



Integrated Method of Ozonation and Anaerobic Process for Treatment of Atrazine bearing Wastewater

Saba Khurshid*, Abdur Rahman Quaff*† and Ramakar Jha*

*Department of Civil Engineering, National Institute of Technology, Patna-800005, Bihar, India

†Corresponding author: Abdur Rahman Quaff; arquaff@nitp.ac.in

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ABSTRACT

The paper presents the treatment of atrazine-contaminated wastewater by ozonation followed by an anaerobic process using Upflow Anaerobic Sludge Blanket (UASB) reactor. The experiment was performed with 100 ppb synthetic solutions of atrazine prepared in ultra-pure water. The corresponding initial Chemical Oxygen Demand (COD) is 226 mg.L⁻¹. The initial pH was adjusted to 9.5. The atrazine-bearing synthetic wastewater was ozonated with an ozone dose of 9.4mg/l for 40 minutes of optimum ozonation time, resulting in a 35% reduction in the initial concentration of atrazine. Along with atrazine reduction, there was a COD removal of 54.42%. Further, it was degraded with an anaerobic process, resulting in the final reduction in atrazine concentration of 81% and the corresponding removal in COD of 86.7%. The process of ozonation led to the mineralization of atrazine and enhancement in the biodegradability of the wastewater. Using ion chromatography, the ozonated wastewater sample was analyzed for ionic by-products before and after ozonation. The ion chromatography results showed the breaking of the atrazine compound and the formation of Cl⁻, NO₃⁻, SO₄²⁻, and F⁻ as intermediate products. Further, the BOD₅/COD ratio increased, reflecting the increased biodegradability. This ozonated wastewater was treated in a UASB reactor where the pesticide was degraded to 19 ppb, and COs degraded to 30 mg.L⁻¹. The overall removal of atrazine pesticide and COD were 81% and 86.7%, respectively, in the integrated system of ozonation followed by anaerobic degradation.

INTRODUCTION

The disposal from agrochemical industries contains many toxic substances of great environmental and health concern. This industry produces large amounts of organic wastewater with a significantly high COD. It has been found that pesticides are among the priority substances polluting water propagating to surface and groundwater (Philip & Ghosh 2006). In a monitoring program, pesticides have been widely noticed in European countries ranging from surface water to streams, rivers, lakes, reservoirs, and ditches (Oller et al. 2011). Some of these pesticides are recalcitrant, resistant to biological decay, and noxious for aquatic species. Among a wide range of recalcitrant chemicals released from this industry, atrazine is frequently found in water bodies worldwide (Philip & Ghosh 2006). It has been addressed as an emerging contaminant as it disrupts the endocrine system and is carcinogenic. The term "Emerging Contaminants" (ECs) has been defined in various ways. Still, fundamentally, it refers to any naturally occurring or artificial compounds that disrupt the endocrine system resulting in abnormal reactions. (Oller et al. 2011). Atrazine is among a series of an

s-triazine group of herbicides mainly used to control annual grass and broad-leafed weeds in maize, sorghum, pineapple, sugarcane, macadamia nuts, and many other crops (Philip & Ghosh 2006). It is also used on roadway grasses, golf course turf, and residential lawns. Due to its widespread use and solubility in water, it is found in surface and groundwater, exceeding its maximum contaminant level of 3 µg.L⁻¹ (Ghosh et al. 2005). The World Health Organization has established a limit of 2 µg.L⁻¹ for drinking water. (Ghosh et al. 2005). The European Union banned using atrazine as its degradation products remain in the soil even after 6 months (USEPA 2007). This reveals that it has a very high persistence in the environment. Atrazine is a pesticide commonly used as a model compound in research because it is a potential endocrine disruptor and is carcinogenic (USEPA 2007). Also, it remains hard to degrade due to its triazine ring, as shown in Fig. 1. (Mohammed & Mustafa 2017).

