

# Treatment of Atrazine through Ozonation: Effect of Contact Time on COD and Atrazine Removal

Khurshid Saba, Quaff Abdur Rahman\* and Jha Ramakar

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

\*arquaff@nitp.ac.in

## Abstract

In this work, degradation of atrazine, an herbicide, is explored through the advanced oxidation process of ozonation. Ozonation can degrade organic as well as inorganic compounds. The study evaluated and analyzed the effect of contact time of ozonation on concentration of atrazine removal as well as chemical oxygen demand (COD) removal of the treated sample. The study also analyzed the effect of initial pH on COD removal. The synthetic sample prepared was having an initial concentration of atrazine as 100 ppb with corresponding COD as 203mg/l.

The atrazine removal efficiency was found to be increasing with the increase in ozonation time. Atrazine was observed to degrade more when the pH was alkaline. So, the initial pH was kept as 9.9 and the ozone dose was 9.8 mg/l. The optimum ozonation time was 40 minutes which resulted in COD removal of 55.40 % and atrazine removal of 36.33%. The results showed that atrazine is destroyed by ozone very rapidly.

**Keywords:** Atrazine, herbicide, advanced oxidation process, ozonation.

## Introduction

Pesticide industry is considered as one of the major pollutants to the environment due to its high COD of around 6000-7000 mg/l, BOD of about 2000-3000 mg/l, TDS of 12000-13000 mg/l and highly alkaline or acidic nature<sup>13</sup>. This industry generates highly polluted wastewater because it contains different types of pesticides, harmful chemicals, aromatic amines, organic chemicals with complex structures which are highly soluble in water. The accumulation of these pesticides and chemicals in the environment causes bioaccumulation and biomagnification which in turn are very harmful to human health. These harmful substances also affect other living organisms and aquatic life disrupting the whole ecosystem.

Hence the treatment and removal of pesticides from water sources has been an area of great interest to water companies and research scientists over a decade. The major industries that contribute in pollution of aquatic environment in India comprise of 57% pesticides, 15% surfactants, 17% pharmaceuticals, 7% personal care products and 5% phthalates<sup>12</sup>. These all contains many emerging pollutants. Atrazine is also among them which is regarded as a new

emerging organic pollutant and is frequently detected pesticide in water sources in an unacceptable range. It is considered as a priority pollutant by the European Commission<sup>11</sup>.

Atrazine has been selected for the present study because of its complex structure, solubility in water (33mg/l at 20°C) and difficulty in degradation by conventional methods. Atrazine is widely used for control of weeds and grass in maize, pineapple, sorghum, macadamia nuts, sugarcane and other crops<sup>7</sup>. Some of the pesticides similar to atrazine and of the same group are simazine, propazine and cyanazine. These pesticides belong to the triazine group of pesticide. Atrazine has a half-life period of approximately 200 days<sup>7</sup>. It has been found that atrazine and its intermediates persist in the soil even after about one year of application. This represents its ability to contaminate groundwater<sup>2</sup>.

Atrazine is carcinogenic and a potential endocrine disruptor and so its exposure has a very harmful effect on human and aquatic life. EPA has classified it as restricted use pesticide and has set its limit in surface water as 0.003mg/l<sup>6</sup>. The WHO has fixed its permissible limit as 2 µg/l in drinking water<sup>7</sup>. Some of the properties of atrazine are tabulated in table 1. Its use is increasing day by day and it is amongst the major products imported in India. Since atrazine is hard to degrade, so a lot of research work is being done to find a suitable method to treat this micropollutant. Basically, two advanced technologies are being explored extensively for these kinds of pollutants; first is adsorption and second is advanced oxidation processes (AOPs).

