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Comparative Study of Biotreated Leachate Before and After Using AOPs Treatment for Removing COD, BOD and Color

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ABSTRACT

In this research, a comparative study of the treatment the biotreated (UASB-AERATED LAGOON) leachate effluent before and after using advanced oxidation processes The combined application of biotreated processes (UASB + aerated lagoon) and advanced oxidation processes (AOPs) for treating leachate effluent offers significant advantages. This integrated approach allows for efficient decolorization, outperforming the use of biotreated leachate alone. The UV/H₂O₂ process also yielded significant pollutant removal rates in biologically treated effluent, achieving up to 74% COD, 71% BOD and 52% color reduction. Among the AOPs studied, UV/H₂O₂ showed the highest decolorization efficiency, reaching up to 98%. Ozonation was particularly effective as a pretreatment for raw, untreated leachate, achieving substantial reductions 93% in color, 88% in BOD and 77% in COD. Additionally, ozonation of the initial leachate provided superior results in terms of decolorization, COD removal and BOD removal compared to other AOPs. The Photo-Fenton process emerged as the most effective AOP, delivering the highest removal efficiencies across all parameters, especially for COD (82%) and color (92%). Its efficacy is attributed to the synergy between UV light and the Fenton reaction, which generates abundant hydroxyl radicals. Notably, the photo-Fenton treatment achieved the highest BOD removal efficiency. The order of COD removal efficacy across AOPs was UV/H₂O₂ > UV > ozone > photo-Fenton. Although ozone proved highly effective for COD and color removal in the initial leachate, the performance of UV/H₂O₂ may have been influenced by the low pH level used. However, combining UV or H₂O₂ with ozone further enhanced decolorization rates. Overall, UV/H₂O₂ emerged as the most efficient AOP for both COD and color removal. Applying UV and H₂O₂ to biotreated leachate shows strong potential for industrial use. In conclusion, this study proposes combining biological processes with tailored AOPs for efficient landfill leachate treatment. Initial ozonation prepares raw leachate, while UV-based AOPs and the photo-Fenton process excel in later stages. Customizing AOPs based on leachate properties like pH and organic content boosts pollutant removal, reduces environmental risks and meets discharge standards, offering a scalable solution for leachate management.

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1. Introduction

Human life is inevitably associated with the generation of substantial amounts of waste and wastewater. Various methods, including dumping, incineration, recycling and sanitary burial, are employed in different regions to manage waste and effluents based on the volume of waste and available technologies. Open dumpsites, which are the oldest and most prevalent solid waste landfills globally, can significantly impact the environment and human health in negative ways. One of the contributors to this pollution is leachate, a highly contaminated wastewater produced during waste disposal. Leachate results from rainwater infiltration and the decomposition of organic matter within solid waste (Faridun et al., 2019). The characteristics and quantity of leachate depend on several factors, such as waste composition, dumpsite lifespan, waste material stabilization, compaction level, initial moisture content, rainwater infiltration rate, regional climate, season, temperature, evaporation, transpiration and on-site management practices (Costa et al., 2019; Salem et al., 2019). Leachate typically contains significant quantities of both organic and inorganic pollutants, ammonium, heavy metals, hazardous organic compounds, pathogenic microorganisms and toxic substances. Leachate is a critical factor in water source pollution (Shu, J et al., 2019). Leachate is one of the important factors that pollute water sources (Fallah et al., 2021; Rezaei et al., 2009).

Landfill leachate contamination is recognized as one of the major environmental health challenges in many developing countries, primarily due to the lack of cost-effective treatment technologies and regulatory standards for waste disposal (Alzamora BR et al., 2020). This contamination is driven by the rapid increase in municipal solid waste (MSW) generation globally, resulting in

an estimated production of 2.2 billion tons of MSW per year (Cetrulo TB et al., 2018). Unlike specialized waste disposal facilities, such as incinerators and recycling plants, engineered landfills are often seen as the most feasible solution for managing large volumes of MSW, as they can contain waste while reducing risks of groundwater, surface water and air pollution (Yatsunthea T et al., 2020).

Consequently, a significant number of countries, particularly China (0.1%) and members of the European Union, utilize landfills as their primary method for MSW disposal (Ozbay G et al., 2020). However, leachate can escape due to damage or chemical degradation of protective liners, such as high-density polyethylene (HDPE) geomembranes (Sauve G et al., 2020). The leachate produced in landfills poses substantial environmental and public health hazards due to the release of toxic substances, harmful microorganisms and noxious gases into groundwater and the atmosphere. Leachate is a dark, complex liquid containing various toxic organic and inorganic compounds, including microbial contaminants (Amoatey P et al., 2021). Common pollutants in leachate include dissolved organic compounds, trace ions, xenobiotic organics, ammonia and coliform bacteria (Ankit ShL et al., 2021). Additionally, leachate can release persistent organic pollutants, heavy metals and emerging contaminants into the environment (Nika MC et al., 2021).

In many developing countries, unsustainable production and consumption patterns have led to increased MSW generation, a rise in landfill sites and thus more frequent leachate contamination events (Siddiqi SA et al., 2021).

This poses a severe environmental and health risk, especially in regions lacking engineered landfill infrastructure (Baawain MS et al., 2020). Studies have shown elevated levels of lead (Pb), cadmium (Cd) and chromium (Cr) in groundwater samples, exceeding critical

thresholds and posing cancer risks due to leachate contamination (Teng C et al., 2021). Research by (Propp VR et al., 2021) also revealed high concentrations of heavy metals, such as nickel (Ni), cadmium (Cd) and manganese (Mn), in crops irrigated with leachate-contaminated surface water, which highlights a potential carcinogenic risk to humans and animals (Abiriga D et al., 2021).