Atrazine is difficult to degrade with conventional coagulation, filtration, precipitation, reverse osmosis, etc., due to its high chemical stability and minimal biodegradability (Pathak 2011). Although biological

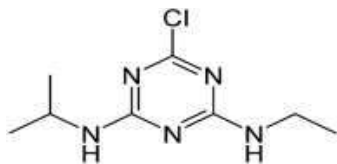
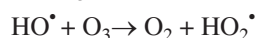
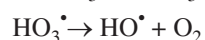
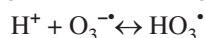
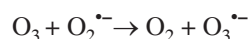
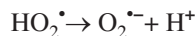
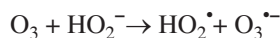
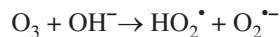


Fig. 1: Structure of atrazine.

processes are popular for treating such organic pollutants, many operational difficulties exist. Biological methods usually fail because of such toxic compounds as these compounds inactivate waste-degrading microorganisms. The low biodegradability of such compounds is another reason for low efficiency (Philip & Ghosh 2006). Removal of atrazine by adsorption is also considered a good technology. Still, the demerit is that the atrazine-contaminated wastewater from industries contains not only atrazine but also a large amount of dissolved organic matter, which decreases the adsorptive capacity of the adsorbent (Ghosh et al. 2005). There are studies on removing atrazine by aerobic and anaerobic processes, but they are neither efficient nor practicable because of operational difficulty (Ghosh et al. 2005). So the new idea is to partially pre-treat such toxic substances by Advanced Oxidation Processes (AOPs), forming more readily biodegradable intermediates (Covinich et al. 2014). Nowadays, ozone technology plays an important role in the degradation of refractory organic pollutants in an eco-friendly way (Hulsey et al. 2008). AOPs are chemical processes that are environmentally safe and prevent contaminants from moving from one phase to another. Rather, it degrades contaminants into harmless products in a short reaction time (Saleh et al. 2020). They can eliminate inorganic contaminants like cyanides, sulfides, nitrites, and dissolved organic contaminants, including halogenated hydrocarbons, volatile organic compounds, aromatic compounds, and nitrophenols, detergents, pesticides (Covinich et al. 2014). It can completely oxidize organic pollutants to CO_2 , water, and salts. AOPs are generally categorized as ozone-based treatment, electrochemical AOP (eAOP), ultraviolet (UV)-based treatment, catalytic AOP (cAOP), and photo AOP (AOP). The effluents from pulp and paper mills and those from the chemical, petrochemical, textile, and other sectors can be treated using AOPs (Oller et al. 2011). The ozonation-based process of AOPs plays an important role in water treatment and can degrade refractory organic pollutants in an environmentally friendly way (Saleh et al. 2020). Ozone, an oxidizing gas, interacts directly or indirectly with inorganic and organic substances by producing hydroxyl radicals. Ozonation's best performance occurs at alkaline pH (Wang 2020). At alkaline pH the molecular ozone and the oxygen radicals, including the hydroxyl radical are present which

reacts with almost all organic and inorganic compounds (Oller et al. 2011). The breakdown of ozone produces free radicals (HO_2^\bullet and HO^\bullet), which interact with various contaminants (Venkatesh et al. 2014). The mechanism of ozone decomposition at alkaline pH in aqueous solution is shown in the following equations.



The main factors affecting the ozonation process are pH, ozone dose, contact time, the type and amount of oxidizable organic compounds, the presence of ozone scavengers, and the ozone mass transfer (Oller et al. 2011). Numerous studies have looked at the use of ozone for the decomposition of pesticides and are well-reputed (Oller et al. 2011). Meijers et al. (1995) conducted a study on 23 pesticides using ozonation. Among them, six pesticides were removed efficiently: dimethoate, chlortoluron, diuron, isoproturon, motoneuron, and vinclozolin (Saleh et al. 2020). In another study, ozonation was used to degrade 40 pesticides (Ormad et al. 2010). Maldonado et al. (2006) conducted a study to observe the effect of ozone on five pesticides. In a study, when nano-ZnO (nZnO) was added to the ozonation process to remove atrazine from contaminated water, it was observed that the removal efficiency was higher than with the ozonation alone. The nZnO catalytic ozonation method successfully removed atrazine with an initial concentration between 0.5 and 5 $\text{mg}\cdot\text{L}^{-1}$. When the initial loading concentration was raised to 5 $\text{mg}\cdot\text{L}^{-1}$, the removal rate dropped to 90.2% (Pérez-Lucas et al. 2020). When ozonation was combined with UV light, it increased the removal of fluroxypyr to 92% (Saleh et al. 2020). Ozone helps to decompose detergents, chlorinate hydrocarbons, phenols, pesticides, and aromatic hydrocarbons (Derco et al. 2021). This literature shows that AOPs are powerful and efficient treatment methods for degrading recalcitrant materials or mineralizing stable, inhibitory, or toxic contaminants (Legrini et al. 1993, Venkatesh et al. 2015). At the first stage of degradation, AOP alters the compound's structure, making it more biodegradable. Further, it degrades the compound and reduces its toxicity. In the last step, it leads to the mineralization of organic compounds. Hence, AOPs can transform recalcitrant compounds into inorganic substances (CO_2 and H_2O_2) and lead to total and partial mineralization,

