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Treatment of coke oven wastewater using ozone with hydrogen peroxide and activated carbon

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ABSTRACT

Demand of metallurgical coke results in generation of large amount of coke oven wastewater. Treatment of this wastewater was done with ozone which was used in combination with activated carbon (AC) and H_2O_2 to increase the degradation of chemical oxygen demand (COD). To optimize the parameters which influence the COD degradation of coke oven wastewater Response surface methodology (RSM) was used. The optimized condition for treatment with ozone and activated carbon is pH 5, 13.5 min of reaction time and 2 g/L activated carbon while for the treatment using ozone along with H_2O_2 was pH 9.5, 3.5 g/L H_2O_2 concentration and 27.5 min of reaction time. The maximum degradation of COD achieved in the O_3/AC was 76.79% while in the O_3/H_2O_2 process the COD removal was 75.8%. Study of both the treatment processes suggests that both the processes follow pseudo second order kinetics with constants 16.10×10^{-5} L/min·mg for the O_3/AC process and 7.04×10^{-5} L/min·mg for the O_3/H_2O_2 process. The O_3/AC process is more acceptable in terms of fast rate of COD degradation, economy and efficiency of the process as it requires less time and hence proposed treatment scheme which could degrade COD of large volume of wastewater.

Keywords: Coke oven wastewater; Response surface methodology; Ozone; Hydrogen peroxide; Activated carbon

1. Introduction

Advancement of human civilization is usually correlated with rapid urbanization causing an increased demand for construction materials. Steel being one of the major materials has experienced a large hike in production due to the increasing demand [1]. Metallurgical coke prepared in a coking plant is of great importance in the iron and steel industry mainly for reduction of iron ore to pig iron [2,3]. In a coking plant, coal of coking grade is converted into coke via pyrolysis, in the absence of O_2 and at temperatures of around 1200°C. The volatiles present in the coal are released and is known as coke oven gas which is used for manufacturing benzene, toluene, naphthalene, tar and dyes [3]. During the process of quenching of hot coke, washing the ammonia stills and processing and purification of by-products, water is consumed at a rate of approximately 4000 m^3 per 1000 tons of coke produced [4]. A huge quantity of wastewater is thus discharged into the atmosphere (at the rate of 0.3–4.0 m^3 per ton of coke produced) [5]. The effluent

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contains toxic contaminants such as organic contaminants (polynuclear aromatic hydrocarbons, phenolic compounds, and heterocyclic hydrocarbons containing oxygen, nitrogen, sulfur) and inorganic pollutants (sulfate, thiocyanate, cyanide) most of which are refractory, toxic and carcinogenic in nature [6–8]. Thus, pollution caused by coke oven wastewater is a serious issue in the world [9].

As the concerns about the ill effects of coke oven wastewater are increasing various researches have been carried out to develop different treatment methods to effectively degrade the contaminants present in the coke oven wastewater [10–13]. Conventional treatment process such as bio-treatment, chemical oxidation, adsorption via activated carbon, reverse osmosis and air stripping have been carried out in many studies, but they were not effective in degrading contaminants present in coke oven wastewater [14–16]. Biological treatment methods seem to be an effective alternative treatment methods, but the prolong treatment time and high sensitivity of the biological degrading agents – bacteria and fungi poses a major threat to its commercial large scale implementation. The chemical oxidation process has its drawbacks – excessive sludge generation and the high cost of chemicals [17]. The adsorption process is not economic and is a tedious process as regeneration of the used activated carbon is often troublesome.

In this context, advanced oxidation processes can be considered to be an alternative to the above-mentioned treatment procedure. In such processes hydroxyl radicals are generated which has the ability to degrade most of the organic pollutants present in the wastewater [18]. Ozone as an oxidizing agent have recently received a lot of attention from the scientific community due to its high oxidative capacity and ability to degrade a lot of organic which is non-biodegradable in nature [19–22]. From Eq. (1), high oxidation capacity of ozone is due to its high standard reduction potential (E°) of about 2.07 V (standard hydrogen electrode) [23].

$$O_3 + 2H^+ + 2e \leftrightarrow O_2 + H_2OE^0 = 2.07V \quad (1)$$

Ozone usually degrades the organic component of the wastewater in two ways – directly or indirectly. In the first case, ozone molecule attacks an unsaturated bond and breaks it up while in the second case, ozone produces a hydroxyl radical in chain reactions which disintegrate organics into water and carbon dioxide. The indirect oxidation because of the chain reaction mechanism is usually favored and for this few modifications are necessary – increasing initial pH, adding H_2O_2, UV radiation or solid catalyst [24]. A major problem associated with the treatment of wastewater with O_3 are its high cost and low mass transfer rate for which it is not popularly accepted industrially [25]. O_3 along with activated carbon (AC) has proved to be efficient in this regard as the catalytic property of AC increases COD removal to a great extent [26]. The addition of H_2O_2 increases the release of hydroxyl ions which again speeds up the COD removal. For implementation in an industry, which generates a very high volume of wastewater, a treatment procedure is needed which effectively degrades effluent of varying characteristics at a very fast pace. Thus this study aims in establishing a method which is not only effective but also very fast.