**Table 1**  
**Properties of Atrazine**

<b>IUPAC name</b>	<b>2-chloro-4(ethylamino)-6(isopropylamino) -s-triazine</b>
Empirical formula	C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>
Rel. molecular mass	215.69 g
Density	1.2 g/cm <sup>3</sup>
Boiling point	not distillable
Melting point	173-175°C
Vapour pressure	4 x 10 <sup>-5</sup> Pa
Solvolyis/solubility	Approx. 33 mg/L in water, 18 g/L (at 27°C) in methanol

AOPs are chemical methods that degrade organic substances into harmless products<sup>4</sup>. Since advance oxidation process of ozonation has been reported to be good for the treatment of organic as well as inorganic substances and has a lot of

advantages over other methods, so it is being implemented in treatment of water and wastewater. AOPs are of several types, for example O<sub>3</sub>, O<sub>3</sub>/UV, O<sub>3</sub>/UV/TiO<sub>2</sub>, Fenton oxidation and electro coagulation. Ozone based AOP has many benefits. First, it reduces the cost of other oxidants and catalysts required for treatment. Secondly, it is an effective way to reduce the COD for the compounds that cannot be completely oxidized by common methods.

AOPs are raising great interest for the removal of those organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability. The prime mechanism of AOPs function is the generation of highly reactive free radicals. The main advantage of ozone based AOP is that it does not produce more toxic compounds than removed ones and does not introduce foreign matter to the medium. It is highly reactive and has an oxidation potential of 2.07 eV while that of chlorine is 1.36 eV. In this method, oxidation of pollutant is done by oxidizing agent having an oxidation potential higher than oxygen.

The highly reactive free radical produced by the unstable gas ozone, which quickly degrades from O<sub>3</sub> to O<sub>2</sub>, is more stronger and less discriminating than chemical oxidants. It can therefore degrade a variety of organic contaminants in water (Eq. 2 and 3)<sup>8</sup>:



Ozonation process has two pathways: i) direct ozonation by molecular ozone ii) hydroxyl radical oxidation. Hydroxyl radicals ( $\cdot\text{OH}$ ) are very effective in destroying organic compounds because they are reactive electrophiles. Oxidation by ozone dynamically depends on the pH of the solution. Hydroxide ions enhance ozone decomposition under higher pH condition while in strongly acidic conditions the ozone decomposition is very insignificant<sup>10</sup>. The oxidation by ozone is directly affected by the solution pH<sup>1,18</sup>. From the literature, it is established that AOP of ozonation helps in decomposing pesticide and also eliminates toxic chemicals<sup>9</sup>. Ozonation results in the degradation of organic contaminants like herbicides, pesticides, pharmaceuticals<sup>16</sup>. In a study, the impact of ozonation on five pesticides was studied<sup>11</sup>.

Ormad et al<sup>14</sup> also studied the removal of pesticide by ozonation. The combination of physical or chemical methods with biological processes may be used as a working option for the treatment of pesticide containing wastewater<sup>5</sup>. Chemical methods have the ability to completely degrade the pesticide contamination during water and/or wastewater treatment. Ozonation has proven to be effective and promising tool in treatment of toxic and recalcitrant

chemicals<sup>16</sup>. It is a cost-effective technology if used judiciously. The main objective of this study is to explore the potential of ozonation for the treatment of pesticide industry effluent.

## Material and Methods

**Materials:** The pesticide used in this study was Atrazine of analytical grade from Sigma-Aldrich with purity of 99.8%. Acetonitrile (99.9%) and methanol (99.7%) used were of HPLC grade (Merck) purchased from Angel Scientific. NaOH and H<sub>2</sub>SO<sub>4</sub> chemicals used for changing the pH were from 'NICE' company. Ultrapure water was prepared using a Milli-Q system.

**Preparation of Synthetic Water:** Synthetic water was prepared using Milli-Q filtered water to minimize interferences and effect of any ozone consuming impurities. The characteristics of synthetic water are shown in table 2. Four different sets of samples having pH 3, 5, 6.9, 9.9 are prepared using NaOH and H<sub>2</sub>SO<sub>4</sub> to observe the degradation of atrazine at different pH. It is because it has been interpreted from the literature that degradation of atrazine increases by increasing pH<sup>10</sup>.