transforming them into more biodegradable substances. It has been reported that chemical oxidation for complete mineralization is usually expensive. Its combination with a biological treatment is widely reported to reduce operating costs (Covinich et al. 2014). Once these substances became biodegradable, it is treated through the biological process. The anaerobic process is more economical than the aerobic process. Among the anaerobic process, the UASB reactor has been extensively used to treat various wastewaters (Lettinga & Hulshoff Pol 1991, Ghosh et al. 2005). A number of aerobic and anaerobic treatment methods have been studied for the degradation of atrazine (Pathak 2011). But the bacterial culture in actual field is a difficult and is not feasible at all. Reports show that the anaerobic method is better than the aerobic method for aliphatic and aromatic compounds (Mandelbaum et al. 1993). Atrazine degrades more rapidly under anaerobic conditions than in aerobic environments (Kearney et al. 1965, Ghosh et al. 2005). Atrazine may completely degrade and mineralize through the economically viable method of biodegradation, which also yields simple chemicals like carbon dioxide, water, nitrogen, and organic materials (Baghapour et al. 2013). Biodegradation is the best method for eliminating atrazine and other herbicides from the environment. A study examined atrazine removal by two *Pseudomonas* bacteria (fluorescence and aeruginosa) and found that atrazine was significantly degraded by *Pseudomonas* bacteria (Baghapour et al. 2013). Combining biological and chemical processes may produce a more practical way to improve the treatability of refractory effluents by increasing the BOD₅/COD ratio (Oller et al. 2011).

MATERIALS AND METHODS

The herbicide 'atrazine' used in the experiment was of analytical grade from Sigma- Aldrich with a purity of 99.8%. All the chemicals used were of HPLC grade. Acetonitrile (99.9%) and methanol (99.7%) used were of HPLC grade of Merck company purchased from Angel Scientific. NaOH and H₂SO₄ were used for adjusting pH. Ultrapure water was prepared using a Milli-Q system. Sucrose (C₁₂H₂₂O₁₁), ammonium chloride (NH₄Cl), and potassium dihydrogen orthophosphate (KH₂PO₄) were used in the experiment and were of analytical grade.

Synthetic Water Preparation

An aqueous solution of atrazine was prepared by dissolving atrazine in Milli Q filtered water. This was to minimize the interferences and effects of any ozone-consuming impurities. The observed characteristics of the prepared synthetic wastewater are shown in Table 1. For ozonation, the pH was increased to 9.5 using NaOH.

Table 1: Characteristics of synthetic wastewater.

S.No.	Parameters	Observed values
1.	COD (mg.L ⁻¹)	226
2.	TDS (mg.L ⁻¹)	6.7
3.	pH	6.3
4.	Alkalinity (mg.L ⁻¹ as CaCO ₃)	40
5.	Conductivity (μS.m ⁻¹)	9.4
6.	Atrazine (ppb)	100

Analysis of Atrazine

The atrazine concentration was measured by Thermo Fischer SCIENTIFIC Ultimate 3000 HPLC (High-Performance Liquid Chromatography) using a reversed-phase C18 column of 250x4.6 mm with a particle size of 5 μm at a wavelength of 220nm. The mobile phase was acetonitrile: water (70:30 v/v) with a flow rate of 1mL.min⁻¹. The injection volume was 20 μL. The column temperature was set at 25°C. All the analytes were filtered through a 0.45 μm syringe filter.