Although coke oven wastewater disposal is of great challenge in the present scenario yet very few studies have dealt with the treatment of coke oven wastewater with ozone as an oxidizing agent. In this present study, two sets of experiments were conducted – in one ozonation was done along with AC while in the second ozone was purged along with H_2O_2. The study aims to optimize the parameters influencing the process using response surface methodology such that maximum COD removal was obtained and thus provide an effective and comprehensive approach to treat coke oven wastewater.

2. Materials and method

2.1. Wastewater and chemicals

20 L of wastewater was collected from Durgapur Project Limited, West Bengal and immediately after transportation it was transferred to lab iceboxes at 4°C to avoid any changes to the physiochemical properties of the effluent. The wastewater was analyzed and the initial COD was 3690 mg/L, total suspended solids (TSS) was 115 mg/L, pH 9.3 and it had a yellowish brown colour. The chemicals required for the study are H_2O_2 (30% by v/v), NaOH and H_2SO_4 (96% v/v). All the solutions were made with distilled water. The AC used for the experiments were prepared by activation of rice husk ash using o-H_3PO_4 in 1:1 ratio and then carbonization for 120 min at 350°C. Silica was recovered from the rice husk ash before activation of the carbonaceous mass [27].

2.2. Experimental setup

Experiments were conducted in a 5 L batch reactor made of acryl nitrate and ozone was injected from the bottom at the rate of 4.7 g/h through a diffuser. Ozone gas was generated by ozone generator manufactured by Creative Oz-Air (i) Pvt. Ltd., India. The ozone generator took oxygen from the atmosphere and converted it into ozone and delivered into the reactor by a centrifugal pump. The reactor was equipped with 4 baffles and a propeller to ensure proper mixing of the reaction broth. The pH of the wastewater was adjusted to the required level using either NaOH or H_2SO_4. Fig. 1 shows the details of the experimental setup used for the study.

2.3. Analysis

COD was analyzed using the general methods prescribed by APHA [28] and reactor digestion method for a COD range of 0–1500 mg/L using automatic COD analyzer of LoviBond, Germany . The exterior morphology of the activated carbon used for the study was characterized using scanning electron microscope (SEM model: Hitachi 3000). X-ray diffraction (XRD) was used to study the nature of activated carbon before and after it has participated in the treatment process. ExpertPRO diffractometer using Ni-filtered Cu Kα radiation at scanning rate 6° per minute was used within a range of 10° and 90°. Further, to understand the surface chemistry of the activated carbon, Fourier transform infrared spectrograph analysis within the range of 400

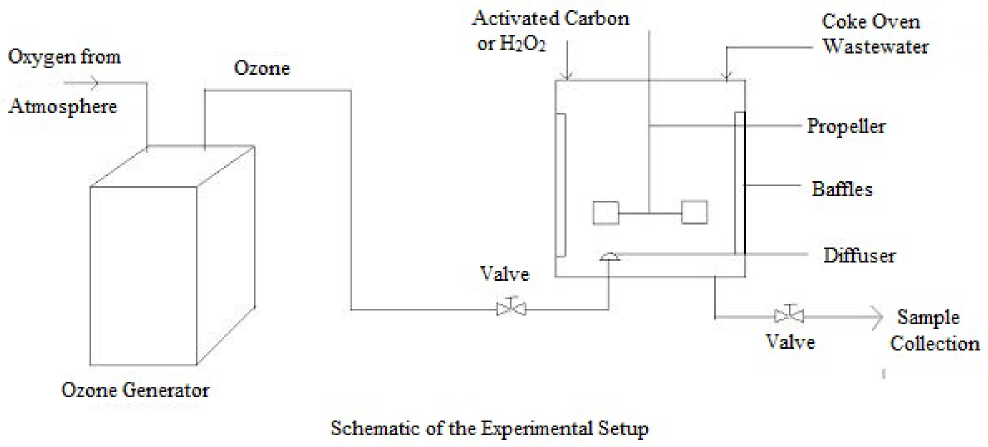

Fig. 1. Experimental setup used for the study.

cm^{-1} to 4000 cm^{-1} was done using ParkinElmarFTIR-2000. The removal efficiency of the process was measured using the following equation:

$$\%\ \text{Removal of COD} = \left(1 - \frac{C_f}{C_i}\right) \times 100 \tag{2}$$

where C_i and C_f stands for the initial and final COD values (mg/L) respectively.

