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Industrial wastewater treatment using hybrid techniques and data modeling using RSM-ANOVA approach

Pratima Gajbhiye*[a] and Anand Mohan Yadav[b]

[a]Department of Chemical Engineering, School of Chemical Engineering and Physical Sciences, Lovely Professional University, Jalandhar-144 411, Punjab, India

[b]Meerut Institute of Engineering and Technology, Meerut-250 005, Uttar Pradesh, India

E-mail: pratima.24280@lpu.co.in

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Sonochemistry is nowadays used to treat both water and wastewater. The aim of this work is to examine and determine the effect of combined treatment of sonochemical effect, ultrasound (US), ozonation (O_3) and sonocatalysis. In this work, we have optimized the concentration of copper oxide catalyst for ozonation and sonocatalysis, the power intensity along with operating parameter at different concentrations of copper oxide (CuO) catalyst was done treating the real industrial wastewater. The optimum conditions obtained from experiments were for pH 3 and catalyst loading 0.5 g/L. The key observation was that it achieved less energy consumption for the US/O_3/CuO combined system with 75.6% of COD reduction. The combined effect is responsible for the production of hydroxyl radicals which treats the waste water. The modeling was also done using the Box-Behnken Design (BBD), where the combined effect of US, O_3 and CuO catalyst loading was applied. The analysis of variance (ANOVA) was applied to fit the model. The determination of coefficient (R^2) and the adjusted determination of coefficient (Adj. R^2) for response % COD removal found to be 0.9998 and 0.9995 respectively, indicating a reasonable fit of the model to the experimental data.

Keywords: Ultrasound, ozonation, sonocatalysis, ANOVA, RSM, Box-Behnken Design.

Introduction

Anthropogenic sources are the major cause of pollution for land, air and water thus causing environmental degradation. Though various environmental protection acts have been made to control release of harmful chemicals like dyes, aromatics, phenols, organic, inorganic wastes, heavy metals, mining wastes etc., its release still continued in many parts of the water bodies by the industries. These releases are responsible for life-threatening diseases like cancer, genetic mutation, mutagenic effects in humans and aquatic life too[1–5]. The waste water treatment varies as the type of waste keeps changing. There is no specific treatment which can be applied to all the types of waste water from industries.

Different processes used for the treatment of waste water include adsorption, flocculation, reverse osmosis, aeration techniques, microbial degradation, etc. These methods though are used for treatment of waste water, but drawbacks of some of these processes include high cost of set up, skilled labor, also inability of the microorganism to act on it and sometimes the secondary product produced is of toxic nature also. Thus developing imperative techniques that are eco-friendly which does not produce harmful chemicals is essential. Advanced oxidation methods are such methods which does not produce any harmful products[6–9].

Advanced oxidation processes are defined as the processes that generate hydroxyl radicals in sufficient quantities to be able to oxidize majority of the complex chemicals present in the effluent.

Advanced oxidation processes include chemical oxidation processes, ultraviolet (UV) based processes (semiconductor/UV or ultraviolet-visible (UV-Vis)), critical water oxidation, ultrasound, electron beams, Fenton and photo-Fenton processes, cavitation, ozonation, photo catalytic oxidation-reduction processes. In all these mentioned processes, hydroxyl radicals are produced to oxidize the complex chemicals present in the waste water. Even single process can be

used for the treatment of waste water, but combining them to form a hybrid process is always preferable. It improves water quality as the COD reductions are better compared to single and dual processes apart from low power requirement.

Cavitation is the process of formation of vapour phase of a liquid due to reduced pressure, even at ambient temperature. A liquid is said to cavitate when vapour bubbles form and grow due to reduction in pressure. Micro bubbles so formed, caused cavities which occurs in a very small interval of time, releasing large energy causing the temperature to reach to 5000°C[10,11]. Cavitation can be achieved by passing ultrasound (sound waves) into liquid medium. Cavitation is also the cheapest technique available for pretreatment of waste water. When ultrasound is passed through a liquid medium, it causes mechanical vibration. If the liquid medium contains dissolved gas that every liquid has, tiny micro bubbles will be formed, grown and violently collapsed by the action of the sound wave[12]. Under such extreme condition water molecules dissociates into $OH^{\bullet}$ and $H^{\bullet}$ radicals. $OH^{\bullet}$ radicals are strongly oxidizing agent, so it rapidly reacts with pollutant and produce carbon dioxide and water. The combined effect of hydroxyl radicals which are highly reactive and high impact of cavity collapse leads to the breaking and oxidation of most of the organic contaminants, which is generally not achieved by traditional methods[13].