Extraction of Atrazine

The extraction of atrazine was done by liquid-liquid extraction technique (Aslam et al. 2013). Samples were extracted using the QuEChERS method. 10 mL of sample was taken in a polypropylene 50 mL centrifuge tube. Then 10 mL of dichloromethane was added and vortexed for 45 seconds. Further, 3g of MgSO₄ was added to it and vortexed for 45 seconds. Then it was centrifuged at 4000 rpm for 10 min. After that, the supernatant was taken in a cleanup tube, vortexed for 45 sec, and then centrifuged at 4000 rpm for 10 min. Again, the supernatant thus obtained was evaporated to dryness at a temperature of 45°C. It was then redissolved in methanol for HPLC analysis (Dong et al. 2016).

Analysis of Intermediate Products after Ozonation

Ion Chromatography analyzed the sample for ionic components before and after ozonation. Analysis of sulfate, nitrate, chloride, and fluoride was performed using Ion Chromatography Model 882, Compact IC plus, Metrohm, Ltd. with Anion Dual 2 column Metrosep, 6.1006.530. The instrument was operated in suppressed conductivity detection mode using 50 mM H₂SO₄. The eluent was a mixture of sodium bicarbonate (NaHCO₃) and sodium carbonate (Na₂CO₃). The flow rate was 0.7 mL.min⁻¹. Each sample run was for 35 min and started with the injection of 20 μL of the sample. Before injection, the samples were filtered through a 0.22μm pore size syringe filter.

Ozonation Procedure

Ozone was generated from the air by an ozone generator

Table 2: Operating parameters of ozonation.

Parameters	Value
Gas flow rate (liters per minute)	1.5
Ozone concentration (mg.L ⁻¹)	9.4
The volume of the sample (mL)	500
Ozone output (g.h ⁻¹)	0.42

and an oxygen concentrator from Eltech company. Oxygen was supplied to the ozone generator through the oxygen concentrator, producing 93%±3% pure oxygen. The maximum ozone production capacity of the ozone generator was 10 gm.h⁻¹. The gas flow rate was fixed at 1.5 L.min⁻¹, and an ozone dose of 9.4 mg.L⁻¹ was supplied. The volume of the sample ozonated at a time was 500 mL.

The ozone output (P) was calculated using the formula shown in equation (1). The values are tabulated in Table 2.

$$P = (R * C * 60) / 1000 \quad \dots(1)$$

where,

P = Ozone output (gm.h⁻¹)

R = Flow rate of feed gas (m³.h⁻¹) or (LPM)

C = Ozone conc. (mg.L⁻¹)

The KI starch method was used to measure the amount of ozone in the feed gas (Baird et al. 2017). An ozone destructor destructed the residual ozone in the off-gas.

Anaerobic Degradation

A laboratory-scale UASB reactor made of transparent plexi glass of vertical cylindrical shape tube of 5 cm diameter with a total volume of 2.08 L was used for biological analysis. The UASB reactor has an effective working volume of 1.68 liters. The remaining 0.4 liters were kept for gas liquid solid (GLS) separation arrangement. The overall height of the UASB reactor was 1.06 meters, and the effective height was kept at 0.86 m. The biomass in the UASB reactor was conditioned sludge prepared using fresh sludge fed with sucrose as a carbon source at 300 mg.L⁻¹. The details of conditioned sludge are given in the next heading.

Seed Sludge

Fresh sludge collected from the UASB reactor from Barauni Dairy Plant, Bihar, India, was used as the seed sludge for this study. The sludge was fed with the synthetic wastewater from the start-up to the steady state condition containing sucrose, ammonium chloride, potassium di hydrogen orthophosphate (KH₂PO₄) in the ratio 300:10:1. The sludge was then acclimatized to the changed environment for 17 days as it was never exposed to atrazine earlier. The system was used for further experiments once the sludge got stabilized

Analyses

The line diagram for the integrated system is shown in Fig. 2. Standard methods were used to analyze the sample (Baird et al. 2017). The COD was measured by the closed reflux method, and pH was measured with a pH meter (PCS Tester 35). Atrazine concentration was analyzed through HPLC. The liquid-liquid extraction method was used for the extraction of atrazine. Every time 500 mL of prepared synthetic wastewater was taken for treatment. All the parameters and the atrazine concentration were analyzed for all the samples. The KI starch titration method measured the amount of ozone in the feed gas (Baird et al. 2017). Alkalinity and VFA were determined by the method suggested by DiLallo & Albertson (1961). Liquid displacement method adopted for collection of biogas in the anaerobic process.