The ozone consumed (OC) during the removal of COD by ozonation is given in the following equation [29].

$$OC = \frac{Q_G}{V} \times \frac{\int_0^t \left(1 - \frac{C_{AG}}{C_{AGo}}\right) dt}{\left(C_o - C\right)} \tag{3}$$

where Q_G is the gas flow rate (mL/min), C_{AG} is the off-gas ozone concentration (g/m^3), C_{AG0} is the input ozone concentration (g/m^3), V is the sample volume (mL), t is the time (min), and C_0 and C correspond to the initial and final (at time t) COD (mg/L), respectively.

2.4. Design of experiment

There were two sets of experiments that were carried out simultaneously in this study; in one case, activated carbon (AC) was used along with ozone while in the other H_2O_2 was used along with ozone for the wastewater treatment. While in the O_3/AC process, adsorption aids the oxidation process, in the O_3/H_2O_2 process the oxygenation was with free oxygen radical which generated as H_2O_2 and is considered of the indirect type [26]. Optimum pH, the dosage of H_2O_2 or AC, the time for reaction is to be identified for the maximum COD removal. Response surface methodology (RSM) was used for the design of experiments; its modeling and optimization of the parameters is to be done for the response variables; namely COD degradation. RSM is a collection of mathematical and statistical techniques useful for developing, improving and optimizing the process and is used to evaluate the relative significance of several affecting factors even in the presence of complex interactions of the factors [30–32]. The main objective of the RSM is to determine the optimum conditions of the system or to determine the operating conditions, which is usually done in three consecutive stages – (i) design experiments (ii) RSM via regression and (iii) optimization.

This optimization process follows three major steps – carrying out designed experiments as suggested by RSM then evaluating the coefficients in a mathematical model along with the prediction of the responses and examining the adequacy of the model [33]. The design experiments were carried out in the reactor as described above while the operating parameters were varied according to various literature surveyed. For the O_3/AC experimental set, pH was varied within the range 3–7, the dose of AC was kept between 1 g/L to 3 g/L and the reaction time was from 7 min to 20 min, while for the O_3/H_2O_2 experiment, the dose of H_2O_2 was varied within the range of 2 g/L to 5 g/L while pH and time for reaction were varied between 7 to 12 and 20 min to 60 min respectively. Statistically designed 20 experiments were conducted with the different combination of independent variables, as suggested by the design expert software. RSM provides a quantified relation between the independent variables on which the process behavior depends and the process output or behavior as shown in Eq. (4).

$$Y = f\left(x_1, x_2, x_3, x_4 \ldots x_n\right) \tag{4}$$

where Y is system behavior or system response because of the various independent parameter x_1, x_2, x_3 etc. The independent variables are known as factors [34].

For three process parameters, the number of design experiments is given by Eq. (5)

$$N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 6 = 20 \tag{5}$$

as shown by Sahu et al. [34].

The result obtained after each run was analyzed and the response obtained was correlated with three independent parameters for the COD removal by ozonation using an empirical second degree polynomial equation (Eq. (6)) such as

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \left(\sum_{i=1}^{n} \beta_{ii} x_i\right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j + \epsilon \tag{6}$$

where β_0 is the constant coefficient, β_i is the linear coefficient, β_{ij} is the interaction coefficients, β_{ii} is the quadratic coefficients.

The results obtained were in terms of COD removal and Ozone consumption was applied in the RSM to find the best operating conditions which would result in maximum removal of COD and minimum consumption of O_3. At the end of each of the run, the samples were analyzed for COD removal. The statistical software package was used for regression analysis of experimental data and for plotting of the response surface.

2.5. Kinetic study

For the determination of reaction mechanism, kinetic study for COD removal of the coke oven wastewater using O_3/AC and O_3/H_2O_2 was done. Batch experiments were performed to determine adsorption kinetics. In 5L reactor vessel, 4L of coke oven wastewater solution were prepared; AC and H_2O_2 were added according to the optimized value given by response surface methodology and the pH was set in accordance with the optimized value. The flask was placed in a constant speed incubator shaker at 140 rpm. After different time intervals, a part of the solution from the specified flask was separated from the adsorbent by filtration and was analyzed to determine the COD content. The pseudo first order equation is given by Eq. (11) [27].

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{7}$$

q_e and q_t is defined as given in Eq. (8) and Eq. (9)

$$q_t = \frac{V\left(C_o - C\right)}{w} \tag{8}$$

$$q_e = \frac{V\left(C_o - C_e\right)}{w} \tag{9}$$

where C_0 is the initial COD concentration (mg/L), C_e is the equilibrium concentration of COD (mg/L) and C is the concentration of COD (mg/L) at time t (min). V is the total volume of wastewater (L) and w is the amount of adsorbent added (g) [27]. Replacing q_e and q_t by Eqs. (8) and (9) respectively in Eq. (7), we get Eq. (10),

$$\ln\ln\left(\frac{C_o - C_e}{C - C_e}\right) = k_1 t \tag{10}$$

where k_1 is the rate constant for pseudo first order model (min^{-1}).

