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Intensification of catalytic wet air oxidation for industrial effluent treatment using ozone and ultrasound as pretreatment

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ABSTRACT

The current work deals with the application of combined oxidation schemes (ozone, ultrasound and wet air oxidation) for improving the treatment of an industrial wastewater. The effect of temperature (150–180°C), oxygen pressure (1.42–1.92 MPa), catalyst dosage (0.1–0.2 kg m^{-3}) and type of catalyst (activated charcoal and ruthenium on carbon) on the reduction in chemical oxygen demand (COD) of a real industrial wastewater has been investigated initially. Under the optimized set of operating parameters (temperature as 180°C, total pressure as 1.92 MPa and catalyst loading as 0.2 kg m^{-3}), pretreatment using ozone, ultrasound and combination of ozone and ultrasound has been applied with an objective of intensification. The combination of ozone and ultrasonic irradiation followed by catalytic wet air oxidation (CWAO) effectively intensified the mineralization of industrial wastewater giving 80% COD reduction as compared with 60% COD reduction for the case of CWAO alone. The pretreatment also enabled use of less stringent conditions for obtaining similar levels of mineralization. Overall, the work has clearly demonstrated the beneficial results of combining ozonation and ultrasound with CWAO.

Keywords: Catalytic wet air oxidation; Ozonation; Ultrasonic irradiation; Wastewater treatment; Process intensification

1. Introduction

The pesticide and chemical industries are considered to generate wastewaters containing toxic and non-biodegradable compounds that can remain in the environment even after conventional wastewater treatment approaches [1]. Treatment of wastewater containing possibly bio refractory compounds such as pesticides, pharmaceutical drugs and other emerging contaminants is subject of considerable concern due to the toxic and possibly carcinogenic effects leading to potential health hazards for aquatic and human life [2–3]. Existing wastewater treatment methods such as adsorption, extraction, and chemical oxidation suffer from limitations such as limited applicability and low efficiency [4–5]. A promising way to achieve the degradation of biologically and chemically stable molecules is based on the application of wet air oxidation (WAO), which utilizes conditions of high temperature and pressure for mineralization. WAO is a promising treatment technology especially for wastewater streams that are too dilute to incinerate and too concentrated for biological treatment. In WAO, organic compounds are decomposed at a temperature in the range of 180 to 315°C and total pressure in the range of 2 to 15 MPa. In a typical oxidation scheme based on WAO, the organic compounds present in the effluent are first carbonized and the dissolved oxygen then reacts through different oxidizing species including hydrogen peroxide and hydroxyl radicals formed in-situ to yield the final oxidation products. The main advantages of WAO are as follows: (a) increased utilization of oxygen giving higher treatment rates, (b) mineralization of organics in short treatment times, (c) removal of inorganic constituents such as salt or brine and (d) recovery of heat of combustion [6–7]. A main disadvantage of the WAO process is the requirement of significantly higher temperatures and pressures, which can be reduced with the use

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of catalysts and the process is described as Catalytic Wet Air Oxidation (CWAO). There have been different homogeneous and heterogeneous catalysts reported in literature for use in the WAO [8–12]. CWAO using a homogeneous catalyst leads to the presence of metal ions in the effluent and hence an additional step is necessary to recover these toxic ions due to stringent environmental regulations. Use of the heterogeneous catalyst offers ease of separation from the liquid stream and also allows recycle of the catalyst that can make the process cost efficient. There have been some earlier reports dealing with the mineralization of refractory molecules using CWAO based on the use of heterogeneous catalyst. Noble metals such as Ru, Rh, Rd and Pt generally show higher catalytic activity for use in the CWAO and also higher resistance to metal leaching than catalysts based on the metal oxides. Maugans and Akgerman [8] investigated the wet oxidation of phenol in the presence of a Pt/TiO_2 catalyst, whereas Gomes et al. [13] investigated the treatment of olive mill wastewater using iridium and platinum supported on carbon as the catalyst. Though platinum has been commonly used as a catalyst with significant efficacy, higher catalyst costs can lead to uneconomical operation at commercial scale. Ruthenium is also an active metal that can play a catalytic role in the oxidation of refractory molecules and can be easily supported on carbon or graphite [10]. Moreover, ruthenium is cheaper than platinum. Vaidya and Junghare [10] reported excellent efficacy of Ruthenium catalyst supported on TiO_2 for the WAO of piperazine. Considering these aspects, ruthenium supported on carbon (5 wt %) as catalyst has been selected in the present study, which is in accordance with the generally reported loading for WAOs [9–10]. It is also important to understand that though CWAO has been very successful on laboratory scale of operation especially for effluent streams with significant COD levels, commercial use of CWAO has not been very common possibly attributed to the higher fixed and working capital investment as well as use of harsh process conditions, which gives rise to process safety issues.

A novel approach based on the combined operation of advanced/chemical oxidation process (ozone and ultrasound operated individually as well as in combination) as the pretreatment followed by the CWAO has been presented in the current work for the treatment of an actual industrial effluent obtained from a local industry, for the first time. Use of pretreatment can allow the use of less harsh conditions of temperature and pressure in the CWAO as well as reduce the treatment time required for similar extents of mineralization which can give lower treatment costs. The combined process based on ultrasound and ozone belongs to the class of advanced oxidation processes (AOPs) that rely on the production of hydroxyl radicals under mild experimental conditions and subsequent attack on the pollutants [14–15]. The main advantages of such oxidation processes are as follows: (a) use of ambient temperature and pressure conditions, (b) higher rates of oxidation, and (c) applicability for degradation of wide range of pollutant molecules. There are some shortcomings of the AOPs which makes their commercialization difficult as follows: (a) only wastes with relatively lower pollutant load (COD < 5.0 g L^{-1}) can be treated effectively; (b) use of oxidants like hydrogen peroxide, ozone, Fenton's reagent which can also add to effluent load if used in excess; (c) complete mineralization is difficult and also treatment costs can be higher [16]. Considering all the advantages and drawbacks of the AOPs, it appears to be beneficial to use them as a pretreatment for the conventional approaches for treatment of the industrial effluents in different combinations as investigated in the present work.