RESULTS AND DISCUSSION

Reduction in COD

The oxidation of atrazine by ozonation led to the decline in the COD of the wastewater sample. As the ozonation time increases, the reduction in COD also increases. After a certain time, it was observed that COD removal was almost constant, as shown in the Fig. 3. From this result, it is observed that the COD reduction of 54.4% was observed after 40 min of ozonation. The COD of synthetic wastewater declined with certain ozonation times, whereas additional ozonation proved ineffective in reducing COD. Although in literature, it has been reported that COD content was found to increase with increased ozonation time due to the formation of tiny organic molecules such as aldehyde, ketones acetic acid, which are not completely mineralized (Venkatesh et al. 2015). Reduction in

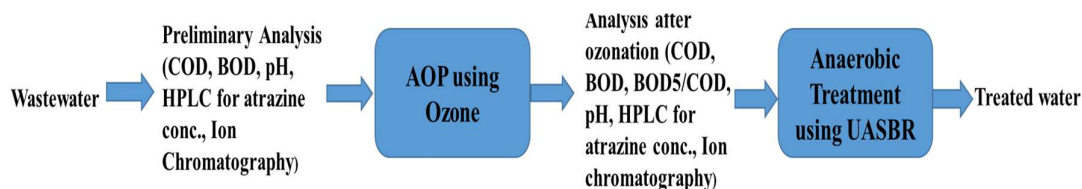


Fig. 2: Line diagram for an integrated system.

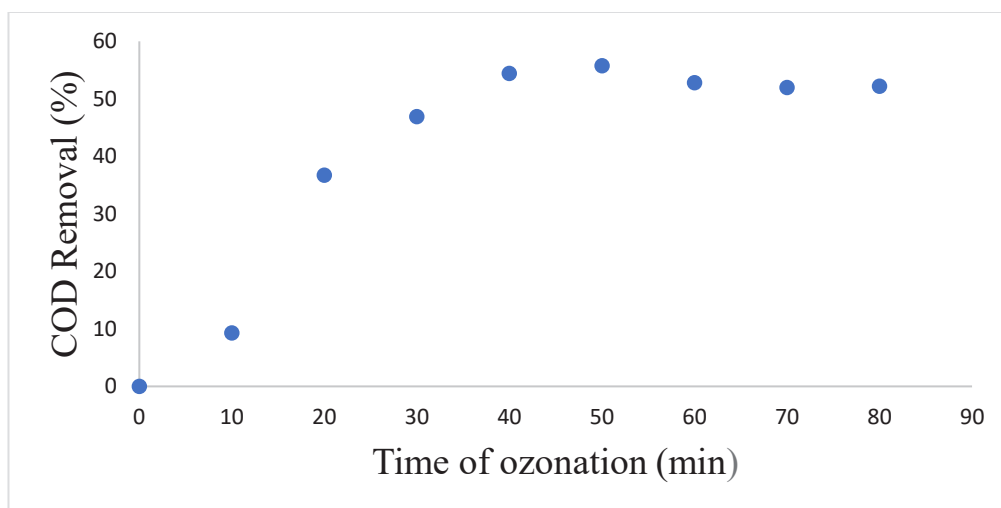


Fig. 3: COD removal Vs. Time of ozonation.

COD value led to partial oxidation but not full mineralization. The results reveal that ozone contact time had a notable effect on COD removal. The ozonated wastewater was treated with a UASB reactor for further reduction of COD.

The COD removal achieved after the anaerobic degradation was 86.7%, as represented in Fig. 7.

Enhancement of Biodegradability

The atrazine-containing wastewater inhibit the anaerobic biodegradation process in the UASB reactor. The ozonation process enhances these types of wastewater by increasing biodegradability. The enhancement of biodegradability can be checked by the increasing value of the BOD₅/COD ratio. The BOD₅/COD ratio of wastewater increased with ozonation resulting in enhanced biodegradability of ozonation by-product. Ozone treatment breaks long-chain compounds making them biodegradable (Oller et al. 2011). After 40 min of ozonation, the biodegradability ratio increased from zero to 0.27. An increase in the ratio of BOD₅/COD indicates an improved biodegradability of recalcitrant substrates. This indicates that ozonation changes the functional groups in herbicide to produce more biodegradable by-products, which are easily eliminated by biological treatment.