Ozone is an oxidizing agent that can react with chemicals having multiple bonds such as C-C, C-N, N-N, etc. Ozone is also considered as highly reacting species with high reduction potential. The use of Cu-O as a catalyst is known since decades due to its high efficiency, simplicity, stability and low cost. We propose here in this work, a combination of combined treatment of sonochemical, ultrasound (US), ozonation (O_3) and sonocatalysis.

Response surface methodology (RSM) and artificial neural network (ANN) are the optimization tools used in various processes. In the present study, Box-Behnken Design (BBD) was chosen from other RSM design due to its simplicity, feasibility, efficiency and also the minimum number of test runs required than other RSM designs. Already this kind of modeling has been done in our previous work[14–16].

The variables studied were CuO loading, time and O_3 flow rate keeping US constant throughout the experiment at 90 W. The process input variables were varied to different levels to observe their effect on COD removal. The obtained result of experimental design matrix performed using BBD was used to obtain mathematical model by using BBD-RSM quadratic model. The relationships and interactional relationships of the variables were determined by fitting the second order polynomial equation to data obtained. The quality of the fit of the model was evaluated using analysis of variance (ANOVA) and test of significance.

Experimental

Materials:

Ferrous ammonium sulphate, copper oxide and hydrochloric acid (98%) were procured from the local industry. In all the experiments, the waste water used was collected from the industry. NaOH, potassium dichromate were purchased from Loba Chemie.

The sonochemical reactor was equipped with a vertical ultrasound horn (operating at 90 watt power). The power was supplied using generator. Ozone was injected using the ozone generator as shown in Fig. 1 in which the rate of generation of ozone was controlled till 400 mg/h.

Method:

In all experiments, pH of waste water was controlled first. In a 250 ml beaker around 100 ml of the industrial waste water was added having pH 1.38. To this was then added, dilute NaOH for adjusting the pH to 3. The CuO catalyst was then added to the beaker containing sample and stirred using the magnetic stirrer for uniform distribution of catalyst in all regions of the beaker. Ozone was then injected in the

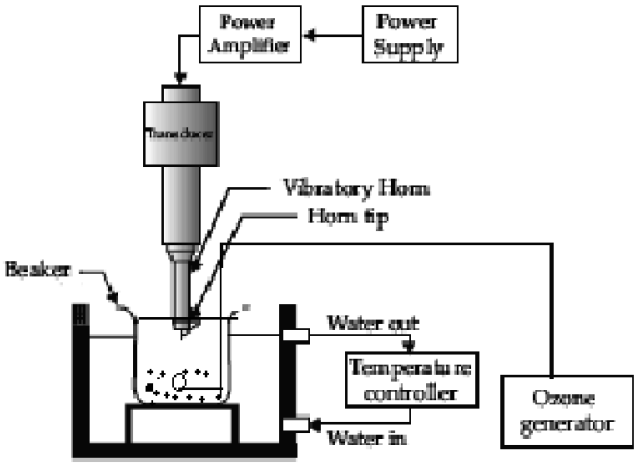

Fig. 1. Schematic representation of US/O_3/CuO system.

solution at a rate of 100, 250 and 400 mg/h. The ultrasound was passed in the solution by using the sonicator which is operated at 90 W.

Thus combined effect of ozone, ultra sound and CuO catalyst has been used to treat the polluted water. Then some amount of sample was pipetted out after every 30 min of interval and was analyzed.

Analysis:

The sample pipetted out was analyzed for chemical oxygen demand (COD) by using the COD digester. The amount of oxygen required for oxidation of organic compounds present in the sample is called as COD. The sample was transferred in the COD bottle and was diluted up to 20 ml of volume with distilled water. Then 10 ml of potassium dichromate (0.25 *N* $K_2Cr_2O_7$) and 30 ml of concentrated H_2SO_4 (98% pure) was added. After that a pinch of $HgSO_4$ was added and the bottle was set for heating in COD digester for about 120 min at 150°C. After heating, the bottles containing solution, it is allowed to cool for 40–45 min and are then titrated against ferrous ammonium sulphate (FAS) (0.1 *N*) using indicator. The obtained burette reading was used to calculate the COD using the below formula:

COD in ppm = (Blank reading – Sample reading) × Normality of FAS × 8000/(Volume of sample).