To mitigate the environmental impact of leachate, efficient and affordable treatment methods are crucial (Parvin F et al., 2021). Given the complexity of leachate as a pollutant, preliminary treatments-such as coagulation-flocculation, air stripping and chemical oxidation-are necessary to reduce COD, total dissolved solids and overall toxicity (Iravanian A et al., 2020). For many years, conventional biological treatments and classical physico-chemical methods have been considered the most appropriate technologies for manipulation and management of high strength effluents like landfill leachates. There are many advantages of destructive technologies for the treatment of nonbiodegradable pollutants. The AOPs generate free radicals, which act as strong oxidants to destroy the organic pollutants. In AOPs, oxidant agents such as H_2O_2 , O_3 , UV and ultrasound Fenton, are used alone or in a combination (Sarria et al., 2002).

Latest investigations on the degradation of organic pollutants are focused on the combination of biological and physical-chemical treatments. This saves a considerable amount of energy in comparison with what is needed to achieve the full mineralization of the pollutants by chemical oxidation. Torres et al. (2003) and Marco et al. (1997) reported the degradation of generated chlorophenol from bleaching process during paper production by sequential biological-AOP using *T.versicolor* and $UV/TiO_2/Ru_xSe_y$ obtaining a 99% chlorophenol removal after 96 h and 20 min with a 97% reduction in chemical oxygen

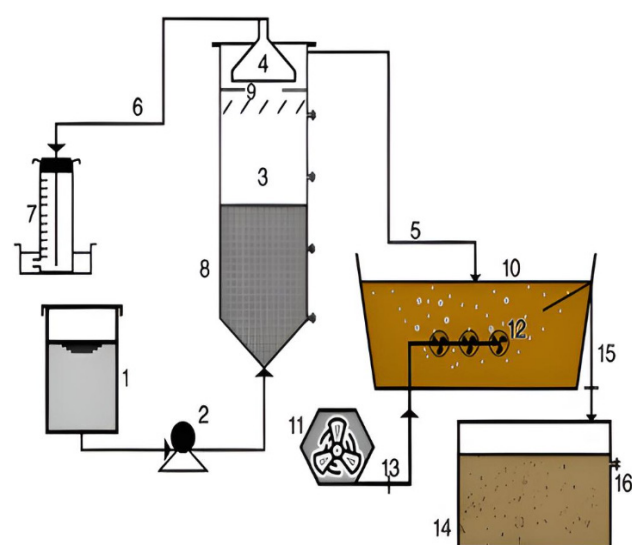
demand. A biological treatment does not prove to be so effective in color removal from treated leachate within permissible limits. Therefore, post treatment seems to be essential to bring anaerobically treated effluent to the recommended quality. In addition to these systems, advanced oxidation processes (AOPs) are the emerging post treatment options. The main advantages of AOPs include a lack of byproducts of environmental concern, high process rate and efficiency (Pedroza et al., 2007). These treatment processes are considered very promising methods for the remediation of pollutants containing non-biodegradable organic (Kos et al., 2008). Post treatment involves the application of UV and AOPs a schematic of chemical oxidation experimental set-up is presented in (Figure 2) in color and COD removal and disinfection of leachate. Post treatment is accomplished by UV and AOPs, including O_3 , H_2O_2 , UV/H_2O_2 , Fe^{+2}/H_2O_2 . According to Yasar et al. (2006), all processes show good performance for the removal of color and COD from the combined industrial biotreated (UASB) effluent. These systems are feasible to quickly remove both the parameters. AOPs (O_3 , H_2O_2/UV and $UV/H_2O_2/Fe^{+2}$) result in over 90% and 80% removal for color and COD, respectively, UV and Fe^{+2}/H_2O_2 results in slightly less color removal of 76% and 68%, respectively and COD removal 57% and 60%, respectively. Overall it can be said that the photo-Fenton process appears to be the most effective technology, whereas ozonation appears to be similar with proper optimal conditions for pH and temperature. In a study, advanced oxidation processes (AOPs) such as Fenton, ultraviolet light (UV), hydrogen peroxide (UV/H_2O_2) and photo-Fenton processes were investigated in laboratory scale experiments as an effective alternative for leachate treatment (Tikhe et al., 2014). The other study showed that the photo-Fenton process was the most effective treatment process under acidic conditions at pH 2.5 - 3.5 and produced a higher percentage of COD removal and color

removal. Although these techniques are not economically acceptable for the treatment of large-scale effluents, the combination of AOPs with a biological process could significantly decrease the overall cost of leachate treatment (Neyens et al., 2006). Fang and colleagues used an up flow anaerobic sludge blanket (UASB) reactor at 37 °C to treat landfill leachate. The process achieved COD removal ranging from 66% to 90% within a 6-day hydraulic retention time. The UASB effluent, containing 1500 mg/L COD, was then subjected to Fenton coagulation. By adjusting the initial pH to between 4-6 and using a hydrogen peroxide concentration of 300 mg/L, they achieved 99.3% COD removal in just 30 minutes (Fang et al., 2005). Literature review revealed that though the sequential biological and advanced oxidation techniques have been studied, there is no available literature on using UASB+Aerated Lagoon as the pretreatment step followed by AOP (UV/H₂O₂/O₃) process. The objective of this study was to compare the effects of AOPs on biotreated leachate performance in reduction (COD, BOD and TOC) and comparison conclusions with before using AOPs. In this work the sequential biological degradation-advanced oxidation process for leachate was evaluated. Biological degradation was carried out using laboratory scale (UASB-AREATED LAGOON) process and AOP in a batch recycle photochemical reactor.

2. Material and Methods

Samples were collected at specific time intervals from the reaction vessel and transferred into 5 ml glass vials. These vials were filled completely to avoid any headspace and then sealed using Teflon-lined silicon septa and screw caps. Immediate analysis was conducted on the samples to prevent any further reactions. The concentration changes of phenol were determined using a spectrophotometer (DR 2500, HACH) following established methods (Cortez et al., 2011). The initial and biotreated

solutions were also analyzed using the standard methods procedure, (Primo et al., 2008) pH measurements were carried out using a pH meter (Shu et al., 2006). To adjust the pH, 250 mL of leachate sample was mixed with H₂SO₄ to achieve pH values of 2.5, 3 and 3.5. The mixture was stirred for 15 minutes using a magnetic stirrer and pH testing occurred every 5 minutes. Once the pH stabilized, the sample was settled for 1 hour and supernatant samples were taken for COD measurements.