Mineralization of Atrazine

The removal of COD represents the mineralization of organic contents of atrazine. The untreated wastewater, as well as ozonated wastewater samples, were analyzed through Ion Chromatography (IC) for ionic components like fluoride, nitrate, chloride, and sulfate. The chromatogram obtained from IC is shown in Fig. 4 and Fig. 5. Ozonation resulted in the release of nitrogen atoms connected with triazine bonds of

atrazine molecules. Sulfate, chloride, and fluoride were found in unozonated and ozonated water samples. These anions show the presence of other chemicals in the unozonated water sample. Similar observation on the presence of anions in real wastewater has been reported by other researchers (Liang et al. 2009). F⁻, Cl⁻, SO₄²⁻ concentrations before ozonation were 0.015 mg.L⁻¹, 0.166 mg.L⁻¹, and 0.618 mg.L⁻¹, respectively. The concentration after the treatment was 0.062 mg.L⁻¹ F⁻, 0.335 mg.L⁻¹ Cl⁻, 0.143 mg.L⁻¹ NO₃⁻ and 22.205 mg.L⁻¹ SO₄²⁻ respectively. The formation of nitrate and increased concentration of other ions signify the degradation of atrazine into other compounds.

Ozone treatment is paired with a biological process to entirely remove the organic content of specific wastewater because treatment is typically not considered complete until compound mineralization is almost complete. In this regard, several research projects have also been conducted recently (Covinich et al. 2014).

Degradation of Atrazine

The concentration of atrazine pesticide decreased with the ozonation time. The rate of ozonation applied for this experiment is mentioned in the previous section, including materials and methods. The decrease in the concentration of pesticide was analyzed through HPLC. The retention time obtained for atrazine was 1.537 minutes. The identification and concentration of atrazine in the aqueous solution were based on the retention times and area of the chromatogram of the samples tested. The maximum atrazine removal was observed at 40 min of ozonation.

Further, ozonation has a very mild or no effect in removing atrazine. So, the optimum time of ozonation

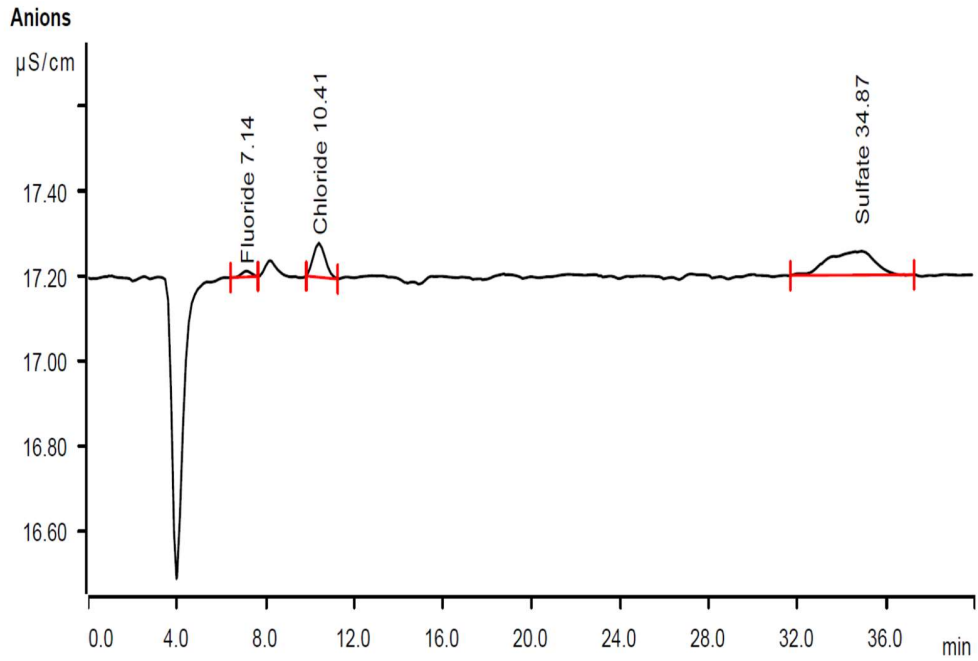


Fig. 4: Ions present in the synthetic wastewater before ozonation.