The pseudo second order kinetics is given by Eq. (11) [35].

$$q_t = \frac{t k_2 q_e^2}{1 + t k_2 q_e} \tag{11}$$

where k_2 is the pseudo second order rate constant (g/min·mg), t is the time (min) replacing q_e and q_t with Eq. (8) and Eq. (9) in Eq. (11), we get Eq. (12)

$$\frac{1}{\left(C_o - C_e\right) - \left(C_o - C\right)} = \frac{1}{\left(C_o - C_e\right)} + K_2 t \tag{12}$$

3. Results and discussion

3.1. Optimization of independent parameters for the O_3/AC process

The parameters influencing COD removal have been optimized by RSM using design expert software to get the values of the influencing parameters, viz. initial pH of wastewater, the AC dose and the reaction time for which the COD removal is maximum and the ozone consumption is minimum. The experiments suggested according to RSM and their obtained responses have been tabulated in Table 1.

The ratio of maximum to minimum range in the process was less than 10 hence no transformation was chosen and quadratic order model was selected for COD removal analysis while square root transformation was chosen for ozone consumption response as this ratio exceeded 10 [36]. The design expert software showed that the R^2 value for the linear is 0.107, for 2FI model is –0.026, for cubic it is 0.978 while for quadratic it was 0.988 and hence suggested a quadratic model to generate a regression model for the COD removal percentage. It is observed that the predicted R^2 of 0.743 is in reasonable agreement with the adjusted R^2 of 0.938 as the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio which is greater than 4 is desirable and the value, in this case, is 15.02. Thus it indicates an adequate signal and this model can be used to traverse the design space [36]. The final regression function for COD removal in terms of factors is given below (Eq. (13)):

$$\begin{aligned}\%\ \text{COD removal} = {} & [-47.055 + (27.621 \times \text{pH}) + (11.797 \\ & \times \text{AC dose}) + (5.214 \times \text{time}) + (-0.520 \times \text{pH} \times \text{AC dose}) \\ & + (-0.241 \times \text{pH} \times \text{time}) + (-0.217 \times \text{time} \times \text{AC dose}) \\ & + (-2.319 \times \text{pH}^2) + (-1.316 \times \text{AC dose}^2) + (-0.097\ \text{time}^2)]\end{aligned} \tag{13}$$

The ozone consumption (OC) was optimized using RSM and such that the amount of ozone consumed per Kg of COD removed was minimum. The quadratic model was chosen for O_3 consumption. The final regression model of this response in terms of factors is given below in the form of an equation (Eq. (12)).

$$\begin{aligned}\sqrt{\text{OC}} = {} & [0.674 + (-0.131 \times \text{pH}) + (0.218 \times \text{AC dose}) \\ & + (-0.022 \times \text{time}) + (0.00227 \times \text{pH} \times \text{AC dose}) + (0.0012 \\ & \times \text{pH} \times \text{time}) + (0.000236 \times \text{AC dose} \times \text{time}) + (0.0109 \\ & \times \text{pH}^2) + (-0.0208 \times \text{AC dose}^2) + (0.00044 \times \text{time}^2)]\end{aligned} \tag{14}$$

From Table 1, it is clear the values of ozone consumption are less than 3 Kg O_3/Kg COD in most of case, ensuring the feasibility of the overall process [37].

3.1.1. ANOVA analysis

Based on the analysis done by ANOVA on the regression model (Eq. (13)), it has been found that pH and time of reaction have a significant effect on COD removal. Table 2 shows

Table 1
Experiments as suggested by RSM and their corresponding response for the treatment with ozone and activated carbon

Run	Factor 1	Factor 2	Factor 3	Response 1	Response 2
	pH	Activated carbon dose (g/L)	Reaction time (min)	% COD removal	Ozone Consumption (Kg O_3/Kg COD)
1	5.00	2.00	13.5	76.87	1.891
2	7.00	3.00	7.00	63.63	1.184
3	5.00	0.32	13.5	70.60	2.058
4	3.00	3.00	20.0	73.38	2.934
5	8.36	2.00	13.5	51.16	2.841
6	7.00	1.00	7.00	57.49	1.311
7	3.00	1.00	20.0	68.73	3.132
8	3.00	1.00	7.00	52.84	1.426
9	5.00	2.00	13.5	76.87	1.891
10	5.00	2.00	24.4	76.77	3.426
11	3.00	3.00	7.00	57.23	1.317
12	7.00	1.00	20.0	66.73	3.226
13	1.63	2.00	13.5	47.28	3.073
14	5.00	2.00	2.57	50.77	0.544
15	5.00	2.00	13.5	76.87	1.890
16	7.00	3.00	20.0	61.30	3.512
17	5.00	2.00	13.5	76.87	1.890
18	5.00	2.00	13.5	76.87	1.890
19	5.00	3.69	13.5	72.86	1.994
20	5.00	2.00	13.5	75.58	1.923