- | | |
|--------------------------|------------------------|
| 1. INLET TANK | 9. Deflector baffles |
| 2. Peristaltic pump | 10. Aerated lagoon |
| 3. UASB reactor | 11. Air blower |
| 4. Gas separator | 12. Air nozel |
| 5. Effluent outlet | 13. Air flow |
| 6. Gas outlet | 14. Sedimentation tank |
| 7. Gas collection system | 15. Lagoon outlet |
| 8. Sludge blanket | 16. Ultimate outlet |

Figure 1. Schematic view of the UASB Reactor, Aerated Lagoon and Sedimentation Tank

2.1. Experimental Setup

The schematic diagram of the experimental setup for biodegradation using an Upflow Anaerobic Sludge Blanket (UASB) reactor and an aerated lagoon is shown in (Figure 1). The UASB reactor, constructed from PVC material, has a cylindrical shape with a diameter of 15 cm and a height of 170 cm. Sampling valves are strategically placed at 20 cm intervals along the

vessel and the top of the cylinder serves as the gas outlet.

To initiate the reactor, approximately 4 liters of sludge obtained from activated sludge, which had been stored in a sealed container for one month, was used as inoculum material. This sludge was mixed with 7 liters of leachate diluted to a chemical oxygen demand (COD) of 1000 mg/L to provide necessary nutrients. The UASB reactor was also equipped with a peristaltic pump (KT-20, Model PDP-B-V, Italy).

Further details, including system specifications and operational information, please given in (Table 1).

Table 1. Characteristics of Bio Treated (UASB- AREATED LAGOON) Leachate

Leachate Parameter	Bio treated (UASB- AREATED LAGOON)
pH	7.6-8.3
Color (PtCo)	980
BOD ₅ (mg/L)	1960
COD (mg/L)	960

In the initial stage, diluted leachate with a COD concentration of 2000 mg/L entered the reactor from the bottom to the top, with a volumetric loading of 1 g/L/d. The hydraulic retention time (HRT) was 1 day. The organic loading of the system varied between 1 and 20 kg/m³/d of COD. The reactor pH ranged from 7 to 8, which is optimal for anaerobic microorganisms. We measured pH, COD, temperature and BOD. Due to faster results than BOD, COD measurements served as the daily indicator of pollution load in biological treatment. COD was determined using the digestion method with the HACH spectrometer DR-5000 (USA product). An aerated lagoon supplemented the anaerobic treatment system. The pilot study used a tank with dimensions of 0.5 × 0.5 × 0.5 m³, equipped with a barrier to

prevent short-circuiting. Lagoon ventilation was achieved by installing a diffuser at the tank bottom, maintaining dissolved oxygen levels at 2-3 mg/L. The aerated lagoon's effluent was directed to a sedimentation unit (0.2 × 0.5 × 0.5 m³) with a retention time of 6 hours. (Figure 1) illustrates the UASB reactor, aerated lagoon and sedimentation tank. To establish the aerated lagoon, we introduced 10 liters of fresh brown sludge from a sewage treatment plant with an active sludge system. To prevent organic shock, we gradually replaced the leachate with twice the pollution every 5 days until the COD reached 3000 mg/L. The aerated lagoon's mixed liquor suspended solids (MLSS) concentration was 3500 mg/L, suitable for aerobic treatment (Tchobanglous et al., 2019).

We investigated retention times of 2, 4, 6, 8, 10 and 12 hours by adjusting the flow rate to optimize organic compound removal. Dissolved oxygen levels in the lagoon were maintained above 3 mg/L. Total nitrogen (TN) and total phosphorus (TP) concentrations were determined using persulfate digestion and persulfate UV oxidation methods with the HACH spectrometer DRB-5000 (USA product). Portable meters (Partech 740 monitor and solitech 10 sensors) measured total suspended solids. Volatile fatty acids (VFA) were quantified following standard methods (5560 C) (APHA, AWWA et al., 1998). To calculate filtered Chemical Oxygen Demand (COD_F), samples were filtered using Whatman GF/C glass microfiber filters.

(Figure 2) depicts the experimental setup for advanced oxidation. The cylindrical reactor (250 mL volume) was made of quartz glass. A 125W UV lamp immersed in the glass tube provided irradiation. The lamp included a cooling water space within the reactor vessel. The reaction mixture filled the chamber between the reactor walls and UV lamp system, with an air bubbler ensuring suspension of the photocatalyst.

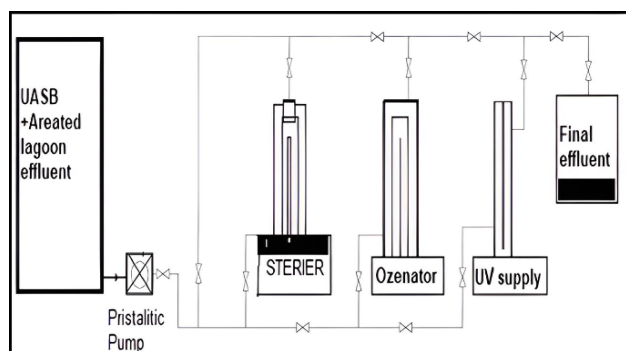


Figure 2. AOP Unit Used in the Experimentation

2.2. AOPS Setup

Ozonation was performed in a bubble column reactor made of plexiglass. The internal diameter and height of the reactor were 3.5 cm and 35.5 cm, respectively. Ozone was introduced at a rate of 100 mg/hr through a diffuser at the bottom of the reactor using an ozone generator (Enalay HGOZ 1000). Ozonation time varied from 5 to 25 minutes for solo experiments. For combined O_3/H_2O_2 experiments, 112 mg/L of H_2O_2 was added to the sample, followed by varying ozonation times. A hydrogen peroxide reactor consisted of a graduated Pyrex glass cylinder with a magnetic stirring setup. Analytical-grade hydrogen peroxide (35% w/w) from Merck was used and the H_2O_2 dose ranged from 112 to 373 mg/L. Additionally, peracetic acid was prepared in different concentrations (1%, 5% and 15%) following standard methods (Cortez et al., 2011). For each concentration, a fixed dose of 1 ml/L was used. UV irradiation, both alone and in combination with H_2O_2 (H_2O_2/UV), took place in a cylindrical reactor with an internal diameter of 3.5 cm and a volume of 330 ml. To enhance UV absorbance, the reactor was wrapped with aluminum foil (Figure 2).