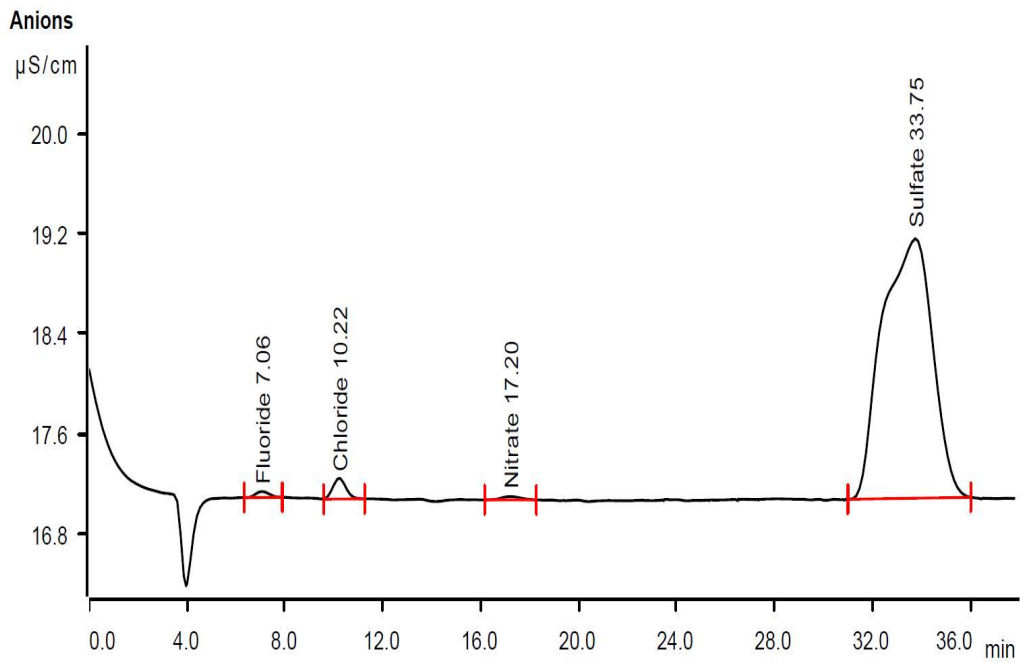


Fig. 5: Ionic product present in the sample after 40 minutes of ozonation.

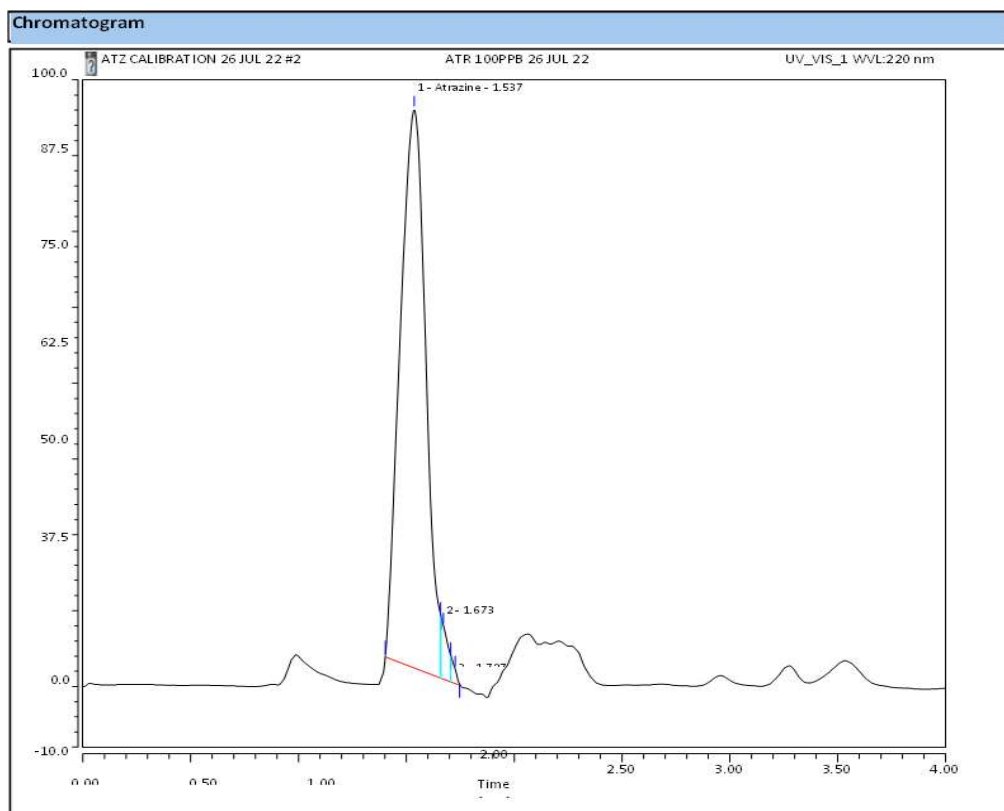


Fig. 6: A typical HPLC chromatogram (Area vs. Time).