In recent years, application of cavitational reactors based on the use of ultrasound for wastewater treatment has been of significant interest and combination with other AOPs has been reported to yield synergistic results [17]. Cavitation is defined as the formation of the vapor filled bubbles or cavities in the liquid due to the alterations in the pressure field either in a flowing liquid or in a medium subjected to ultrasound [18–19]. The cavitational effects can eliminate the mass transfer resistances associated with treatment processes such as ozonation and hence combined operations can be more effective. Ozone possesses an oxidation potential of 2.07 eV and is capable of oxidizing organic and inorganic molecules [20]. Ozone decomposes in water under specific conditions such as presence of irradiations giving hydroxyl radicals, which are also strong oxidizing agents [21]. Considering these aspects, ultrasound and ozonation, either operated individually or in combination, have been investigated as pretreatment strategy in the present work.

There has been not much work reported in the literature on the combined use of CWAO and ultrasound/ozone. Ingale and Mahajani [22] investigated the mineralization of refractory waste by a novel SONIWO (sonication followed by CWAO) technique and reported that 66% COD reduction was observed using the SONIWO technique, whereas only 36% COD reduction was obtained using CWAO alone. Dhale et al. [23] also studied the subcritical mineralization of sodium salt of dodecyl benzene sulfonate using a hybrid process of sonication followed by wet oxidation using homogeneous catalysts (SONIWO) and reported that sonication as a pretreatment was able to eliminate the induction period and also resulted in enhanced oxidation.

Overall, the current work has focused on the use of ultrasound/ozone as pretreatment followed by CWAO for the treatment of a real industrial effluent, for the first time. Pretreatment of the industrial waste prior to CWAO can make the process economical as these can possibly reduce the severity of the required conditions. The work also focuses on comparing different treatment strategies and optimization of operating parameters. The main objective of the work was to develop an optimized hybrid approach with reduced treatment time and possibly less harsh conditions for CWAO. The possible advantages expected from the hybrid approach are as follows:

(a) Pretreatment can breakdown the higher molecular weight pollutants to simpler molecules possibly leading to higher overall mineralization extents.
(b) CWAO after pretreatment can be carried out at less harsh conditions.
(c) Pretreatment of waste streams is at ambient conditions and hence the overall process can be economical as the required treatment time using CWAO may be reduced with requirement of less harsh conditions.

2. Materials and methodology

2.1. Materials

The wastewater was procured from specialty chemicals industry. The reagents used for COD analysis (potassium dichromate, ferrous ammonium sulfate, ferroin indicator, mercuric sulfate, silver sulfate) as well as activated charcoal were obtained from S. D. Fine Chemicals, Mumbai, India. Ruthenium on carbon (5%) catalyst was procured from Sigma Aldrich, Bangalore, India. Oxygen with a minimum stated purity of 99.5% was obtained from Industrial Oxygen Company Ltd., India. All the chemicals were used as received from the supplier without any further purification. Distilled water was used for the preparation of solutions, which was prepared in the laboratory using distilled water plant.

2.2. Experimental setup

The high pressure reactor used in the present work for CWAO studies was procured from Amar equipments Ltd., India. A schematic representation of the experimental set up is shown in Fig. 1. The reactor was equipped with an electrically heated jacket, a 6-blade turbine agitator and a variable speed magnetic drive. The temperature and the speed of agitation were controlled by means of a Schneider controller. The gas inlet, gas release valve, cooling water feed line, pressure gauge and rupture disk were also provided to the reaction vessel. The liquid sample line and thermocouple well were immersed in the reaction mixture. A chilled water condenser was fitted at the location of the sample exit line to avoid flashing of the sample. The reactor was also provided with a cooling coil.

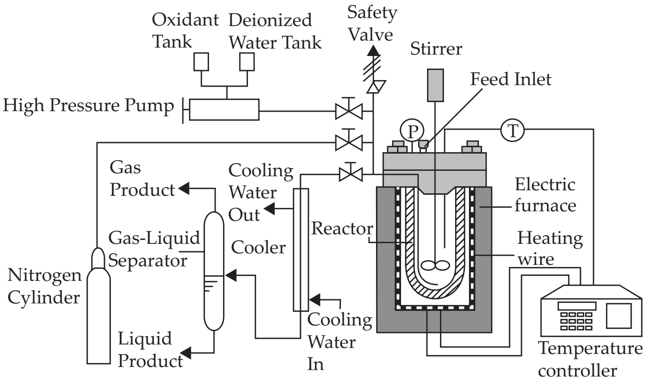

Fig. 1. Schematic of wet air oxidation set-up.