A low-pressure mercury UV lamp (Pen ray 35C9 Upland, CA USA) with radiation intensity of 5 m W/cm² (at the surface of the lamp) and wavelength of 254 nm was used. The UV lamp was placed at the center of the reactor to ensure uniform distribution of UV irradiation and no lamp cooling was provided. All the experiments

were performed in batch mode and at ambient temperature. UV irradiation time was varied from 5 to 25 min for UV solo experiment and for H_2O_2/UV . 112 mg/L of H_2O_2 was added to the sample and then UV irradiation time was varied from 10 to 60 sec. Disinfection by solar radiation was undertaken using a rectangular (40×5×5 cm) reactor made of Plexiglas. (Table 1) show the characteristics of (UASB+ Aerated Lagoon) treated leachate.

2.3. Ozone

Ozone has proved to be a powerful oxidizing agent and its oxidizing ability is owed to nascent oxygen atoms and hydroxyl radicals. It reacts, directly or indirectly, with complex compounds, breaking them into simpler and smaller molecules. The ozonation process minimally generates toxic byproducts and its prior application to wastes also enhances their biodegradation (Sevimlim et al., 2004). Consequently, no additional disposal problems are associated with the ozone treatment technique. However, process conditions like pH, temperature, initial leachate concentration, ozone dose and exposure time influence the performance of the ozonation process (Arslan et al., 2001, WU et al., 2001).

According to (Yasar et al., 2007), ozonation shows best results for post treatment of anaerobically (UASB, AREATED LAGOON) treated effluent for color and COD removal as compared to the pretreatment of combined industrial wastewater of the same nature. However, the efficiency of the ozonation process increases at elevated pH while temperature shows an adverse effect on removal efficiency as an increase in temperature (>30°C) results in continuous decrease of color and COD degradation. The effect of ozone on COD and biodegradability of leachate is also dictated by reaction time. Many studies (Tizaoui et al., 2007) reported an overall increase in COD removal as the reaction time of oxidation increased. This is because of

higher ozone doses. For instance, COD removal increased from 4% at 5 min reaction time to 10% at 60 minutes at an inlet ozone concentration of 63 mg/L (normal temperature and pressure) (Cortez et al., 2011) COD removal was observed when leachate was treated for 60% instead of 20 minutes.

2.4. UV Light

Ultraviolet (UV) light plays a crucial role in breaking chemical bonds by providing the necessary energy. When UV irradiation interacts with molecules, it can cleave chemical bonds, resulting in fragmented by-products. These by-products may either degrade further or become excited and prone to oxidation. Even strong bonds, such as the double oxygen bond (O=O) in molecular oxygen (O₂) or the double carbon-oxygen bond (C=O) in carbon dioxide (CO₂), can dissociate due to UV exposure. High-efficiency UV lamps are essential for delivering the required energy in applications like leachate treatment processes. However, selecting the appropriate UV lamp pressure and radiation intensity involves balancing cost and efficiency requirements. The duration of exposure to UV light has a direct effect on the removal of color and COD (chemical oxygen demand) from leachate. Notably, the reduction in color depends on the initial concentration of leachate. Even when using a high-intensity UV lamp, significant improvements in color removal may not be achieved if the leachate concentrations are already high. UV systems offer several advantages, as highlighted in numerous studies. These benefits include compact design, ease of operation, low maintenance requirements, rapid treatment and the absence of disinfection byproducts. However, it's essential to recognize that UV disinfection alone does not provide residual protection and bacteria can become reactivated after a few days of treatment (ZHOU et al., 2002).

2.5. UV/H₂O₂

The use of ultraviolet light in combination with hydrogen peroxide enhances the rate of generation of free radicals OH^{*} significantly. This occurs because UV light supplies energy required for the dissociation of H₂O₂ into hydroxyl radicals. Photolysis of aqueous hydrogen peroxide has been investigated by many researchers (Yasar et al., 2007). In the UV/H₂O₂ process, photon energy is high enough to break the chemical bonds of the organic compounds which enables the process to treat leachates that contains different organic contaminations. A low concentration of H₂O₂ did not generate enough OH^{*} in solution. Addition of H₂O₂ above optimum will lead to decrease in hydroxyl radical concentration due to free radical scavenging by the excess H₂O₂ (Chen et al., 1997).

UV/H₂O₂ process is efficient in mineralizing organic pollutants. A disadvantage of this process is that it cannot utilize solar light as the source of UV light due to the fact that the required UV energy for the photolysis of the oxidizer is not available in the solar spectrum (Neyens et al., 2003). Moreover, H₂O₂ has poor UV absorption characteristics and if the water matrix absorbs a lot of UV light energy, then most of the light input to the reactor will be wasted. Finally, special reactors designed for UV illumination are required, while residual H₂O₂ should be addressed (Crittenden et al., 2005). The major factors affecting this process are the initial concentration of the target compound, the amount of H₂O₂ used, leachate pH, presence of bicarbonate and reaction time. Specifically, the kinetic rate constant for the degradation process is inversely proportional to the initial concentration of the pollutant. As a result, leachate dilution should be done at an optimum level (Gogate et al., 2004). Moreover, there is an optimum concentration for H₂O₂. Beyond this limit, the presence of H₂O₂ is detrimental to the degradation reaction due to scavenging action.