Results and discussion

Effect of sonication:

The rates of degradation were studied using ultra-sonication method only and were done at pH 3. Fig. 2 shows that how the degradation get affected due to change in the treatment time. It clearly shows that the 26.36% degradation of industrial waste water can be achieved in 120 min.

Effect of ozone:

For the destructions of organics from waste water, ozonation treatment is also considered as an effective approach[19]. It is also considered as one of the clean technology for removing pesticides and dyes. Ozonation combine with ultrasound result in more formation of free hydroxyl radicals. When used alone, about 46% degradation was achieved but when the process was combined with copper oxide after 120 min, the degradation achieved was 57.89%. When ozone treatment was combined with the catalyst loading along with sonication it produced a reduction of 63.15% in COD at 0.5 g/L of catalyst loading and it reached to 75.6%.

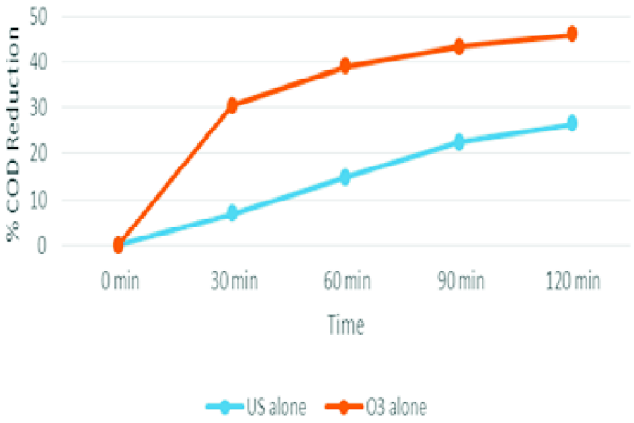

Fig. 2. Comparison of US and O_3 effect.

Effect of catalyst (CuO) loading:

The reactivity of the catalyst was found to be enhanced when combined with ultra-sonication as it improves the rate of mass transfer. Experiment involving sonocatalytic degradation of industrial wastewater sample using CuO were conduct at different loading of CuO (0.11 g/L, 0.5 g/L, 0.77 g/L, 1.01 g/L) which are shown in Fig. 3. It was observed that as the CuO loading increase from 0.1 to 0.5 g/L, the extent of degradation also increases from 48.75 to 63.15% after 120 min and beyond this optimum, the degradation slows down. Even if the catalyst loading is increased, the effect is not seen positive. This could be due to the fact that higher con-

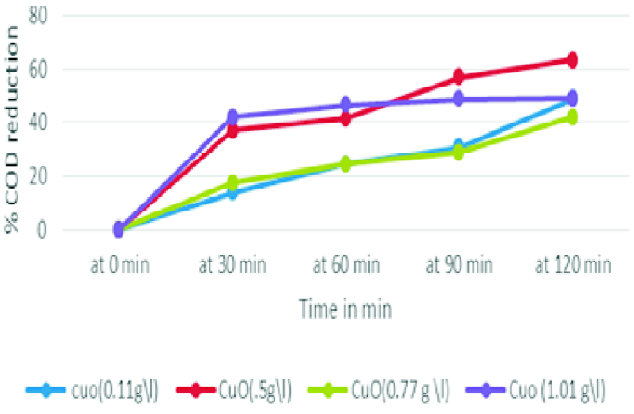

Fig. 3. Effect of catalyst loading on COD removal.

Table 1. Effect of catalyst loading

Time (min)	CuO (0.11 g/L)	CuO (0.5 g/L)	CuO (0.77 g/L)	CuO (1.01 g/L)
0	0	0	0	0
30	14	37.1	17.5	42.1
60	24.6	41.4	24.6	46.5
90	30.7	57.89	29	48.9
120	48.8	63.15	42.1	49.1

centration of the suspended particles disturbs the transmission of ultrasound in water medium[18].