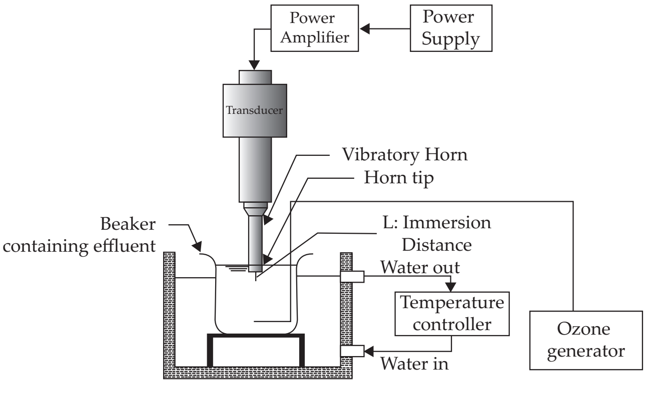

Fig. 2. Schematic representation of experimental setup for combined pretreatment of ultrasound and ozonation.

Ultrasonic horn (Dakshin India Ltd., Mumbai) equipped with a generator operating at a frequency of 20 kHz and power rating of 240 W was used for the pre-treatment. The tip diameter of the transducer was 2.1 cm giving an active acoustical vibration area as 3.46 cm^2. The calorimetric energy efficiency obtained for the ultrasonic horn was 10.5% (the actual power dissipation into the solution and hence available for cavitational activity was 25.2 W). Experiments were conducted in a glass reactor surrounded with a water bath to maintain a constant operating temperature.

Ozone generator (Model-DO400) was obtained from Eltech Engineering, Mumbai, with a rated maximum output flow of 400 mg/h. Ozone was generated from air by a laboratory-scale discharge generator and continuously bubbled into the pretreatment vessel using a bubble diffuser. A stirrer with a speed of about 200 rpm was used to provide sufficient contact between the effluent solution and ozone. A schematic diagram of the experimental set-up used for ozonation experiments has been shown in Fig. 2 (For experiments involving only ozone, ultrasonic horn was replaced by mechanical agitation).

2.3. Experimental methodology

In a typical experiment for CWAO, the reactor was filled with 0.5 dm^3 of effluent solution. All the experiments were performed at initial pH 12 to avoid corrosion of SS-304 reactor. The pH was adjusted using 0.2 M NaOH solution. The reactor was then purged with nitrogen, prior to the start of the experiment to ensure an inert atmosphere inside the reactor. The speed of agitation was adjusted to a pre-decided value and the reaction temperature was set as per the required value. After reaching the desired temperature, sample was withdrawn which was considered "zero" time for the reaction. Oxygen from the cylinder was then sparged into the liquid phase directly beneath the impeller to attain the desired partial pressure of oxygen. Exotherm of the reaction was controlled with the help of cooling water circulated through the cooling coil. The amount of oxygen fed into the reactor was in excess as compared with the theoretical requirement. Samples were withdrawn at regular intervals from the sample port. The entire system was operated in batch mode. Experiments were conducted using different loadings of Ru/C catalyst over the range of 0 to 0.2 kg m^{-3}. The effect of process parameters such as stirrer speed, temperature, pressure, initial pH and presence of free radical scavenger on the extent of degradation was investigated. The range of operating parameters considered in the work was temperature as 150 to 180°C, total pressure as 1.42 to 1.92 MPa, and catalyst loading as 0 to 0.2 kg m^{-3}.

A glass reactor (1 L volume) placed in water bath was used for the pretreatment experiments. Water bath was used to maintain a constant temperature of reaction mixture. For the experiments involving the use of ultrasound, an ultrasonic horn was immersed in the reaction mixture to a depth of 1 cm. The power dissipation for ultrasonic horn was set at 100 W with on and off time as 7 and 3 sec, respectively (duty cycle of 70%). For the experiments involving the use of ozone, a diffuser was incorporated at the bottom of the reactor. Ozone gas at a rate of 100 mg h^{-1} was introduced into the reaction mixture.

2.4. Analysis

COD analysis was performed using the standard dichromate reflux method [24]. Total organic carbon (TOC) analysis was performed using the ANATOC II total organic carbon analyzer procured from SGE International Pvt. Ltd., Australia.

The initial COD loading of effluent was 14,800 mg L^{-1}. As per the analysis done by specialty chemical industry, the wastewater stream mainly comprised of phenol, pentachlorophenol, 4 hydroxyphenylethane, sodium pentachlorophenate, 1-Hydroxyethylidene,1-diphosphonic acid as major constituents.

3. Results and discussion

3.1. CWAO of industrial effluent

Heterogeneous CWAO is a three phase reaction. During the treatment, pH changes are generally expected [12], and hence it is important to select an optimum level of the initial pH so that the operation is feasible and there are no corrosion issues. The natural pH of the effluent received was 5 and hence preliminary experiments were performed using this natural pH as the initial pH.

3.1.1. Change in pH of effluent during CWAO

WAO is based on a free radical mechanism and hence change in the pH of solution can occur, which can alter the concentration of hydroxyl radicals in the solution leading to different rates of reaction. It is important to note that SS-316 reactor was used for the experiments and to avoid any corrosion damage, effluent pH was proposed to be initially adjusted to pH of 12 using NaOH. To confirm this requirement, the results obtained in the initial phase of experimental work based on the use of effluent with pH of 5 (as received from industry) have been given in Fig. 3 which clearly confirms the reduction in the pH. It was observed that at 180°C, the pH of the effluent decreased rapidly from 5 to 2 during the initial one hour of oxidation and then increased to 9. The initial decrease in the pH is due to the degradation of pollutant molecules to low molecular weight organic acids and the reversal in trend suggests complete mineralization of organic acids to carbon dioxide and water. Lin and Ho [12] also reported similar trends of change in pH for the treatment of high strength industrial wastewater. The pH of effluent was reported to decrease rapidly with increasing oxidation time initially and after specific time, the pH of effluent increased and the rate of increase was dependent on the oxidation temperature. At 200°C temperature and $Cu(NO_3)_2$ loading of 500 mg L^{-1}, the pH of effluent was also reported to decrease to 4.5 after an hour of oxidation and reversed beyond that due to the degradation of acids. Considering this result, all the experiments have been performed starting at pH of 12 so as to avoid generation of strongly acidic conditions during the treatment.