2.6. Fenton and Photo-Fenton Processes

Fenton and photo-Fenton oxidation processes are effective for treating bio-treated leachate. The photo-catalytic treatment process efficiency is significantly higher than the simple Fenton process for bio-treated leachate as photo-Fenton provides almost complete color removal and significant COD reduction (BALCIOGLU I.A. et.al, 1999). The mechanism of Fenton's oxidation is based on the generation of hydroxyl radicals by the catalytic decomposition of the H_2O_2 in acidic media (Barusinski et al., 2000, Malato et al., 2007). Photo-Fenton process combining with aerobic biological processes have been successfully used for the treatment of saline industrial wastewater containing almost 0.6 g/l α -methyl phenylglycine (Mosteo et al., 2008). In that study, the optimal conditions were observed when 6 ml of H_2O_2 (70%) and 1 ml of $FeSO_4$ (0.5 M) were added to 50 ml of OMWW (reaction time = 6 days, pH = 4.2) (El-Gohary et al., 2008). In another study, Dias et al. (2000) investigated the use of Fenton process for the pretreatment of OMWW. COD removal up to 83% was achieved, at pH values ranging from 2 to 3 (initial COD = 23400 mg/L, reaction time = 90 min, $H_2O_2/Fe^{2+} = 10$). Fenton's oxidation has been applied for the pretreatment of landfill leachate. Petruzzelli et al. (2007) reported that under optimal conditions (initial COD = 10915 mg/L, reaction time = 120 min, $H_2O_2/Fe^{2+} = 13$ w/w, pH = 3.2) almost 50% COD removal was observed.

2.7. Application of Combined Systems

The mechanism of action of combined AOPs is not so straightforward. The application of an O_3/UV system enhances the disinfecting characteristics of ozone significantly (Benitez et al., 1996). However, it is desirable that UV irradiation should follow ozonation because simultaneous application of UV and ozone retards the efficacy of ozone due to the decomposition of ozone to molecular oxygen.

During the treatment of effluent by an H_2O_2/UV system, UV irradiation followed by H_2O_2 produces two hydroxyl radicals that react with organic contaminants or undergo an H_2O_2 decomposition-formation cycle. This decomposition formation cycle helps maintain nearly constant concentration of H_2O_2 during the treatment process (Zhouh et al., 2002). However, an excessive H_2O_2 dose may hinder the penetration of hydroxyl radicals because of its character to scavenge hydroxyl radicals (Glaze et al., 1987).

3. Results and Discussion

3.1. Ozonation

Ozone is commonly employed for leachate treatment due to its potent oxidative properties resulting from the decomposition of O_3 into nascent oxygen (O^{\cdot}) and hydroxyl radicals (Camel et al., 1998). Ozone effectively reduces pollutants (such as *Aeromonas salmonicida*, *Aeromonas liquidfaciens*, *Pseudomonas fluorescens* and *Yersinia ruckeri*) by up to 99%, even in systems containing suspended and dissolved particles. In a study, the impact of ozonation time on the removal of COD, color and BOD (biochemical oxygen demand) was investigated using 99.5% pure oxygen fed into the ozone generator. Initially, COD, color and BOD removal increased with ozonation exposure time, up to 25 minutes and then stabilized. This behavior can be attributed to variations in the susceptibility of different organic compounds to oxidation (Azbar et al., 2004).

Despite ozone being a highly oxidizing agent, pH values significantly influence COD removal, with higher pH values enhancing removal efficiency (Fallah et al., 2021).

Results suggest that initial leachate decolorization can be achieved efficiently at a constant pH of 6.2 through ozonation, achieving 62% removal within 25 minutes (Figure 3). Additionally, ozonation experiments on biotreated leachate effluent (from

UASB and Aerated Lagoon processes) were conducted at a constant pH of 6.2, using 5% ozone concentration and a pure oxygen supply of 1.5 l/min. These experiments yielded promising results: 93% color removal, 88% BOD reduction and 77% COD removal within 25 minutes (see Figures. 3, 4 and 5). Notably, the color removal initially increased with ozone dosage but reached a plateau, likely due to the prior reduction in leachate intensity through biotreatment.

The reactivity of ozone and its efficiency in leachate treatment depend on the nature and concentration of compounds present (Frontistis et al., 2008).

The higher COD values correspond to greater concentrations of oxidizable pollutants. Therefore, initial COD concentration plays a crucial role in ozonation effectiveness. Emphasize the Photo-Fenton process's potential for effective leachate treatment (Shu et al., 2005).

