Comparative Analysis of the Ultrasound Ozonation Method (USOM) for Flonicamid Degradation in Wastewater

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***Abstract*— Over the past few decades, pesticide use in agriculture has skyrocketed. Pesticides are pollutants found in water sources that threaten both human health and the environment and cannot be properly handled using traditional wastewater treatment methods. In the current study, the extent of COD reduction from ozonation, ultrasound, and the combination of both methods used to study flonicamid decay in aqueous solutions was examined. The degradation was examined at optimal conditions of an ultrasound power of 90 W, a pH value of 2.0, a concentration of 20 ppm, an H_2O_2 loading of 1200 ppm, and a CuO loading of 0.5 g/l. When the US was used in conjunction with multiple approaches, COD was reduced to greater degrees than when the US was used alone. Ozone addition produces better ultrasound findings than simple ozonation. The largest COD reduction compared to other single systems is 92% when US + O_3 + H_2O_2 + CuO are operating together. Overall, it has been proven with clarity that the operation of ultrasound with ozonation and catalysts such as H_2O_2 and CuO results in the greatest COD reduction.**

***Index Terms*—Waste Water Treatment, Pesticide, COD, Ultrasound, Ozonation.**

I. INTRODUCTION

The agriculture industry is one of the fastest growing in India. The use of pesticides and related agrochemicals rises dramatically as a result of the rapid growth rate. The pesticide industry is expanding quickly as a result of the increased usage of pesticides, but it is also having trouble treating its waste water (Ayare and Gogate, 2019). Large levels of non-biodegradable contaminants are present in the effluent produced by the pesticide industry, and standard wastewater treatment techniques do not efficiently remove these contaminants (Bermúdez et al., 2021).
Industrial wastewater that contains non-biodegradable pollutants has been effectively treated using advanced oxidation processes (AOPs). Using sophisticated oxidation techniques, complex molecules can be completely converted into inorganic chemicals, water, and CO_2. Different reagents are used in a variety of sophisticated oxidation procedures to create hydroxyl radicals, which have a powerful oxidising effect (Bermúdez et al., 2021). Due to the growing demand for environmentally friendly technology, product recovery, and purification procedures, the use of ultrasonic power in wastewater treatment and chemical reaction processes has attracted attention (Matouq et al., 2008). Cavitations can also be thought of as an oxidation process since they produce hydroxyl radicals, which are useful for treating wastewater (Patil et al., 2014). According to reports, the ultrasound procedure is a very effective AOP for the breakdown of pesticides found in water. In an aqueous medium, sonolysis involves the compression and expansion cycles of sound waves at a certain frequency that result in the development of cavitation bubbles. By diffusing gas or vapor from the liquid medium, these bubbles expand until they reach an unstable size that causes a violent implosion, which in turn produces extremely high temperatures and pressures. approximately 4200K and 975 bar, resulting in the so-called "hot spots" that enable the breakdown of the water molecule to generate HO•, which has a high oxidation potential and is capable of oxidizing recalcitrant pollutants, leading to the degradation of the toxic compounds and producing harmless

products, such as H_2O, carbon dioxide (CO_2), and inorganic ions (Chincholi and Gogate, 2019).

According to a review of the literature, published ultrasonography investigations primarily use simulated industrial waste water to examine the effects of various operational conditions (Pirsaheb and Moradi, 2020). Investigated the simultaneous sonocatalytic treatment of industrial waste water containing phosphate. They determined that the operation of sonocatalysis (with TiO_2 as the catalyst) in combination with ozone and H_2O_2 results in the greatest COD reduction (Rossi et al., 2020). The use of sonochemistry to break down pesticides in simulated industrial effluent from a factory producing diazinon, one type of pesticide, They discovered that as solution volume and diazinon content increased, so did the ability to break down pesticides (Weavers and Hoffmann, 1998). When used alone or in conjunction with other cutting-edge oxidation processes, sonochemical reactors have been studied by Patil et al. for the treatment of waste water containing imidacloprid (Wilde et al., 2014) They found that waste water containing imidacloprid can be cleaned up well by using cavitation and different oxidation processes together.