US/O_3/CuO degradation generally occurs faster than the respective individual processes. The beneficial effect of hybrid technology combining catalyst and sonolysis could be due to many reasons. It could be due to formation of more hydroxyl radicals which are actually responsible for the treatment of waste water. Also it is already known that the rate of mass transfer is always more if catalysts are used. Reports showed that when all the three systems are combined, there is less energy consumption[19].

Modeling:

The predicted values of response % COD removal have been calculated by using quadratic models and are given in Table 2. According to the presented results in Table 2, it was adduced that there is a good agreement between RSM-BBD predicted values and experimental data. The summarized ANOVA results for the quadratic model, which indicate the significance and adequacy of the model, are given in Table 3 for % COD removal. The model prediction found to be significant with *p*-value < 0.0001 for response % %COD removal as mentioned in Table 3. The model *F*-value (3407.45) for % COD removal indicates that the given model is statistically significant. There is only 0.01% chance that a model *F*-value this large could occur due to noise. The adequate precision, which measures signal to noise ratio and value of 4 is desirable, the ratio of 217.118 for response indicates adequate model discrimination. The determination of coefficient (R^2) and the adjusted determination of coefficient (Adj. R^2) for response % COD removal found to be 0.9998 and 0.9995 respectively, thus indicating a reasonable fit of the model to the experimental data. The low value of the coefficient of variation for response % COD removal was found to be 0.65% which also confirmed good reproducibility of the given quadratic model as given in equation.

Table 2. BBD-RSM experimental design matrix

Run No.	CuO (g/L)	Time (min)	O_3 (mg/h)	Actual % Reduction	Pred. % COD Removal
1	0.5	120	100	63.15	63.20
2	0.1	60	100	28.10	28.03
3	0.5	120	400	76.50	76.24
4	0.5	30	100	37.10	37.39
5	0.5	60	250	55.80	55.77
6	1	60	100	40.40	39.98
7	0.5	60	250	55.80	55.77
8	0.1	30	250	23.50	23.23
9	1	60	400	52.90	52.85
10	0.1	60	400	34.30	34.72
11	1	120	250	65.60	65.62
12	0.1	120	250	54.30	54.09
13	1	30	250	39.80	40.03
14	0.5	30	400	45.30	45.02
15	0.5	60	250	55.80	55.77
16	0.5	60	250	55.80	55.77
17	0.5	60	250	55.80	55.77

Table 3. BBD-RSM experimental design matrix

Source	Sum of squares	DoF	Mean square	*F*-Value	*p*-Value prob > *F*
Model	3120.03	9	346.67	3407.45	< 0.0001
CuO	382.50	1	382.5	3759.65	< 0.0001
Time	1594.36	1	1594.36	15671.14	< 0.0001
O_3	215.65	1	215.65	2119.64	< 0.0001
CuO×time	7.35	1	7.35	72.22	< 0.0001
CuO×O_3	9.68	1	9.68	95.13	< 0.0001
Time×O_3	7.80	1	7.80	76.67	< 0.0001
CuO^2	832.43	1	832.43	8182.02	< 0.0001
$Time^2$	8.36	1	8.36	82.21	< 0.0001
O_3^2	54.72	1	54.72	537.85	< 0.0001
Residual	0.71	7	010		
Lack-of-fit	0.71	3	0.24		
Pure error	0.00	4	0.00		
Cor. Total	3120.74	16			

R^2 = 0.9998; Adj. R^2 = 0.9995; Pred. R^2 = 0.9964; C.V. % 0.65

Equation in terms of coded variables:

$$COD\ \%\ R = 61.71 + 7.09\times A + 14.16\times B + 5.34\times C$$

$-1.32\times A\times B + 1.55\times A\times C + 1.36\times B\times C - 14.28\times A^2 - 1.63\times B^2 - 3.61\times C^2$.