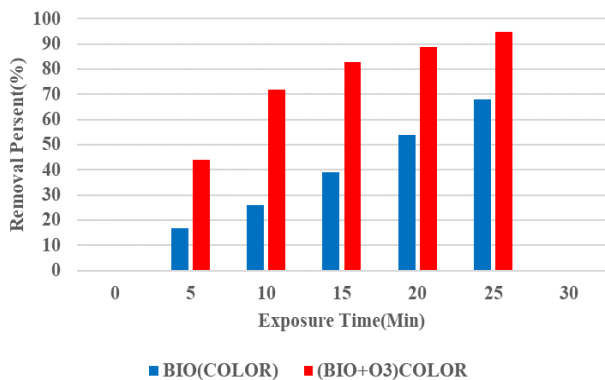


Figure 3. Removal of Color versus O₃ Exposure Time

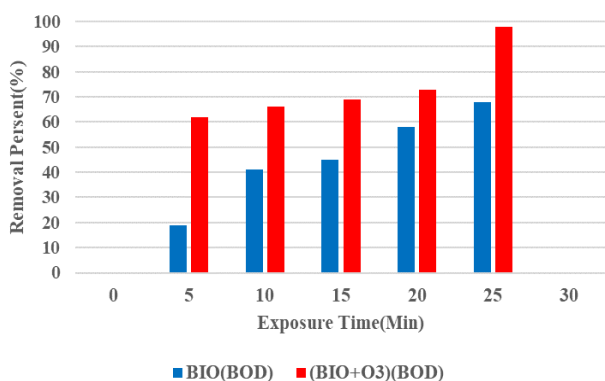


Figure 4. Removal of BOD versus O₃ Exposure Time

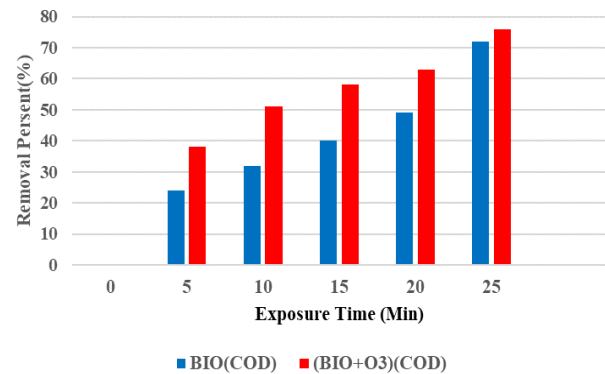


Figure 5. Removal of COD versus O₃ Exposure time

3.2. UV Radiation in Landfill Leachate Treatment

UV radiation has become a well-established method for treating landfill leachate, often paired with advanced oxidation processes (AOPs) to improve treatment outcomes. Leachate is a complex wastewater, typically containing various organic and inorganic pollutants, including colorants, that absorb UV light. This absorption can diminish the overall UV intensity and reduce treatment efficiency, especially in untreated leachate with high color intensity. Despite these challenges, UV irradiation has been effectively used for decades, particularly for disinfecting leachate effluents.

In one study, untreated landfill leachate was exposed to UV radiation alone, aiming to reduce levels of COD, color and BOD. The results showed that after 20 minutes of exposure, the highest removal efficiencies were observed: COD, color and BOD were reduced by approximately 32%, 28% and 37%, respectively (see Figures 6 and 7). Beyond the 25 minutes mark, however, the removal rates declined. This reduction in effectiveness may be due to the intense color of the untreated leachate, which absorbs UV light and interferes with the irradiation process. Generally, UV-supported treatments perform best with aqueous wastes that have lower color intensities, as high color levels can shield pollutants from UV exposure.

The study also explored the effect of UV radiation on leachate that had been pre-treated biologically through an upflow anaerobic sludge blanket (UASB) reactor and an aerated lagoon system. Applying UV radiation to this biotreated effluent produced significantly better results, especially in terms of color removal, with 82% decolorization, as well as strong reductions 84%, 71% in COD and BOD levels (see Figure 6). The improved effectiveness is likely due to the lower initial color intensity of the biotreated effluent, which allowed the UV light to penetrate more effectively and treat remaining contaminants. This finding highlights the importance of integrating UV radiation with pre-treatment steps for highly colored leachate, as it can enhance the overall efficiency of the treatment process.

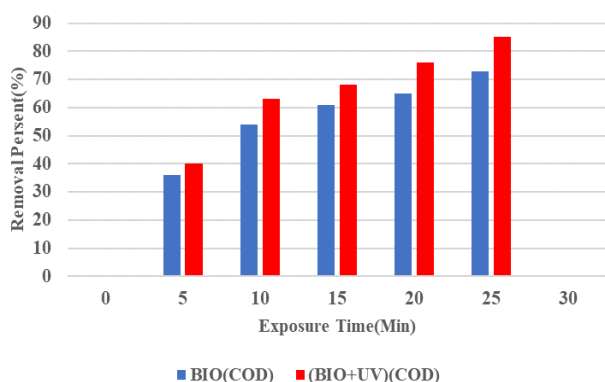


Figure 6. Removal of COD versus UV Exposure Time

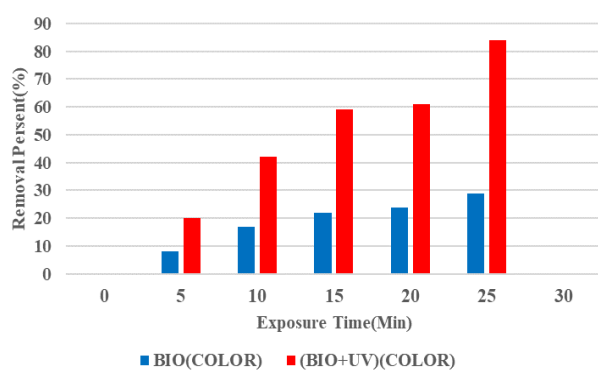


Figure 7. Percentage Removal of COLOR Exposure Time UV

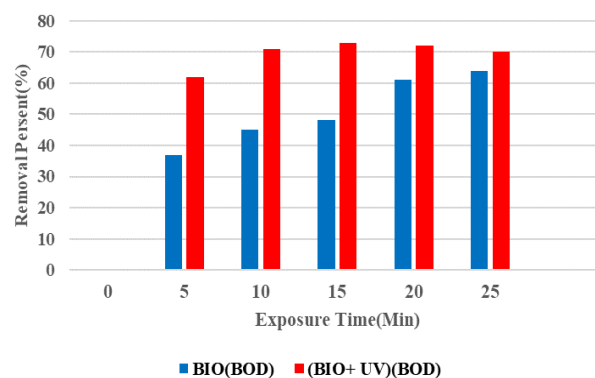


Figure 8. Removal of BOD versus UV Exposure Time

3.3. UV/H₂O₂

The utilization of the UV/H₂O₂ process for treating biotreated leachate yielded significant removal efficiencies for various pollutants. Specifically, the process achieved the following removal percentages:

- (COD): A remarkable 74% removal (as depicted in Figure 10).
- Color: An impressive 52% removal (as illustrated in Figure 11).
- (BOD): A substantial 71% removal (as shown in Figure 9).

The overall contaminant removal efficiency did not meet initial expectations, which may be attributed to the pH-dependent modulation of hydroxyl radical generation. This effect suggests that the production and availability of hydroxyl radicals, essential for effective UV-mediated decolorization, are influenced by solution pH. Enhancing decolorization performance may involve increasing the concentration of H₂O₂ or optimizing the operational parameters of the UV/H₂O₂ system to improve radical generation and sustainability of the oxidation process.