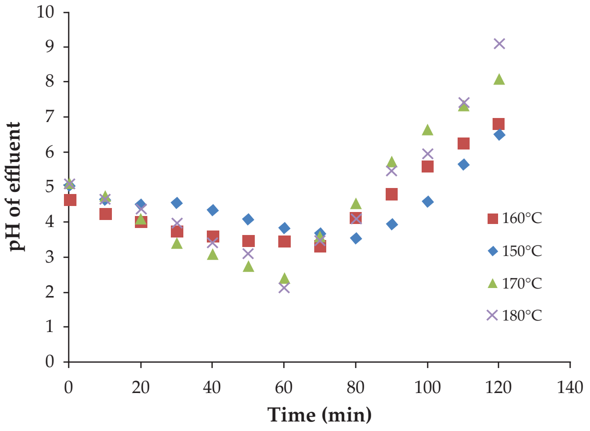

Fig. 3. Variation in the effluent pH with time during the CWAO treatment.

3.1.2. Effect of speed of rotation

Doraiswamy and Sharma [25] presented detailed insights into gas–liquid–solid reactions in the slurry reactor. Typically, due to the high diffusivity of oxygen in the gas phase and its low solubility in water, the gas side mass transfer can be considered to be negligible as compared to the liquid phase mass transfer. The intensity of turbulence in the liquid phase decides the extent of resistance offered to the liquid-phase mass transfer, which is now controlling and hence effect of stirring speed needs to be investigated.

Effect of speed of rotation on the mineralization of effluent was studied over the range of 400 to 900 rpm under conditions of temperature of 160°C, total pressure of 1.42 MPa and catalyst loading as 0.2 kg m^{-3}. The obtained results for the variation in the COD reduction have been given in Table 1 in terms of the kinetic rate constant for mineralization. In the CWAO, oxygen is used in excess during the reaction for complete oxidation of organic pollutants. Hence, the dependency of rate of reaction on oxygen pressure can be considered to be negligible. The kinetic equation for the oxidation can be thus written as follows:

$$\frac{dC}{dt} = -kC^{n} \tag{1}$$

where C is the COD loading, k is the pseudo first order reaction rate constant, t is the time and n is the order of reaction. For the determination of the reaction rate constant, the equation is integrated considering the first order kinetics to yield the following equation:

$$\ln\frac{C}{C_o} = -kt \tag{2}$$

According to the Eq. (2), a plot of $\ln(C_o/C)$ vs. time will be a straight line with slope as reaction rate constant (k). The obtained values of k for varying speeds of rotation have been represented in Table 1. It can be observed from the table that

Table 1
Effect of stirrer speed on kinetics of mineralization using CWAO

Sr No	Stirrer rpm	Rate constant $k \times 10^{-3}$ (min^{-1})	R^2 value
1	400	8.8	0.9663
2	600	9.5	0.9876
3	800	10.3	0.9928
4	900	10.5	0.9823

the mineralization rate constant increased from 0.0088 to 0.0103 min^{-1} with an increase in the stirrer speed from 400 to 800 rpm. For a further increase in the stirrer speed from 800 to 900 rpm, there was only a marginal increase in the rate constant from 0.0103 to 0.0105 min^{-1}. Therefore, it was confirmed that the rate of COD removal was independent of the speed of agitation above an impeller speed of 800 rpm, confirming the absence of resistance to transfer of oxygen in the liquid phase at speeds above 800 rpm. Vaidya and Mahajani [9] have also investigated the effect of stirrer speed on the CWAO of phenol using Ru/TiO_2 catalyst and reported similar existence of an optimum speed. All the further experiments were performed at an impeller speed of 800 rpm.

3.1.3. Effect of temperature

To study the effect of temperature, experiments were conducted over temperature range of 150 to 180°C at constant total pressure of 1.92 MPa with a optimum speed of 800 rpm and catalyst loading of 0.2 kg m^{-3}. The obtained results for the variation in the COD have been given in Fig. 4. COD reduction analysis revealed that about 98% COD reduction was obtained at 180°C in 120 min of treatment. The final COD of the effluent decreased from 6,560 to 240 mg L^{-1} as the temperature was increased from 150 to 180°C clearly confirming an increase in the extent of COD reduction with an increase in the temperature. The kinetic rate constants for the COD reduction at different temperatures have been given in Table 2. It is observed that the value of reaction rate constant increases with an increase in the temperature from 150 to 180°C and the maximum value obtained at temperature of 180°C was 0.0311 min^{-1}.