At the effects of ultrasonic-assisted advanced oxidation processes on the breakdown of acid green-3 dye in wastewater, were able to get 87.09% of the dye broken down in 90 minutes (Patil and Gogate, 2016). For the oxidation of complicated chemical substances in industrial wastewater, a variety of cutting-edge oxidation techniques are combined with ozone ("Ultrasound-Assisted Anaerobic Digestion of Sludge," 2011). Ozonation is an AOP, and ozone (O_3), a potent oxidant, is frequently used in the treatment of wastewater. It produces one oxygen atom (O) and a powerfully oxidizing hydroxyl radical (OH), which can break down the organic molecules in water (Buthiyappan et al., 2019). The primary mechanism for the degradation of complex chemical compounds in trash is the thermal disintegration of ozone in collapsing cavitation bubbles.

II. MATERIALS AND METHODOLOGY

The insecticide group includes flonicamid and is available on the local market for purchase. While cupric oxide (CuO) and the various reagents used for COD analysis (potassium dichromate, ferrous ammonium sulphate, ferroin indicator, mercuric sulphate, and silver sulphate) were acquired from S.D. Fine Chemicals, Mumbai, India, hydrogen peroxide (30% w/w, analytical grade) was purchased from Research Lab Fine Chemical Industries. Freshly prepared distilled water is used to prepare all reagents.

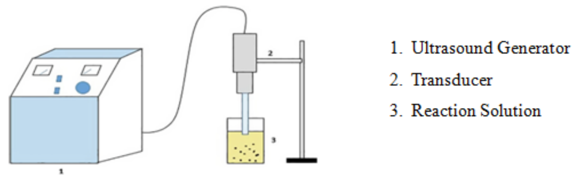

Figure 1: Ultrasonic probe with sonicator

The ultrasound source was an ultrasonic probe sonication **Fig 1** with a frequency of 20 kHz, a power dissipation of 120 W, a tip diameter of 2.1 cm, and a depth of 1 cm into the liquid. For every experiment, a 250 ml glass beaker was used as the reactor, and it was submerged in a water bath to maintain a consistent temperature.

An ozone generator (DOZ400) **Fig 2** bought from Eltech Engineers in Mumbai was used to create ozone from the air. Ozone was continuously bubbled into the reactor at a flow rate of 400 mg/h using a bubble diffuser.

Figure 2: Ozonator

III. EXPERIMENTAL WORK

Throughout the entire experiment, the treatment of waste water with flonicamid was conducted in a 250 ml reactor with 120 ml as the reaction volume. By adjusting the ultrasound power between 60 and 110 W, the greatest COD reduction was examined. Utilizing improved power dissipation, it was possible to examine various parameters, including concentration and pH, in order to determine the degree of COD reduction. Then, at the acquired optimum power dissipation, the investigation of comprehending the impact of various parameters, such as ozone flow rate and catalyst loading (H_2O_2 and CuO), on the extent of COD reduction for the combination approaches was carried out. A 5 ml sample was taken from the reactor every 30 minutes during each experimental run, which lasted 120 minutes. This sample was taken for examination of the COD decrease. To determine the degree of COD reduction, the combination of ultrasound and ozone was studied with all the optimal parameters.

Analysis -
The titrimetric method of COD analysis requires a COD digestion unit for this analysis. A COD digester was used with the following specifications: 1200 oC temperature range, Display: Digital Display, PID Controller, Heater rating: 750 watts, Sensor: PT-100, 120-minute timer with alarm Hole size: 40 mm diameter, 80 mm depth.

Reagents -
Potassium dichromate standard ($K_2Cr_2O_7$), 0.25 M: Fill a volumetric flask with around 12.259 g of $K_2Cr_2O_7$, dissolve it in 100 ml of distilled water, and then dilute it to 1000 ml with more distilled water. Standard solution of ferrous ammonium Sulfate, 0.1 M: After dissolving 39.2 g of Fe $(NH)_2(SO)_26H_2O$ in it, dilute to 1000 ml with distilled water.