Table 2
Analysis of variance (ANOVA) for percentage COD removal

Source	Sum of Squares	d_f	Mean Square	*F* Value	*p*-value Prob > *F*
Model	2008.72	9	223.19	33.021	2.84×10^{-6}
A-pH	0.88	1	0.887	0.131	0.724
B-AC dose	13.45	1	13.457	1.991	0.188
C-Time	500.58	1	500.58	74.062	6.18×10^{-6}
AB	8.68	1	8.68	1.284	0.283
AC	78.93	1	78.934	11.678	0.006
BC	15.97	1	15.975	2.363	0.155
A^2	1240.02	1	1240.023	183.466	9.28×10^{-8}
B^2	24.97	1	24.978	3.695	0.083
C^2	245.98	1	245.989	36.395	0.001

*A: pH, B: AC dose (g/L), C: time (min)

the ANOVA analysis of the first response i.e. percentage of COD removal. Linear term of pH has a much lesser effect on COD removal compared to its second order term. Combined effect of pH and time has a considerable effect on the response. The second order term of time has immense significance. Lower *p*-value and higher *F* value and sum of square indicate the terms which have more significance which indicates the pattern of interactions between the parameters [30,38]. When the values of "Prob > F" is less than 0.05, the model terms are significant hence analyzing the Table 2, we can conclude that percentage removal is highly dependent on the combined effect of time and pH, the square of pH and square of time and the unit power of time. For these terms, the *F* value and sum of square value were highest while the *P* value was lowest. Model terms having values of "Prob > F" greater than 0.1 are not significant, thus indicating that activated carbon dosage is not such an important factor in COD removal. The Model *F*-value of 33.02, sum of square value of 2008.72 and a low *P* value of 2.84×10^{-6} implies the model is significant and can be used to explain the relationship between response and the independent factors appropriately [39]. There is only a 0.01% chance that such a large *F*-value could occur due to noise.

Similarly, the ANOVA analysis for the other response – ozone consumption was done. The analysis of regression model (Eq. (14)) is given in Table 3. It is clear from the ANOVA analysis that ozone consumption is highly depended on the time of reaction. The analysis suggests that quadratic equation describing the ozone consumption model highly depends on the square of reaction time and square of initial pH of the wastewater. It is also dependent on the combined interaction of reaction time and initial pH of the wastewater. It is also evident that the AC dose is not effective in the quadratic equation describing the model. AC added to the process increased the COD removal but it is not a significant factor in determining the ozone consumption. A very low *P* value and a very high *F* value indicate that the regression model is significant and the relation between the response and the independent variable are well established.

3.1.2. Effect of independent factors on COD degradation using ozone and AC

The response surface generated by design expert shows the variation of percentage removal as the factors viz. reaction time, pH and the AC dose. All the results are consistent with the conclusion drawn from ANOVA analysis. Fig. 2(a)

Table 3
ANOVA analysis of the regression model for determining the significant factor responsible for ozone consumption

Source	Sum of Squares	D_f	Mean Square	*F* Value	*p*-value Prob > *F*
Model	1.693	9	0.188	261.637	1.14×10^{-10}
A (pH)	8.9×10^{-5}	1	8.9×10^{-5}	0.123	0.732
B (AC dose)	0.001	1	0.001	1.473	0.252
C (Time)	1.45	1	1.450	2017.019	7.21×10^{-13}
AB	0.001	1	0.001	2.714	0.130
AC	0.010	1	0.010	15.239	0.002
BC	0.001	1	0.001	2.680	0.132
A^2	0.197	1	0.197	274.277	1.35×10^{-8}
B^2	0.002	1	0.002	3.078	0.109
C^2	0.015	1	0.015	22.148	0.001

*A: pH, B: AC dose (g/L), C: time (min)