Interestingly, when applying this process to biotreated effluent leachate (from UASB+ Aerated Lagoon), the results diverged. After 20 minutes of exposure, color increased by 93% (see Figure 11) and after 25 minutes, an impressive 98% of color was removed (see Figure 11). However, the reduction in COD was

not linear over time. Initially, it rapidly decreased to 98% (within the first 20 minutes), but then it gradually declined to 95% (between 20 and 25 minutes, as shown in (Figure 10). This suggests that UASB-ARETED LAGOON-treated effluents may contain compounds that necessitate a more potent oxidizing system. Additionally, the BOD removal was 95% after 20 minutes (Figure 9) and decreased to 93% after 25 minutes (Figure 9). These findings underscore the necessity of tailoring AOP configurations to the unique characteristics of leachate, especially when dealing with effluents that may harbor complex, partially oxidized intermediates resistant to conventional treatment approaches. This nuanced approach to process design can significantly enhance the effectiveness of AOPs in handling variable effluent compositions.

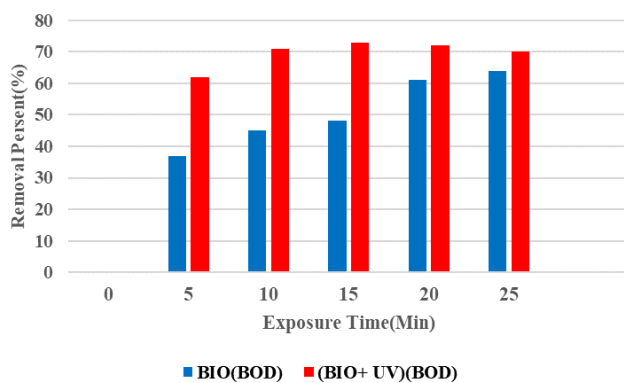


Figure 9. Removal of BOD versus UV/H₂O₂ Exposure Time

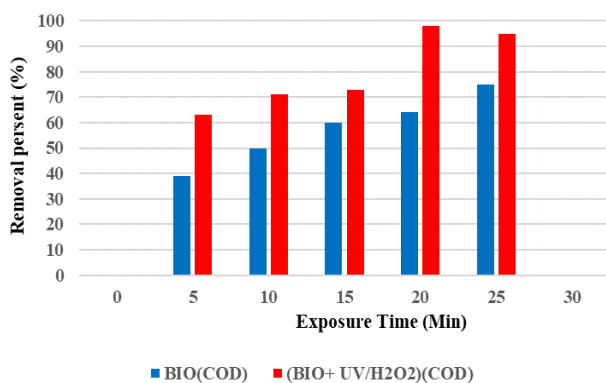


Figure 10. Removal of COD versus UV/H₂O₂ Exposure Time

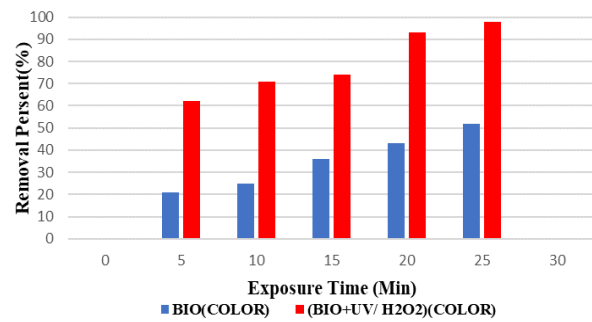


Figure 11. Removal of COLOR versus UV/H₂O₂ Exposure Time

3.4. Photo-Fenton Process

The Photo-Fenton process represents a significant advancement in oxidation technologies. In this process, various tests were conducted using a FeSO₄ concentration of 10 mg/L and a UV exposure time of 30 minutes. The results are:

Color Removal: In the treatment of biotreated leachate using the Photo-Fenton process, optimal color removal was observed after 25 minutes of UV irradiation. At this stage, color removal efficiency reached 49% (as shown in Figure 14), indicating a significant reduction in color intensity, which is a primary indicator of effective treatment.

(COD): The Photo-Fenton process also demonstrated high effectiveness in reducing COD levels. After 25 minutes of UV exposure, COD removal efficiency reached an impressive 63% (refer to Figure 13), underscoring the method's capability in breaking down organic compounds and reducing overall chemical pollution load.

(BOD): The treatment's impact on BOD levels was equally notable. Following 25 minutes of exposure, the process achieved 77% BOD removal (see Figure 12). This substantial reduction in BOD reflects the process's ability to degrade biodegradable organic matter effectively.

However, an intriguing phenomenon was observed when the Photo-Fenton process was applied to effluent leachate pretreated with (UASB) and Aerated Lagoon systems. The UV spectrum between 200-300 nm was found to

primarily disrupt biological substances, signifying the selection of an appropriate wavelength range for optimal degradation. After 25 minutes of UV irradiation, the percentage removal rates for color, COD and BOD were recorded as follows:

COD: 82% (Figure 13), Color: 92% (Figure 14)
Beyond this point, no removal efficiency was observed. These findings emphasize the Photo-Fenton process's potential for effective leachate treatment.