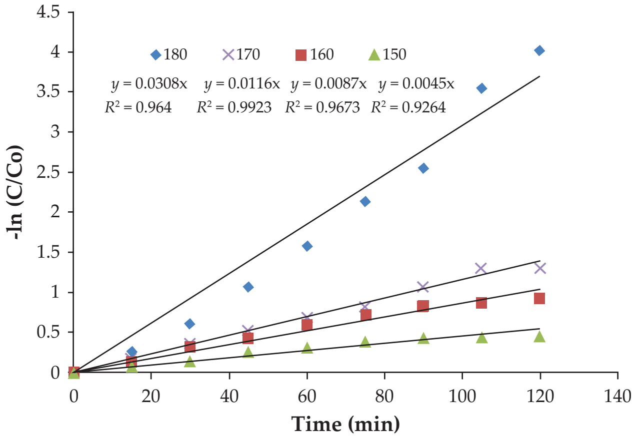

Fig. 4. Kinetics of wastewater mineralization at different temperatures.

Table 2
Effect of temperature on kinetics of mineralization using CWAO

Sr No	Temperature (°C)	Rate constant $k \times 10^{-3}$ (min^{-1})	R^2 value
1	150	4.6	0.92
2	160	8.8	0.9663
3	170	11.6	0.9921
4	180	31.1	0.9568

The dependence of reaction rate constant on temperature can be represented by Arrhenius equation.

$$k = k_0 \exp\left(-\frac{\Delta E}{RT}\right) \tag{3}$$

where ΔE is the activation energy, k_o is pre-exponential factor, R is gas constant and T is the operating temperature. The obtained Arrhenius plot for establishing the activation energy has been given in Fig. 5. The value of activation energy was found to be 95.53 kJ/mol (the R^2 value for the trend line fitting used for estimation of activation energy was 0.9488 confirming very good fitting). Lin and Ho [12] also investigated the temperature dependency of kinetic rate constant for CWAO of high strength industrial wastewater using copper sulfate ($CuSO_4$) and copper nitrate ($Cu(NO_3)_2$) as the catalysts and reported similar range of activation energies. It was reported that the activation energy of wet oxidation decreased from 57.8 kJ mol^{-1} for the case of no catalyst to 46.2 kJ mol^{-1} and 48.3 kJ mol^{-1} for ($CuSO_4$) and ($Cu(NO_3)_2$) as catalyst respectively confirming the similar range of activation energy value as obtained in the present work.

3.1.4. Effect of total pressure

The effect of total pressure on the extent of degradation has been investigated over the range of total pressures as 1.42 to 1.92 MPa at constant temperature of 180°C, speed of rotation as 800 rpm using a catalyst loading of 0.2 kg m^{-3}. The obtained results have been given in Fig. 6. It has been observed that extent of COD reduction increased with an increase in the total pressure from 1.42 to 1.92 MPa. It is also interesting to note here that the rate of COD degradation was fast in the first 60 min of treatment, beyond which the rate of degradation was lower. At 1.92 MPa total pressure, 80% COD reduction was observed in 60 min of treatment. The COD reduction obtained after 120 min was 98% clearly confirming the faster reduction in the first 60 min. Increase in the total pressure increases the availability of oxygen for the reaction, hence increasing the adsorption of oxygen on the catalyst surface leading to enhanced oxidation.

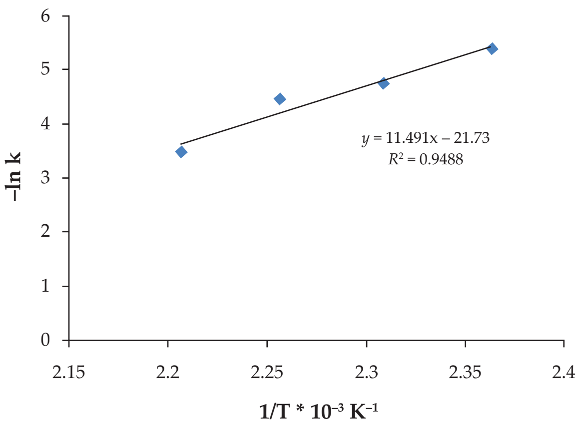

Fig. 5. Arrhenius plot for the catalytic wet air oxidation.

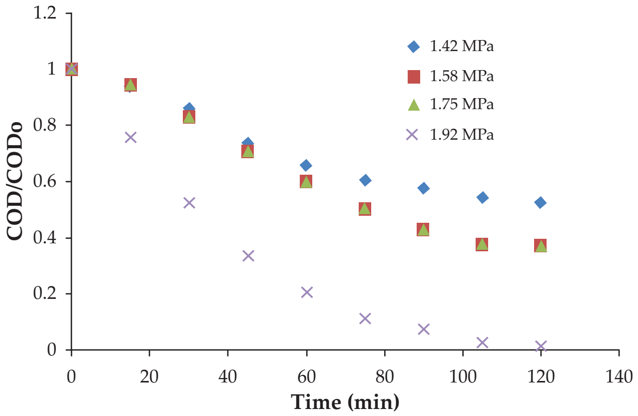

Fig. 6. Effect of total pressure on the extent of COD reduction.

The main purpose of using significantly higher pressure is to maintain the reaction in liquid phase. The slowing of rate of COD reduction after 60 min of treatment is expected as a typical first order kinetic profile.

Vaidya and Mahajani [9] have also reported that the rate of WAO of phenol over Ru/TiO_2 catalyst increased with an increase in the pressure from 0.34 to 1.38 MPa. It was reported that maximum of 96% COD removal is obtained at an operating pressure of 1.38 MPa. It was also reported that the COD reduction followed similar trend of steady increase till an optimum time and slow rate of degradation after the optimum treatment time as also observed in the present work.