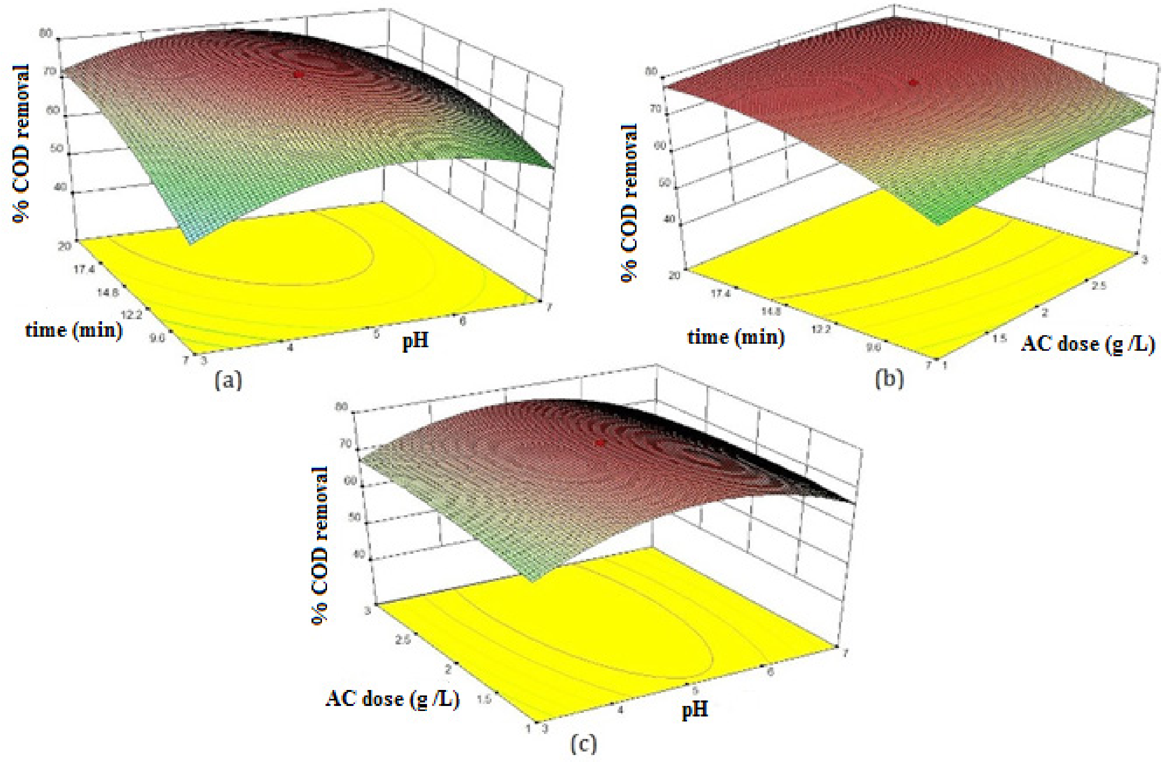

Fig. 2. Response surfaces for degradation of coke oven wastewater using ozone along with activated carbon showing interaction between (a) time and pH (b) time and activated carbon dose and (c) activated carbon dose and pH

shows the dependency of percentage removal on pH and time. The factors pH and time has great influence on the percentage removal. The experiments were carried out with pH ranging between 3 and 7 and it is seen that the percentage removal increases from pH 3 and goes up to a maximum value of 76.79% at pH 5 and decreases gradually with pH. Better COD removal at lower pH may be due to the fact that L type activated carbon (acidic type) was used in the study exhibits a negative charge in water and hence absorbs H^+ ions [38]. Maximum COD removal is achieved at a reaction time of 13.5 min.

The combined effect of activated carbon dose and the reaction time is shown in Fig. 2(b). The factor – activated carbon dose has no major effect on COD removal when varied but reaction time influences the COD removal to a great extent – the COD removal increasing upto 76.79% at a reaction time of 13.5 min. This is because of the fact that the ozonation leads to quick oxidation of contaminants (small organic molecular compounds) which then adsorbed into activated carbon to reduce the organic load in the wastewater [40]. The possible reason that was proposed to justify the increased efficiency of COD removal in O_3/AC process is the catalytic nature of AC which generates highly reactive species from molecular ozone in aqueous media [41,42]. The AC acts not only as a catalyst providing a surface for the O_3 to decompose but also as an adsorbent, absorbing the organics and the by-products of O_3 oxidation [43]. As the COD removal is not highly depended on the AC dose indicating that AC is predominantly catalytic in nature, however, its adsorption characteristics cannot be completely ruled out.

Fig. 2c shows the dependency of percentage removal on the pH and adsorbent dose. The factor pH has great influence on the percentage removal while adsorption dose has negligible or no effect on the response. The experiments were carried out with pH ranging between 3 and 7 and it is seen that the percentage removal increases from pH 3 and goes up to a maximum value of 76.79% at pH 5 and decreases gradually with the increase in initial pH. The maximum removal of COD at a lower pH 5 may be attributed to the reason that the efficiency of the activated carbon is highest at that pH because of the nature of activated carbon [44]. The dosage of activated carbon was varied between 1 g/L and 3 g/L but it is evident from Fig. 2a and Fig. 2c that not much significant change in COD removal are seen as the activated carbon dosage is varied. Activated carbon enhances the COD removal but there is not much effect on COD removal even if the dose of activated carbon is increased which is in accordance with the ANOVA analysis. Insignificant changes in COD removal after the reaction time of 13.5 min indicates that the forward reaction stops nearly after a time period of 13.5 min and hence reaction if continued after 13.5 min it will not yield any significant changes in COD removal.