Final equation in terms of actual factors:

$$\text{COD \% R} = -11.08554 + 92.47431\times\text{CuO} + 0.42083\times\text{time} + 0.088008\times\text{ozone} - 0.064955\times\text{CuO}\times\text{time} + 0.022978\times\text{CuO}\times\text{ozone} + 2.01400\text{E}-004\times\text{time}\times\text{ozone} - 70.53125\times\text{CuO}^2 - 8.05556\text{E}-004\times\text{time}^2 - 1.60249\text{E}-004\times\text{ozone}^2$$

From the ANOVA, Table 3 presented for response %COD, it can be seen that the linear term CuO, time and ozone flow rate, quadratic terms CuO^2, $time^2$ and ozone flow $rate^2$ and cross-product terms (CuO×time, time×ozone flow rate and ozone flow rate and CuO) are the significant terms as their *p*-value is less than 0.05. From the equation, positive coefficient values of the terms indicate their synergistic effect on response, while negative coefficient values of terms indicate its antagonistic effect on response. Fig. 4 shows the effect of process variables on %COD removal: CuO dosage and time whereas Fig. 5 shows the effect of process variables on %COD removal: ozone and time (keeping other variable on mid). Similarly Fig. 6 shows the effect of process variables on %COD removal: CuO dosage and ozone. From Figs. 4–6, it can be clearly seen that time has the most significant effect on COD removal.

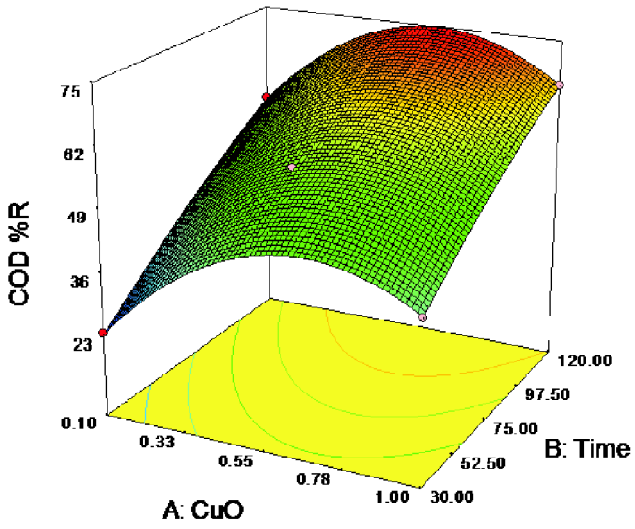

Fig. 4. Effect of process variables on %COD removal: CuO dosage and time.

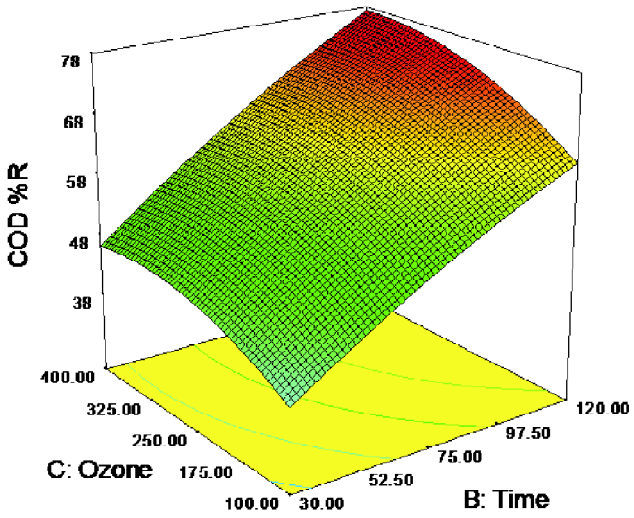

Fig. 5. Effect of process variables on %COD removal: ozone and time (keeping other variable on mid).

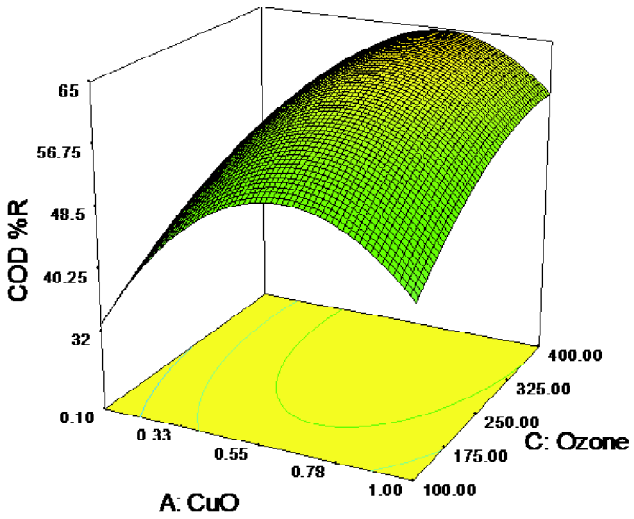

Fig. 6. Effect of process variables on %COD removal: CuO dosage and ozone.