IV. RESULTS AND DISCUSSION

Different operating parameters, such as ultrasound power, pH, concentration, and catalyst loading in terms of COD reduction, were investigated for the application of ultrasound and ozonation for the treatment of wastewater containing flonicamid. The study also looks at how the two effects work together to increase the amount of COD reduction.
Another significant catalyst for accelerating degradation in waste water treatment is copper oxide. To increase the effectiveness of ozonation in terms of the degree of COD reduction, copper oxide was used in the current study at various loadings, including 0.1 g/l, 0.25 g/l, 0.5 g/l, 0.75 g/l, and 1.0 g/l, at a constant pH value of 2.0 and a constant ozone flow rate of 400 mg/l. Figure 14 shows the outcomes in terms of the degree of COD reduction.

Table 1: Rate constants for the breakdown of fluonicamide based on the amount of copper oxide in Ozonation

CuO Concentration (g/l)	Rate Constant (min^{-1})	Extent of degradation (%)	Order	R^2
O_3 + CuO-0.1 g/l	0.005	45.45	1	0.963
O_3 + CuO-0.25 g/l	0.0068	54	1	0.959
O_3 + CuO-0.5 g/l	0.0072	59.09	1	0.965
O_3 + CuO-0.75 g/l	0.0072	57.14	1	0.965
O_3 + CuO-1.0 g/l	0.005	47.82	1	0.948

It has been observed that the amount of COD reduction also increases from 45.45% to 59.09% as catalyst loading increases from 0.1 g/l to 0.5 g/l. This yielded a maximum COD reduction of 59.09% with a CuO loading of 0.5 g/l. Therefore, in subsequent experiments, the optimal value of CuO is set at 0.5 g/l. For the breakdown of phosphate-containing industrial waste water, Ayare et al. achieved 0.75 g/l of CuO. From the data, it can be inferred that the inclusion of solid catalysts can boost cavitational activity by adding more active sites and effectively suspending all the catalysts (Maldonado et al., 2006). When CuO loading is increased past the ideal level, it can be seen that the catalyst particles are getting too close to one another in the same reactor volume, which could lead to agglomeration and only slightly affect the degree of COD reduction ("Uttejana Chaudhari," 1999). First order kinetics is evident in the kinetic analysis of CuO ozonation. **Table 1** shows the specific values of the kinetic rate constants as well as the R2 values. The greatest value of the kinetic rate constant was determined from the results to be 0.0072 min^{-1}. and R^2 score of 0.965 at its highest **Fig 3**.

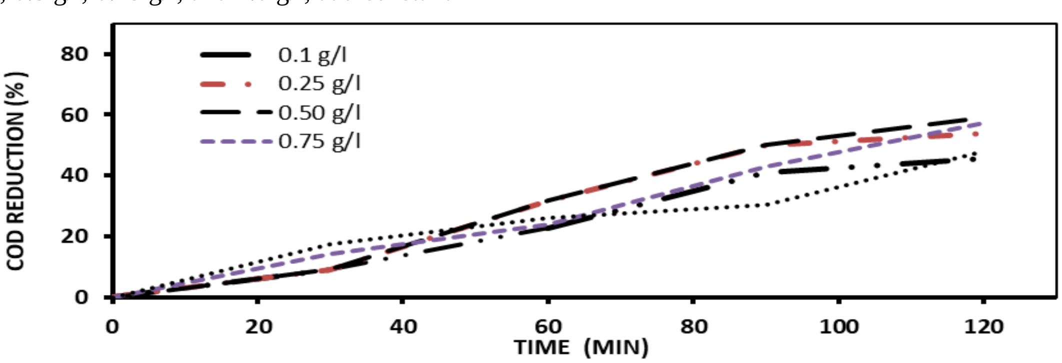

Figure 3: Treatment with different concentration

Table 2: Comparison of synergetic effects of different treatments

Treatment	Rate Constant, min^{-1}	Extent of degradation, %	Order	R^2
US (90 W)	0.008	63.63	1	0.960
H_2O_2 (1200 ppm)	0.008	58.82	1	0.929
CuO (0.5 g/l)	0.004	40.9	1	0.981
US + O_3	0.0091	71.42	1	0.922
US + O_3 + H_2O_2	0.0167	91.3	1	0.880
US + O_3 + CuO	0.013	80.95	1	0.982
US + O_3 + H_2O_2+ CuO	0.0167	92	1	0.850