**Table 2**  
Characteristics of synthetic water

Parameters	Values
Atrazine concentration (ppb)	100
pH	3, 5, 6.9, 9.9
COD (mg/l)	203

**Preparation of Stock solution:** Stock solutions of 100 ppb, 200 ppb, 300 ppb and 400 ppb were prepared in methanol of HPLC grade. All the solutions were stored at 4°C.

**HPLC Operating Conditions:** Thermo Fischer SCIENTIFIC Ultimate 3000 High Performance Liquid Chromatography (HPLC) having ultraviolet detector and integrated with Chromeleon software was used for determining atrazine concentration before and after the treatment. Stainless steel reverse phase C18 analytical column of 250x4.6 mm with particle size as 5 μm from Thermo Fischer was used. Rheodyne injector was used for manual injection of samples. Operating conditions of HPLC were: Mobile phase was acetonitrile/ water in the ratio of 70:30 v/v at flow rate of 1 ml/min, injection volume was 20 μl and detection wavelength was 220 nm. The temperature of the column was set at 25°C. The concentration of the target pesticide was determined on the basis of the retention time and area of the analytes.

**Ozonation procedure and set up:** All the ozonations were conducted in a bubble column reactor made up of acrylic having a capacity of 1 litre. The ozone was produced by corona discharge type ozone generator (Eltech company) with capacity of ozone output of 10gm/hr from pure oxygen as feed gas. Oxygen was supplied to the ozone generator

through an oxygen concentrator (Eltech company) generating  $93\% \pm 3\%$  pure oxygen.

The initial ozone concentration was 9.8 mg/l and gas flow rate were 1.5 LPM. All experiments were conducted at the room temperature. An ozone destructor was connected to destroy residual ozone in the off gas which uses anhydrous  $\text{MnO}_2$  as a catalyst. The setup of the experimental procedure is shown in figure 1.

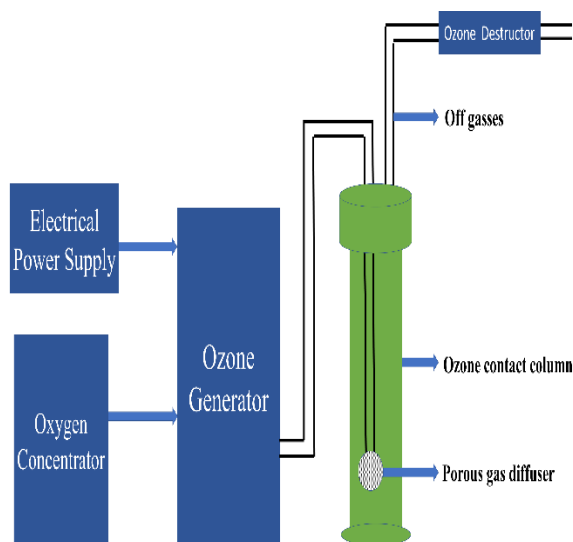


Figure 1: Schematic diagram of ozonation

**Analytical Methods:** For analysis of sample, standard methods were used<sup>15</sup>. The pH was measured with PCS Testr 35 (multi-parameter) from OAKTON company and COD was measured by closed reflux method. Every time 500ml of the prepared synthetic water was taken for the treatment. The variation in pH, chemical oxygen demand (COD), concentration of atrazine was analyzed for all the samples. The experiments were conducted consecutively for contact times of 10, 20, 30, 40, 50 and 60 minutes and samples were analyzed immediately. KI starch titration method was used for determining ozone concentration in the feed gas<sup>15</sup>. The amount of atrazine removal was analyzed with HPLC. All

the samples were filtered through Millipore membrane with  $0.45\mu\text{m}$  pore size.