3.1.3. Effect of independent factors on ozone consumption for ozone and AC process

Similar to COD removal, the Ozone consumption also varies with the factors – pH, COD removal and reaction time. These variations are given in Fig. 3 which shows that

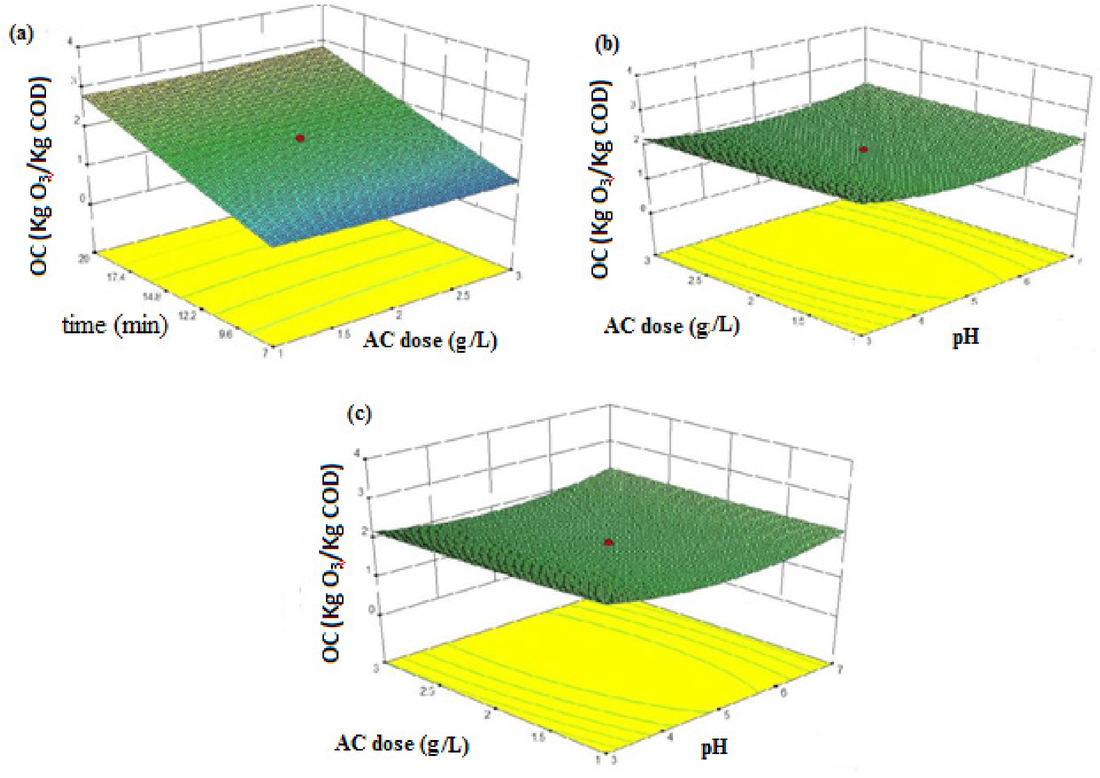

Fig. 3. Variation of ozone consumption with (a) reaction time and activated carbon dose (b) activated carbon dose and pH and (c) activated carbon dose and pH.

the surface generated by design expert is in tandem with the results obtained from ANOVA analysis. It is evident from the RSM surfaces (Fig. 3) that adsorption dosage has no major role in determining the model equation expressing the ozone consumption in the form of a quadratic equation. The major influencing factor that determines the ozone consumption is pH and reaction time. From Fig. 3a it is seen that the ozone consumption increases with reaction time and reaches a minimum of 2.6 kg O_3/kg COD and this is attributed to the fact that even though COD removal shows no further significant change after 13.5 min, yet ozone is purged into the system continuously causing an increase in ozone consumption without any decisive COD degradation. The factor AC has no significant role. Fig. 3b shows minimum ozone consumption around pH 5 and it is higher around pH 7 and pH 3, whereas dosage of activated carbon has no significant effect on ozone consumption. Fig. 3c shows that minimum ozone consumption is at pH around 5 and it increases with time because of reasons mentioned above.