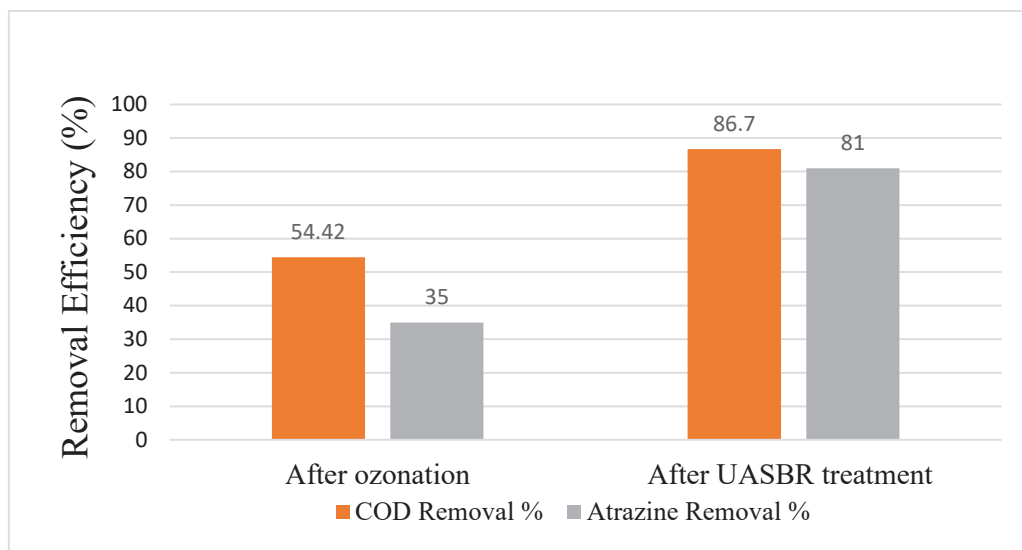


Fig. 7: Graph of removal efficiency of atrazine and COD.

adopted was 40 minutes. The HPLC chromatogram is also shown in Fig. 6.

The removal of atrazine concentration after ozonation was 35%. After the anaerobic treatment using UASBR, the removal of atrazine increases to 81%. The removal efficiency graph for COD and atrazine is shown in Fig. 7.

Observation for Removal Efficiency

Reactor Performance treating Atrazine-bearing Wastewater

The UASB reactor was maintained at a steady state condition. The Hydraulic Retention Time (HRT) was maintained at 16 hours. Initial COD removal was less at this operating condition, but the reactor could achieve more than 85% removal in almost 10 days of operation. After 17 days of operation, there was a COD removal of 86.7% and the corresponding atrazine removal of 81%.

Stability Parameters (pH, volatile fatty acids, and alkalinity)

The reactor's pH and VFA stayed well under the allowed limit. The pH was monitored daily and remained at 6.9-8.2. The VFA/Alkalinity ratio remained in the range of 0.19-0.27. The total biogas production was near about 130 mL.day⁻¹.

The alkalinity was measured daily, and VFA was measured intermittently. The results clearly showed that an integrated chemical and biological method is an effective way to reduce COD. Ozonation helped in the degradation of atrazine into biodegradable components. Hence, ozonation as a pretreatment is a potential process.

CONCLUSION

The results showed that the integrated process of ozonation and anaerobic degradation emerged as a boon for the removal of COD as well as atrazine concentration. The experiment results showed that the atrazine concentration decreased from 100 ppb to 19 ppb, and the corresponding COD value decreased from 226 mg.L⁻¹ to 30 mg.L⁻¹ after the combined treatment. Studies show that atrazine has been degraded efficiently through ozonation, but it was not economical. A new combination developed is economical, eco-friendly, and an efficient idea for the degradation of total organics. It can surely be considered for pesticide removal at the industrial level to treat agro-industry wastewater.

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