## Results and Discussion

Ozonation has proved to be an effective method in degradation of atrazine. The pH as well as time of ozonation play an important role in ozonation. The sample was treated till the ozonation transformed the functional group of atrazine to produce more biodegradable products. The sample could have been treated up to the point when the concentration of atrazine in the sample reaches up to zero which means complete degradation. But then that would have involved very high cost. Here it has been degraded partially up to the point of increased biodegradability and keeping a check over the cost incurred because of ozonation.

**Effect of initial pH on ozonation:** The synthetic water was analyzed at four different pH. Samples with pH 3, 5, 6.9 and 9.9 were prepared using NaOH and  $\text{H}_2\text{SO}_4$ . It was done to study the effect of initial pH on ozonation. The samples were ozonated for a time of 30 minutes and COD reduction was calculated. Figure 2 shows the COD removal at different pH. The maximum COD reduction was observed when the pH was alkaline. So, for the rest of the experiment, pH was kept as 9.9. At high pH, hydroxide ion enhances the ozone decomposition and formation of hydroxyl radicals<sup>3</sup>. It has been observed that rate constant of the reaction of atrazine with ozone is lower than that with  $\bullet\text{OH}$  which indicates that atrazine reacts faster with  $\bullet\text{OH}$ <sup>19</sup>. The pH of the sample reached near to neutral after ozonation. The decrease in pH suggests that the by-products formed are acidic in nature.

**Effect of ozonation on pesticide concentration:** The concentration of atrazine before and after treatment has been analyzed through HPLC. The chromatogram obtained by analyzing analytical standard of atrazine has been shown in figure 3 and calibration plot obtained from HPLC is shown in figure 4. The retention time of atrazine was obtained at 1.483. The HPLC was run at gradient mode and with mobile phase containing as acetonitrile: water (70:30 v/v).