3.1.5. Effect of catalyst dosage

Preliminary experiments with WAO performed at 180°C and 1.92 MPa total pressure without catalyst revealed that negligible extent of COD removal as 4% is obtained in 120 min. Moreover, the effluent stream became dark yellow after treatment in the absence of catalyst. Thermal decomposition occurring due to severe conditions of pressure and temperature results into fragmentation of the macromolecules into smaller molecules and CO_2 though at a significantly low rate. Zhang and Chuang [26] have also reported that the reaction during the period of pressurization and heating (in the absence of any catalyst) was negligible. A heterogeneous catalyst can enhance the oxidation rate in the presence of molecular oxygen and hence Ruthenium supported on carbon as the catalyst was used in the present work. The important characteristics of the heterogeneous catalyst Ru/C used in the present work have been summarized in Table 3.

Effect of catalyst dosage on the extent of COD reduction was studied over the range of catalyst loading 0.05 to 0.2 kg m^{-3} at constant temperature of 180°C, speed of rotation as 800 rpm and total pressure of 1.92 MPa. The obtained results for the extent of COD reduction have been given in Table 4. It can be seen from the table that the extent of COD reduction increased from 4% for the case of no catalyst to 95% for a catalyst dosage of 0.15 kg m^{-3} following a linear trend. A marginal increase in COD reduction was observed for a further increase in catalyst loading from 0.15 kg m^{-3} to 0.2 kg m^{-3} where about 98% COD reduction was observed. The resultant COD at this stage meets the local environmental norms (COD < 250 ppm).

Table 3
Characteristics of heterogeneous catalyst Ru/C

BET surface area (m^2 g^{-1})	627
Micropore volume (cc g^{-1})	0.45
Average pore diameter (A°)	29

Table 4
Effect of catalyst loading on extent of COD reduction using CWAO

Sr No	Catalyst loading (kg m^{-3})	Extent of COD reduction
1	0	4.5
2	0.1	82.3
3	0.15	95
4	0.2	98.2

As the catalyst loading increased, enhanced quantum of active sites are available for the adsorption of pollutant molecules, and hence the rate of reaction increases. The optimum catalyst loading (0.2 kg m^{-3}) where the final COD was below the recommended norms was used in the remaining experiments. Vaidya and Mahajani [9] investigated the effect of catalyst loading on the extent of COD reduction of phenol and reported that the extent of COD reduction increased with an increase in the catalyst loading. It was also reported that 100% COD reduction was observed at 1 kg m^{-3} loading of Ru/TiO_2 catalyst. Lin and Ho [12] studied the CWAO of wastewater using $CuSO_4$ and $Cu(NO_3)_2$ catalysts and reported that extent of COD reduction significantly increased with an increase in the catalyst loading up to 50 mg L^{-1} and after the optimum catalyst loading, only 5% increment in the COD reduction was observed. It is important to note that the extent of increase in the degradation and the actual value of the optimum catalyst loading depend specifically on the type of wastewater and catalyst and hence it is important to establish the same using laboratory scale study as per the methodology described in the current work.

3.1.6. Effect of free radical scavengers

CWAO proceeds with free radical generation and subsequent attack on the effluent molecules resulting into mineralization. In order to study the influence of the radical scavengers on the progress of catalytic wet air oxidation, an experiment was performed in the presence of *t*-butanol at a loading of 5.4×10^{-3} kmol m^{-3} and constant temperature of 160°C. It was observed that the presence of *t*-butanol reduced the extent of COD reduction substantially confirming the dominant contribution of free radicals in the degradation. Vaidya and Mahajani [9] also investigated the dependency of wet oxidation of *phenol* on the presence of *t*-butanol as a radical scavenger and reported that the presence of small amount of *t*-butanol drastically reduced the degradation of phenol.

3.1.7. Reusability of heterogeneous catalyst Ru/carbon

Experiments for reusability were conducted with 0.5 dm^3 effluent solution and 0.2 kg m^{-3} of catalyst loading. After the completion of reaction, the product stream was filtered and the catalyst mass was dried. Around 80% of the used catalyst was recovered, which was again used in the next experiment with 20% of makeup fresh catalyst to keep the catalyst loading constant. With the fresh catalyst, 98% COD reduction was obtained in 120 min of treatment at temperature of 180°C speed of rotation as 800 rpm, and total pressure of 1.92 MPa. In the case of recycled catalyst, 90% COD reduction was obtained indicating the marginal loss of activity of catalyst. Beziat et al. [27] studied the recycling of Ru/TiO2 catalyst for CWAO of carboxylic acids and reported a marginal loss in the activity of catalyst after first recycle and the activity remained stable in the three subsequent oxidation runs. Vaidya and Mahajani [9] also studied the reusability of Ru/TiO_2 catalyst and reported similar results of a marginal loss in the activity of the catalyst.

3.2. Intensification of CWAO

WAO is an energy intensive process as it is operated under conditions of high temperatures (180–315°C) and pressures (2–15 MPa). Due to these aspects, the commercial application for wastewater treatment is hampered especially in the case of the small scale industries as the treatment costs can be significant with requirement of necessary infrastructure for obtaining these drastic conditions. A novel approach for the intensification of WAO in the presence of catalyst has been studied based on the pretreatment using ozone/cavitation which can convert complex pollutant molecules into simpler ones. The aim of the combined process is to make the process cost effective such that the hybrid approach can be used efficiently for treatment of complex streams.