To fully degrade flonicamid from wastewater, the mixed system is to be used in wastewater containing flonicamid. With catalysts H_2O_2 and CuO at optimal values, the combination approach of ultrasonic and ozonation was researched to evaluate the system's degrading efficiency than CuO in terms of the degree of COD reduction. **Table 2** provides a full analysis of combination treatment approaches using optimum values. In comparison to previous combination approaches, the combined treatment method US + O3 + H2O2 + CuO yields the highest degradation value of 92%. First order kinetics is used in the kinetic study of combination treatment techniques.

V. CONCLUSIONS

In the current study, the degradation of flonicamid using a combination ultrasonic-and-ozonation approach was measured under various conditions, and compared to that using simply those two techniques. It determined the ideal operating value for factors like pH (2.0), ultrasonic power (90 W), and treatment time (120 min) at a constant temperature of 32 °C. By employing catalysts like H_2O_2 and CuO, the degradation efficiency can be increased. From the results, it can be seen that using simply ultrasound, a 63.63% reduction in COD was achieved. For the combined US+O3 strategy, the reduction is 71.42%,

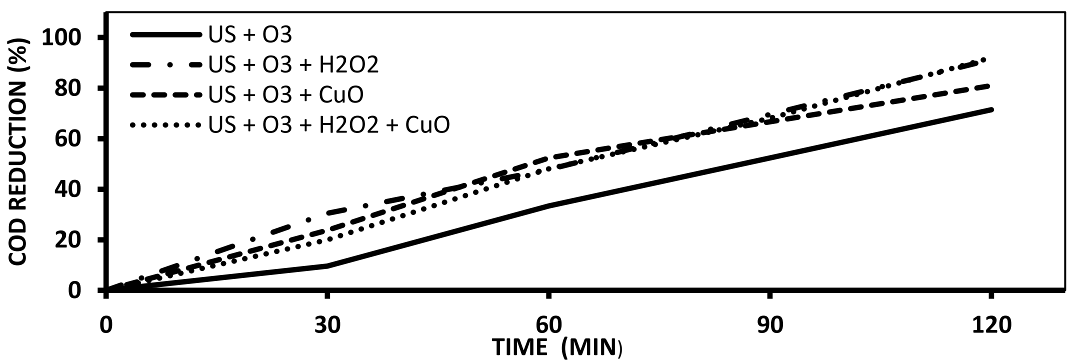

Figure 3: % COD Reduction in Combined Methods

efficacy. At constant pH 2.0, ultrasonic power of 90

W, ozone flow rate of 400 mg/l, H2O2 loading of 1200 ppm, CuO loading of 0.5 g/l, and temperature of 32 oC, the combined systems under investigation were US + O_3, US + O3 + H_2O_2, US + O3 + CuO, and US + O_3 + H_2O_2+ CuO. Fig. 15 displays the COD reduction results that were attained.

Fig. 4, in comparison to US + O_3 + CuO, which reduces COD by 80.95%, the amount of COD reduction employing the combination strategy of US + O_3 + H_2O_2 results in 91.3%. It is clear from the combined ultrasonic and ozonation findings with H_2O_2 and CuO catalysts that hydrogen peroxide has a higher

which is significantly better than the solo system. H_2O_2 and CuO were optimized at 1200 ppm and 0.5 g/l, respectively, resulting in COD reductions of 58.82 % and 40.92%, respectively. The degree of COD reduction was given by the various combined treatment methods, including US + O_3, US + O_3 + H_2O_2, US + O_3 + CuO, and US + O_3 + H_2O_2+ CuO, as 71.42 %, 91.3 %, 80.95 %, and 92 %, respectively. Additionally, it was found that first order kinetics are followed by the entire integrated system. It has been proven that using a catalyst in conjunction with a combination technique results in a higher degradation efficiency than using a system alone. Combining ultrasound and ozone can reduce both the need for ozone and the amount of ultrasonic energy used, which lowers operational expenses. Also, to be noted is the tiny size of activities at the laboratory level. It can be improved in the future on a large scale to reduce the capital cost and improve the techniques.