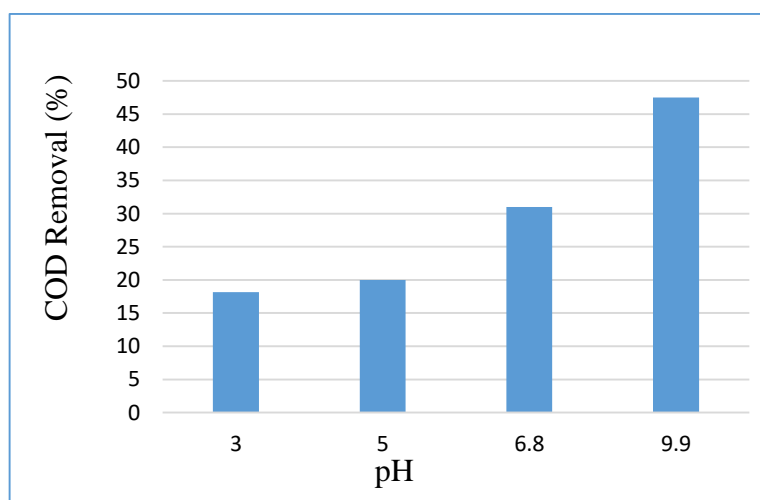


Figure 2: Variation in pH with increase in ozonation time

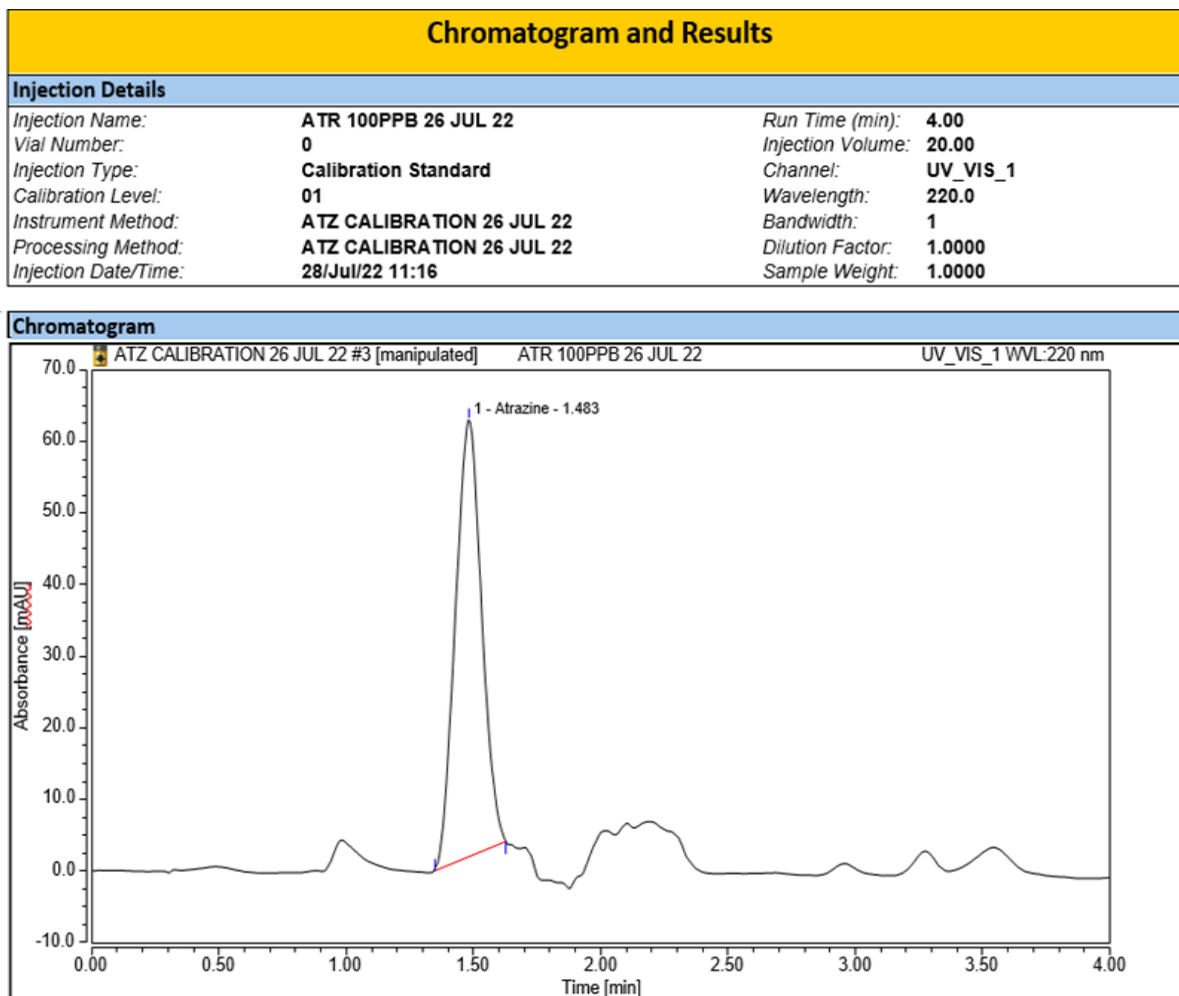