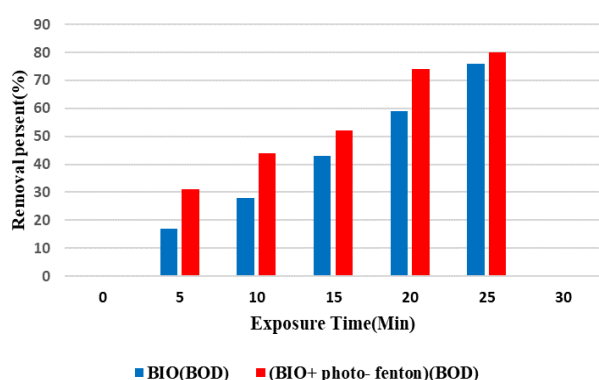


Figure 12. Removal of BOD versus Photo-Fenton Exposure Time

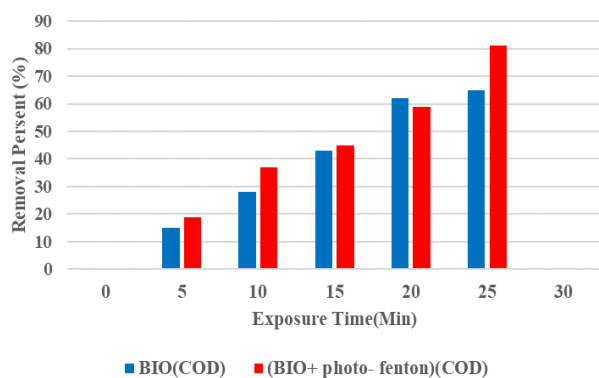


Fig. 13. Removal of COD versus Photo-Fenton Exposure Time

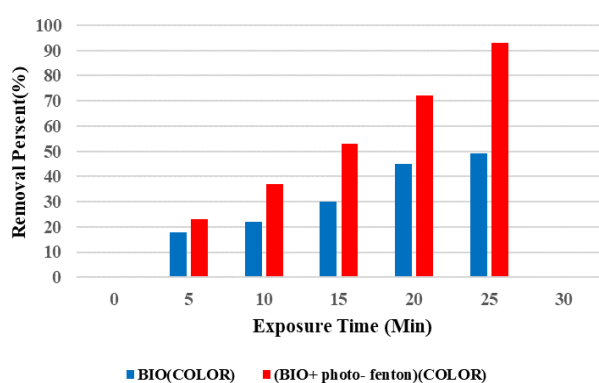


Figure 14. Removal of COLOR versus Photo-Fenton Exposure Time

4. Conclusion

The combined application of biotreated (UASB+ Aerated lagoon) and advanced oxidation processes (AOPs) for treating leachate effluent offers significant advantages. This integrated approach allows for efficient decolorization, surpassing the effectiveness of using biotreated leachate alone.

Ozonation was particularly effective as a pretreatment for raw, untreated leachate, achieving substantial reductions-93% in color, 88% in BOD and 77% in COD.

UV irradiation alone showed limited effectiveness on untreated leachate due to its high color intensity, which impedes UV light penetration. However, when applied to biologically pretreated effluent, UV irradiation achieved notable improvements, including up to 82% color removal and substantial reductions in COD and BOD.

The UV/H₂O₂ process also yielded significant pollutant removal rates in biologically treated effluent, achieving up to 74% COD, 71% BOD and 52% color reduction. The Photo-Fenton process emerged as the most effective AOP, delivering the highest removal efficiencies across all parameters, especially for COD (82%) and color (92%). Its efficacy is attributed to the synergy between UV light and the Fenton reaction, which generates abundant hydroxyl radicals.

The combined application of biotreated (UASB + Aerated lagoon) and advanced oxidation processes (AOPs) for treating leachate effluent offers significant advantages. This integrated approach allows for efficient decolorization, surpassing the effectiveness of using biotreated leachate alone. Among the AOPs studied, UV/H₂O₂ demonstrated the highest decolorization efficiency, reaching up to 98%. Additionally, ozonation of initial leachate resulted in superior decolorization, COD removal and BOD removal compared to

other AOPs. Notably, photo-Fenton treatment achieved the highest percentage removal of BOD. The order of COD removal across AOPs was $UV/H_2O_2 > UV > O_3 > \text{photo-Fenton}$. While ozone proved effective as a strong oxidizing agent, particularly for COD and color removal in initial leachate, UV/H_2O_2 's performance may have been impacted by the pH used (6.4). However, combining UV or H_2O_2 with ozone enhanced the decolorization rate. Overall, UV/HO_2 emerged as the most efficient AOP for both COD and color removal. Simultaneously applying UV and H_2O_2 to biotreated leachate holds promise for industrial implementation.

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مطالعه تطبیقی شیرابه تصفیه شده بیولوژیکی قبل و بعد از استفاده از AOP ها برای حذف COD و BOD و رنگ شیرابه

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چکیده

در این تحقیق به بررسی مقایسه‌ای تصفیه شیرابه خروجی فرایند (UASB - AREATED LAGOON) قبل و بعد از اکسیداسیون پیشرفته (AOPs) پرداخته شده است و شاخص‌های آلاینده مانند COD, BOD و رنگ با لحاظ نمودن pH و دما و زمان تماس در معرض اکسید کنندگان مانند: ازن، UV, H₂O₂/UV و فتو فنتون مورد مطالعه و بررسی قرار گرفتند. زمان‌های تماس ۰، ۵، ۱۰، ۱۵، ۲۰، ۲۵ و ۳۰ دقیقه فرایند اکسیداسیون مدنظر قرار گرفته است. در میان AOP‌های مورد مطالعه، UV/H₂O₂ بالاترین راندمان رنگ‌بری را نشان داد و تا ۹۸ درصد رسید. علاوه بر این، ازن زنی شیرابه اولیه منجر به حذف بهتر رنگ، COD و BOD نسبت به سایر فرایندهای AOP شد. به‌ویژه تصفیه با فتو فنتون بیشترین درصد حذف BOD را به خود اختصاص داد. ترتیب حذف COD در فرایند AOP عبارت بود از: UV/H₂O₂ < UV < O₃ < PHOTO FENTON. در حالی که ازن به‌عنوان عامل اکسیدکننده قوی مؤثر برای حذف COD و رنگ در شیرابه اولیه است اما فرایند UV/H₂O₂ در (pH = 6.4) بیشترین سرعت حذف رنگ را دارا بود و به‌عنوان کارآمدترین فرایند AOP برای حذف COD و رنگ ظاهر شد.

واژگان کلیدی: تجزیه، شیرابه زباله، تصفیه بیولوژیکی، اکسیداسیون شیمیایی