Conclusions

The industrial wastewater treatment was investigated using combined treatment processes based on ultrasound, ozonation and catalyst loading. We observed the effect of sonicator and ozonation as a single process were not found satisfactory. These three systems when combined together gave a remarkable increase in the percentage reduction of COD of the wastewater sample and the same has been validated using the statistical and computational approach. Still

future work can be done on various catalyst modifications. Apart from that also other techniques of Advanced Oxidation Processes can be tried upon for further drop in COD.

References

1. J. Madhavan, P. S. Kumar, F. Grieser, M. Ashokkumar and S. Anandan, *J. Hazard. Mater*., 2010, **177**, 944.
2. J. Madhavan, F. Grieser and M. Ashokkumar, *Sep. Purif. Technol*., 2010, **73**, 409.
3. J. Madhavan, J. Theerthagiri, D. Balaji, Sunitha S. M. Y. Choi and M. Ashokkumar, *Molecules*, 2019, **24**, 3341.
4. D. P. Mohapatra, S. K. Brar, R. D. Tyagi and R. Y. Surampalli, *Chemosphere,* 2010, **78**, 923.
5. M. S. Díaz-Cruz and D. Barceló, *Chemosphere,* 2008, **72**, 333.
6. L. Mohammadi, E. Bazrafshan, M. Noroozifar, A. R. Ansari-Moghaddama, A. R. Khazaei Feizabad and A. H. Mahvi, *Global J. Environ. Sci. Manage*., 2017, **3(4)**, 403.
7. A. Mahvi, A. Maleki, R. Rezaee and M. Safari, *J. Environ. Health Sci. Eng*., 2009, **6(4)**, 233.
8. G. Moussavi, R. Khosravi and M. Farzadkia, *Desalination*, 2011, **278(1)**, 288.
9. M. Sánchez-Polo, U. Von Gunten and J. Rivera-Utrilla, *Water Res*., 2005, **39(14)**, 3189.
10. P. N. Patil and Parag R. Gogate, *Journal of Water Process Engineering*, 2015, **8**, pp. e58-e65.
11. P. N. Patil and Parag R. Gogate, *Ultrasonics Sonochemistry*, 2015, **25**, 60.
12. Nor Elhouda Chadi, Slimane Merouani and Oualid Hamdaoui, *Applied Water Science*, 2018, **8**, 160.
13. Michał Gągol, Elvana Cako, Kirill Fedorov, Reza Darvishi Cheshmeh Soltani, Andrzej Przyjazny and Grzegorz Boczkaj, *J. Mole. Liq*., 2020, **307**, 113002.
14. Anand Mohan Yadav, Ram Chandra Chaurasia, Nikkam Suresh and Pratima Gajbhiye, *Fuel*, 2018, **220**, 826. https://doi.org/10.1016/j.fuel.2018.02.040
15. Anand Mohan Yadav, Suresh Nikkam, Pratima Gajbhiye and Majid Hasan Tyeb, *International Journal of Mineral Processing*, 2017, **163**, 55. https://doi.org/10.1016/j.minpro.2017.04.009.
16. A. Kumari, P. Gajbhiye and V. Rayasam, *Trans. Indian Inst. Met.,* 2019, **72**, 2567. https://doi.org/10.1007/s12666-019-01726-9
17. S. G. Anju, K. P. Jyothi, Joseph Sindhu, Y. Suguna and E. P. Yesodharan, *Research Journal of Recent Sciences*, 2012, **1**,191.
18. Yaneth Bustos, Mabel Vaca, Raymundo López, Erick Bandala, Luis Torres and Neftalí Rojas-Valencia, *Journal of Water Resource and Protection,* 2014, **6**, 16.
19. Abhilasha Dixit, A. K. Mungray and Mousumi Chakraborty, *International Journal of Chemical Engineering and Applications*, 2010, **1**, 247.