3.2.1. Use of cavitation as pretreatment

Experiments were conducted in the glass reactor immersed in a water bath to maintain constant operating temperature and irradiations were introduced using ultrasonic horn. 0.5 dm^3 of effluent solution was placed in the reactor and treated for 30 and 60 min as the pretreatment time at 100 W power output with duty cycle of 70%. The treated sample was then transferred to WAO unit at temperature of 160°C, speed of rotation as 800 rpm, total pressure of 1.42 MPa and 0.2 kg m^{-3} catalyst loading for variable treatment time of 90 and 60 min, respectively. The total time of treatment was kept constant so as to compare the results with only CWAO. The TOC and COD analysis results have been given in Fig 7. It can be seen that there is only a marginal increase in the extent of COD reduction for the use of 30 min and 60 min pre-treatment. Extent of COD reduction obtained at every stage of treatment has been given in Table 5. After 60 min of cavitation pre-treatment, the extent of COD removal was observed to be only 3% which is attributed to the low efficiency of ultrasonic horn in producing enough free radicals for this complex stream. Use of ultrasound may not destroy pollutant molecules completely but can result in the formation of lower molecular weight molecules, which is not clearly reflected in terms of COD reduction. Thus, after the use of ultrasonic cavitation, there is only a marginal change in overall COD but considerable rearrangement of molecules occurs (from complex to simpler), which can enhance the efficacy of CWAO. It was observed that the TOC reduction obtained at the end of combined treatment increased from 61% to 72% with an increase in the sonication time from 30 min to 60 min which suggests that complex molecules in the solution are indeed broken down during cavitation. Ingale and Mahajani [22] studied the approach of sonication followed by CWAO of refractory waste and reported an increase in the COD after pretreatment. However, beneficial results were indeed obtained for the combined system of sonication followed by CWAO (SONIWO) with COD reduction of 66%, whereas only 36% COD reduction was obtained from CWAO alone in three hour of treatment. Dhale and Mahajani [23] also investigated the role of sonication before and after WAO and confirmed similar beneficial effects of using ultrasound as pretreatment.

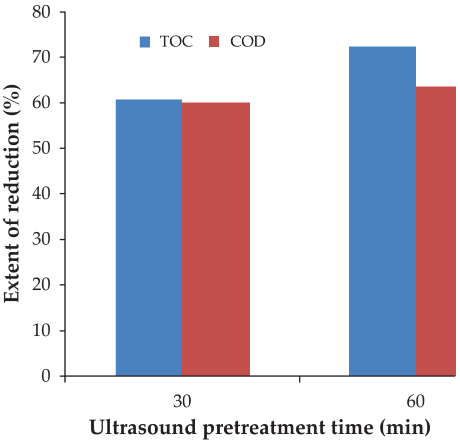

Fig. 7. Effect of ultrasound as pretreatment on extent of COD and TOC reduction using CWAO.

Table 5
Extent of COD reduction during the pre-treatment

Time of treatment (min)	Cavitation (%)	Ozonation (%)	Combination of cavitation and ozonation (%)
30	1	12	18
60	3	20	25

3.2.2. Use of ozonation as pretreatment

Ozonation was also used as a pretreatment with the effluent solution being treated for 30, 45 and 60 min. Ozone gas was introduced just below the stirrer. Samples were withdrawn from the reactor periodically and analyzed for TOC. The pretreated effluent was then transferred to the CWAO reactor where it was treated for 90, 75 and 60 min respectively at constant temperature of 160°C, speed of rotation as 800 rpm, total pressure of 1.42 MPa and catalyst loading of 0.2 kg m^{-3}. After 60 min of ozonation pre-treatment, the extent of COD removal was observed to be 20%. The TOC and COD analysis results have been given in Fig 8. An increment of 5%, 9% and 12% in the extent of COD removal was observed for the three batches pre-treated using ozone for 30, 45 and 60 min respectively. The intensification in the TOC removal obtained using ozonation was much higher as compared with the cavitation. The extent of TOC removal increased from 52.2% to 100% for an increase in pre-treatment time from 30 to 60 min.

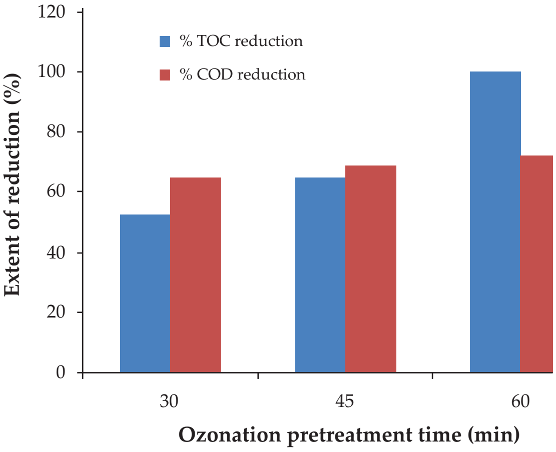

Fig. 8. Effect of ozonation as pretreatment on extent of COD reduction using CWAO.

3.2.3. Combination of ultrasound and ozonation as pretreatment

The combination of ultrasound and ozone was also utilized for the pretreatment of the effluent. Effluent solution was placed in the reactor and treated for 30, 45 and 60 min using optimum conditions for the individual treatment. The treated effluent solution was then transferred to the CWAO reactor where it was treated for 90, 75 and 60 min, respectively, at temperature of 160°C, speed of rotation as 800 rpm, total pressure of 1.42 MPa and catalyst loading of 0.2 kg m^{-3}. After 60 min of combined treatment, the extent of COD removal was observed to be 25%. The results of COD and TOC analysis are shown in Fig. 9 and results for kinetic rate constant have been given in Table 6. It can be observed from the table that as the pre-treatment time increased from 30 min to 60 min, the kinetic rate constant for TOC removal increased from 0.0072 to 0.0155 min^{-1}. The kinetic rate constant based on TOC kinetics for CWAO alone was found to be much less than the one obtained with pre-treatment using ultrasound and ozonation. A twofold increase in the rate constant suggests that the combination of ultrasound and ozonation reduced the induction time as well as gave significant decrease in the TOC of effluent. An increment of 9%, 16% and 20% in the extent of COD removal was also observed respectively with the three batches of varying pretreatment time.