Figure 3: HPLC Chromatogram obtained for Atrazine standard

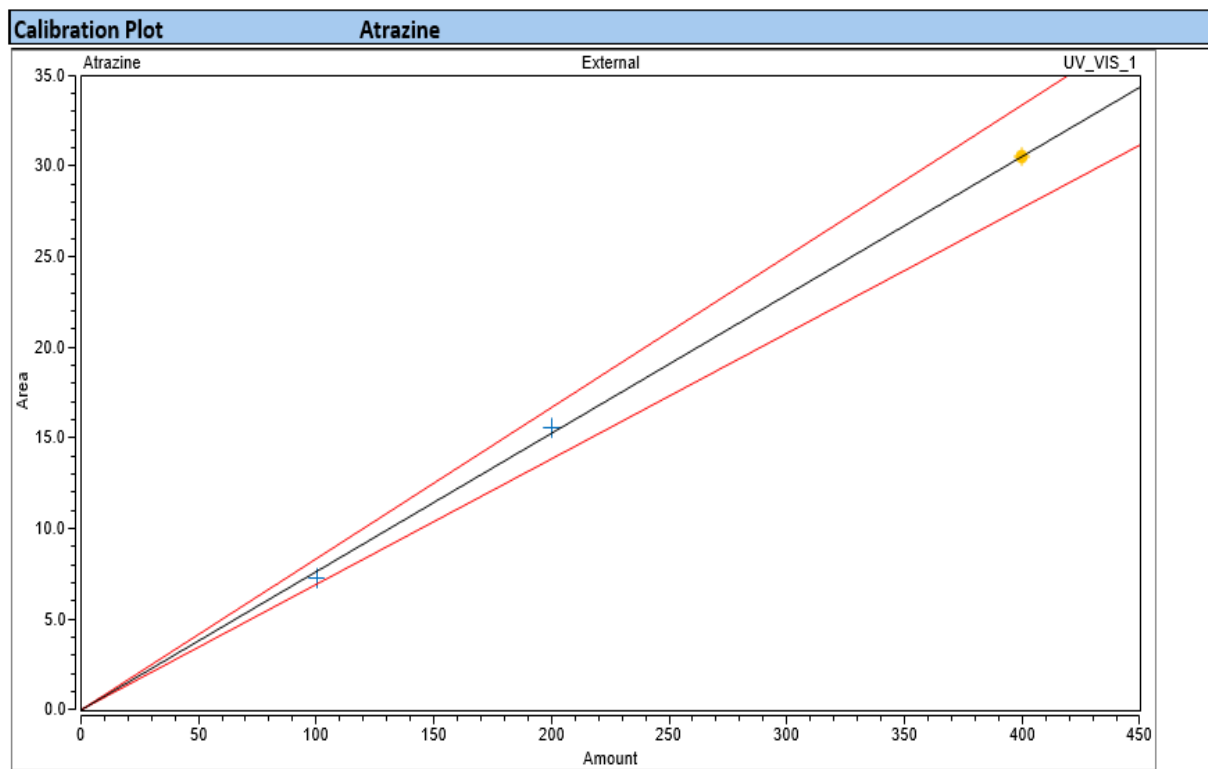


Figure 4: Calibration Plot of Atrazine ( $R^2=0.9992$ )