REFERENCE

[1] *Ayare, S.D., Gogate, P.R., 2019. Sonocatalytic treatment of phosphonate containing industrial wastewater intensified using combined oxidation approaches. Ultrasonics Sonochemistry 51, 69–76. doi:10.1016/j.ultsonch.2018.10.018*

[2] *Bermúdez, L.A., Pascual, J.M., Martínez, M. del M.M., Poyatos Capilla, J.M., 2021. Effectiveness of Advanced Oxidation Processes in Wastewater Treatment: State of the Art. Water 13 15, 2094. doi:10.3390/w13152094*

[3] *Matouq, M.A., Al-Anber, Z.A., Tagawa, T., Aljbour, S., Al-Shannag, M., 2008. Degradation of dissolved diazinon pesticide in water using the high frequency of ultrasound wave. Ultrasonics Sonochemistry 15 5, 869–874. doi:10.1016/j.ultsonch.2007.10.012*

[4] *Patil, A.L., Patil, P.N., Gogate, P.R., 2014. Degradation of imidacloprid containing wastewaters using ultrasound based treatment strategies. Ultrasonics Sonochemistry 21 5, 1778–1786. doi:10.1016/j.ultsonch.2014.02.029*

[5] *Chincholi, M.N., Gogate, P.R., 2019. Ultrasound assisted advanced oxidation processes for intensified Acid Green-3 dye degradation. DESALINATION AND WATER TREATMENT 170, 308–317. doi:10.5004/dwt.2019.24643*

[6] *Pirsaheb, M., Moradi, N., 2020. Sonochemical degradation of pesticides in aqueous solution: investigation on the influence of operating parameters and degradation pathway – a systematic review. RSC Advances 10 13, 7396–7423. doi:10.1039/c9ra11025a*

[7] *Rossi, G., Mainardis, M., Aneggi, E., Weavers, L.K., Goi, D., 2020. Combined ultrasound-ozone treatment for reutilization of primary effluent—a preliminary study. Environmental Science and Pollution Research 28 1, 700–710. doi:10.1007/s11356-020-10467-y*

[8] *Weavers, L.K., Hoffmann, M.R., 1998. Sonolytic Decomposition of Ozone in Aqueous Solution: Mass Transfer Effects. Environmental Science & Technology 32 24, 3941–3947. doi:10.1021/es980620o*

[9] *Wilde, M.L., Montipó, S., Martins, A.F., 2014. Degradation of β-blockers in hospital wastewater by means of ozonation and Fe2+/ozonation. Water Research 48, 280–295. doi:10.1016/j. watres.2013.09.039*

[10] *Patil, P.N., Gogate, P.R., 2016. Combined Treatment Processes Based on Ultrasound and Photocatalysis for Treatment of Pesticide Containing Wastewater. Handbook of Ultrasonics and Sonochemistry 901–929. doi:10.1007/978-981-287-278-4_61*

[11] *Ultrasound-Assisted Anaerobic Digestion of Sludge, 2011. Handbook on Applications of Ultrasound 345–366. doi:10.1201/b11012-19*

[12] *Buthiyappan, A., Chee, M., Raman, A.A.A., Huda, N., Ramesh, S., 2019. Degradation of carbofuran in aqueous solution using persulfate /Fe2+/ultrasound treatment system. Desalination and Water Treatment 164, 176–184. doi:10.5004/dwt.2019.24305*

[13] *Maldonado, M.I., Malato, S., Pérez-Estrada, L.A., Gernjak, W., Oller, I., Doménech, X., Peral, J., 2006. Partial degradation of five pesticides and an industrial pollutant by ozonation in a pilot-plant scale reactor. Journal of Hazardous Materials 138 2, 363–369. doi: 10.1016/ j.jhazmat. 2006.05.058*

[14] *Uttejana Chaudhari, 1999. Water Science and Technology 40 11–12. doi:10.1016/s0273-1223(99)00737-4*