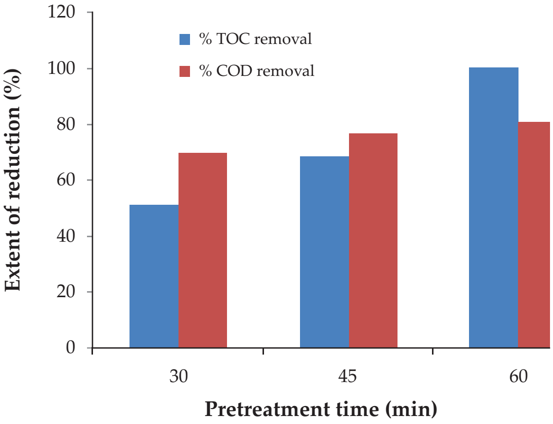

Fig. 9. Effect of ozonation + ultrasound as pretreatment on extent of COD and TOC reduction using CWAO.

Table 6
TOC reduction kinetics using ultrasound + ozonation as pretreatment combined with CWAO

Sr No	Pretreatment time (min)	Rate constant k × 10^{-3} (min^{-1})	R^2 value
1	0	3.5	0.976
2	30	7.2	0.9409
3	45	11.9	0.9326
4	60	15.5	0.92

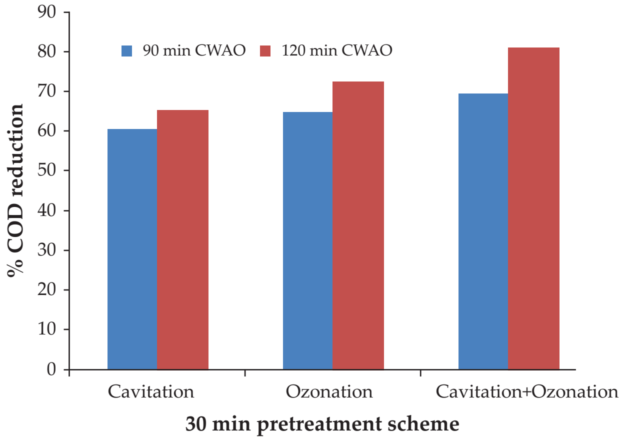

Fig. 10. Comparison of different pretreatment strategies in terms of extent of COD reduction obtained at the end of 120 min of treatment (Results for only 120 min CWAO available in earlier discussion).

3.2.4. Comparison of pretreatment approaches

The three pretreatment strategies discussed in the work viz. ultrasound, ozonation, and combination of ultrasound and ozonation, have potential for the intensification of CWAO up to a certain extent. These three pretreatments (same treatment time) were compared based on the extent of COD removal obtained in the case of CWAO. From the results depicted in Fig. 10, it is clearly observed that there is 4% enhancement in the extent of COD removal using ultrasound alone as a pretreatment followed by CWAO for 90 as compared to the use of CWAO for entire 120 min, whereas for ozonation alone as pretreatment it is 7%. Dhale and Mahajani [23] studied the SONIWO process and stated that cavitation as pretreatment reduces the time required for the generation of a sufficient number of free radicals to initiate the reaction, and does not have significant effect on the extent of COD removal during the pretreatment itself.

The effluent batch was also given CWAO treatment at temperature of 160°C, speed of rotation as 800 rpm, total pressure of 1.42 MPa and catalyst loading of 0.2 kg m^{-3} for 120 min (extended treatment), keeping pre-treatment time constant at 30 min. The results of extent of COD reduction for the varying CWAO treatment time are depicted in Fig 10. In the case of ozonation (ozone flow rate of 100 mg h^{-1} for 30 min), it was observed that extent of COD reduction increased from 65% to 73%, whereas with ultrasound as a pretreatment, the extent of COD reduction increased from 61% to 67%. With the combination of ultrasound and ozonation, it was observed that about 15% increase in the COD reduction was obtained during the extended treatment. The enhanced COD reduction for 90 min and 120 min treatment using CWAO suggests that the combination of pretreatments enhances the rate of oxidation giving higher extent of mineralization even for the extended treatment times.

4. Conclusions

Mineralization of real industrial effluent has been investigated using CWAO. Efforts have been taken to optimize the CWAO parameters in order to make the process energy efficient. Different strategies such as ultrasound, ozonation and combination of ultrasound and ozonation have also been used as a pretreatment for the industrial effluent stream prior to CWAO. Following important conclusions can be drawn based on the main findings of the present work:

- 98% COD reduction is obtained using 0.2 kg m^{-3} loading of Ruthenium supported on carbon catalyst at temperature of 180°C and total pressure of 1.92 MPa using CWAO.
- Combination of ultrasound and ozonation was the best pretreatment strategy giving enhanced reduction at lower temperatures of 160°C and total pressure of 1.42 MPa.
- The pretreatment techniques discussed in the present work can make the CWAO process economically attractive option for industrial wastewater treatment based on the use of less harsh conditions during CWAO and requirement of lower treatment times.

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