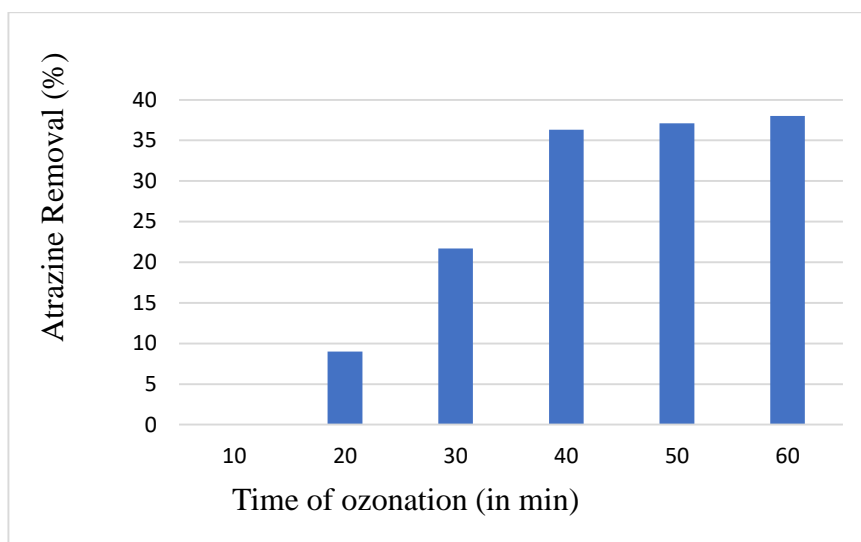


Figure 5: Graph between atrazine removal and time of ozonation

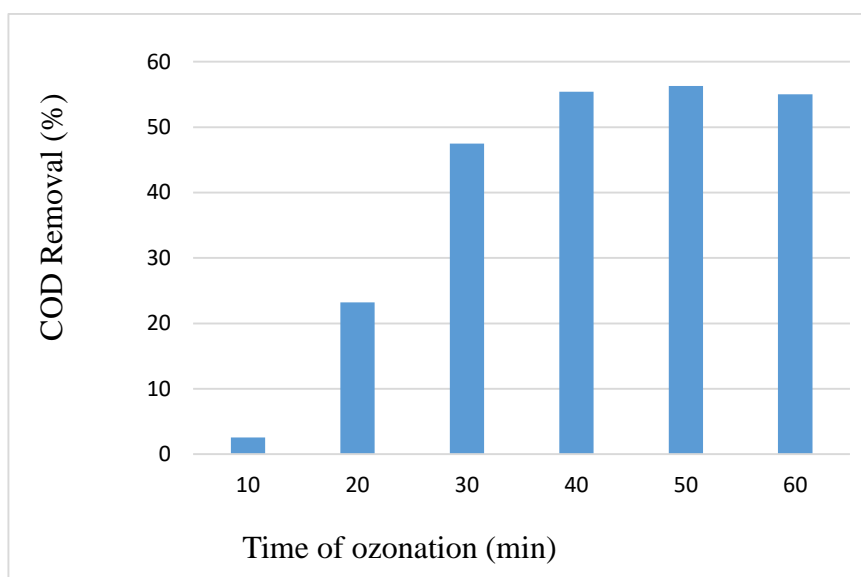


Figure 6: COD removal Vs time of ozonation

It can be seen from figure 5 that for longer ozonation time, there is greater reduction in atrazine concentration. It can also be observed that with increasing time, the atrazine removal percentage also increased but after certain time it is not much significant. Hence, ozonation time of 40 min was taken as optimum ozonation time as it showed good result for decrease in atrazine concentration. The concentration decreased from 100 ppb to 63.67ppb. It is about 36.33% atrazine removal.

**Effect of ozonation on COD (Chemical Oxidation Demand):** Decline in the COD was observed on ozonation of atrazine. The COD values decrease with the increase in ozonation time. The reduction in COD value represents the degradation of atrazine and removal of organic and inorganic contaminants. Also, it represents the extent of oxidation of atrazine molecules by ozonation. It can be observed that there is hardly any reduction in COD value up to 10 minutes but at 30 minutes, COD value reduced up to 47.50 % and at 40 min, COD reduction is around 55.40%. Initially COD

removal value increased but again started decreasing which is mainly because of the destruction of the molecular structure of atrazine, resulting in organic species produced. Though, the highest COD removal has been achieved at 50 minutes but 40 minutes was selected as the optimum ozonation time because atrazine removal after this time of ozonation was not much significant.

After 50 minutes, it was observed that there is an increase in COD concentration. It is because of the formation of smaller fragments of organic molecules like acetic acid, ketones, aldehydes which are not completely mineralized<sup>17</sup>. This signifies that the biodegradable component of the COD is increasing. Hence, it leads to the enhancement of biodegradability. The non-biodegradable component has been broken into the biodegradable component, thereby solving the major problem and fulfilling the ultimate goal. Once the biodegradability is achieved, it can now be coupled with any aerobic or anaerobic process to achieve greater removal efficiency.

## Conclusion

Results shows that ozonation is an effective way to reduce the COD as well as persistent pesticide concentration. The aqueous solution showed best efficiency for high pH and optimum ozonation time of 40 minutes. It led to the decrease in concentration of atrazine as 36.3%. From the present study, it can also be deduced that ozonation can serve as one of the most efficient methods for pretreatment of wastewater at industrial level for pesticide contaminated wastewater.

## Acknowledgement

The authors are thankful to NIT Patna for providing the lab facilities for this research.

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(Received 05<sup>th</sup> December 2022, accepted 13<sup>th</sup> February 2023)