ozonation process.

3.3. Comparing the quality of wastewater before and after ozonation

To ascertain the acceptable limits and standards of environmental pollutants in sewage and effluent for discharge to receiving sources, the sewage discharge standard, or the environmental organization's standard for the discharge of sewage or effluent, has been established and published for the entire nation [45–47]. According to the acquired findings, it can be shown that all of the values are within the permitted range by comparing the outcomes after ozonation with the wastewater output standard (Table 1). In general, it can be claimed that the wastewater generated after ozonation conforms with all regulations and is entirely suited for irrigation and agricultural uses.

3.4. Quality of the treatment plant's effluent in a year

The effectiveness of the wastewater treatment facility was also examined in this study throughout four seasons.

Table 1
Effluent quality before and after ozonation

Parameter	Before ozonation	After ozonation	Irrigation and agricultural standard
Chemical oxygen demand (mg/L)	118	66	200
Dye (Pt-Co)	335	60	75
Total coliforms (CFU/100 mL)	1,100	0	1,000
Fecal coliforms (CFU/100 mL)	1,100	0	400

Table 2
Efficiency of the wastewater treatment plant in four-season

Parameter \ Season	Spring	Summer	Autumn	Winter
pH	5.9	6.9	6.4	7.2
Chemical oxygen demand (mg/L)	137.6	145.8	146.5	162.2
Total suspended solids (mg/L)	70.7	74.8	61.3	64.7

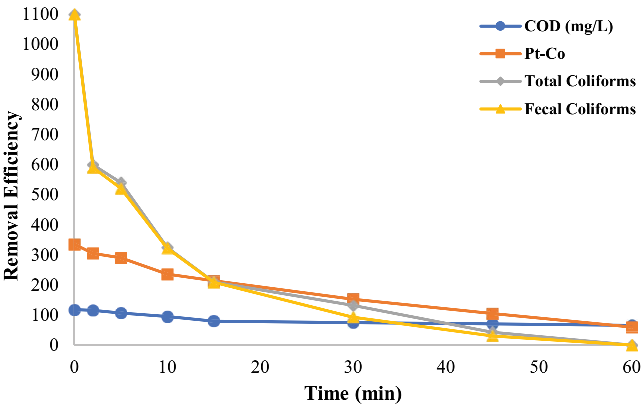

Fig. 3. Effect of contact time of ozonation on removal efficiency.

Table 2 demonstrates that the quantity of COD removal was much greater in the warm (spring and summer) than in the cold (autumn and winter) months of the year. This may be attributed to the bacteria's effective operation and healthy development throughout the typical treatment procedure at this treatment plant. Additionally, certain companies may produce more pollutants during peak working seasons like autumn and winter owing to their seasonality, which might affect the ability of the treatment plant to remove them. On the other hand, given that water usage rises throughout the colder months of the year, this might be the cause of the fall in total suspended solids concentration at these times of the year [48,49]. The findings of previous research that have been done on the effectiveness of industrial treatment facilities are consistent with those of the current study [50,51].

4. Conclusion

This study looked at how ozonation affected the COD values, dye, and microbiological load of industrial effluent. The findings indicate that ozone has little impact on lowering COD, and in this study, the reduction percentage was 18.6%, which is not a substantial decrease. Ozone is quite useful for lowering dye, and in one study, the outcome was 82.1%. The impact of ozone in lowering overall coliform in the ideal period of 60 min was extremely spectacular and 100%; for fecal coliform, the perfect time took 45 min, and the percentage decrease was 100%. Investigations of this treatment plant's seasonal variations revealed that it operates more effectively during the warm months of the year. Additionally, its suitability for irrigation and agricultural use was assessed, and its quality met EPA and WHO criteria.

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Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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