3.1.4. Optimization of independent factors for both responses

The aim of the study was to optimize the independent parameters – initial pH, reaction time and adsorbent dose such that we have minimum ozone consumption and achieve maximum COD degradation. The optimized value of the independent parameters for maximum COD removal with minimum possible ozone consumption is reaction time of 13.5 min, initial wastewater pH of 5.0 and a 2 g/L dosage of AC. At this optimized condition, the COD degradation was found to be 76.79% with an ozone consumption of 2.6 kg O_3/kg COD.

3.2. Optimization of independent parameters for O_3/H_2O_2 process

Three parameters viz., time of reaction, initial pH of the wastewater and H_2O_2 have been optimized by RSM using Design Expert Software for maximum removal of COD from coke oven wastewater and minimum consumption of ozone simultaneously. The list of experiments designed by RSM and the corresponding values of response (% removal of COD and ozone consumption) for each sample obtained at those experimental conditions are shown in Table 4. As suggested by the software, the ratio of maximum to minimum in the process for COD degradation was estimated to be more than 10 hence no transformation was chosen and quadratic order model was selected to analyze data. For developing a regression model for the consumption of ozone, logarithmic transformation was used as the ratio between maximum and minimum exceeded 10 [36].

The design expert software showed that the R^2 value for the linear is 0.785, for 2FI model is –0.738, for cubic it is 0.979 while for quadratic it was 0.986 and hence suggested a quadratic model for the COD removal percentage. It is seen that the predicted R^2 of 0.736 is in reasonable agreement with the adjusted R^2 of 0.984 as the difference is less than 0.2. Adeq

Table 4
Design of experiments and their corresponding responses for COD removal and ozone consumption for ozone and H_2O_2

Run	Factor 1 pH	Factor 2 H_2O_2 g/L	Factor 3 Time min	Response 1 % COD Removal	Response 2 Ozone Consumption Kg O_3/Kg COD
1	7.0	5.0	15.0	60.142	2.148
2	9.5	3.5	27.5	79.748	2.970
3	9.5	3.5	27.5	79.748	2.970
4	12	5.0	40.0	59.754	5.765
5	9.5	3.5	27.5	79.748	2.970
6	9.5	6.1	27.5	70.542	3.357
7	9.5	3.5	27.5	79.748	2.970
8	12.0	2.0	15.0	62.984	2.051
9	7.0	5.0	40.0	59.754	5.765
10	12.0	2.0	40.0	65.180	5.285
11	9.5	3.5	27.5	79.748	2.970
12	13.7	3.5	27.5	48.837	4.850
13	9.5	0.97	27.5	69.186	3.423
14	9.5	3.5	48.5	75.969	5.501
15	9.5	3.5	6.4	75.646	0.73755
16	5.29	3.5	27.5	46.511	5.09259
17	7.0	2.0	40.0	63.630	5.41455
18	9.5	3.5	27.5	79.748	2.97016
19	12.0	5.0	15.0	69.186	1.86741
20	7.0	2.0	15.0	68.863	1.87617

Precision greater than 4 is desirable and the value for this case is 19.85, thus indicating an adequate signal and ensuring that the model can be used to navigate the design space [36]. The final regression function for response in terms of factors that are used in making of statistical model is given as:

$$\%\text{COD removal} = [-98.9101 + (33.2363 \times \text{pH}) + (7.30 \times H_2O_2\ \text{Conc.}) + (0.625 \times \text{time}) + (0.445 \times \text{time} \times H_2O_2\ \text{Conc.}) + (-0.0064 \times \text{pH} \times \text{time}) + (-0.0452 \times \text{time} \times H_2O_2\ \text{Conc.}) + (-1.808 \times \text{pH}^2) + (-1.537 \times H_2O_2\ \text{Conc.}^2) + (0.0086) \times \text{time}^2] \quad (15)$$

Another response – ozone consumption was also optimized using RSM. Ozone Consumption is defined as the mass of ozone gas consumed during removal of a certain mass of COD during ozonation under experimental conditions. Logarithmic transformation was chosen for this response and a quadratic model was used to design the ozone consumption response. The final regression model of this response in terms of factors is given below in the form of an equation (Eq. (16)).

$$\ln(\text{OC}) = [2.085 + (-0.549 \times \text{pH}) + (-0.105 \times H_2O_2\ \text{Conc.}) + (0.087 \times \text{time}) + (-0.00684 \times \text{pH} \times H_2O_2\ \text{Conc.}) + (0.000107 \times \text{pH} \times \text{time}) + (0.000722 \times \text{time} \times H_2O_2\ \text{Conc.}) + (0.0297 \times \text{pH}_2) + (0.00226 \times H_2O_2\ \text{Conc.}^2) + (0.00085 \times \text{time}^2)] \quad (16)$$

From Table 4, it is clear the values of ozone consumption are less than 3 kg O_3/kg COD in most of case, ensuring the feasibility of the overall process [37].

3.2.1 ANOVA analysis

Table 5 shows the ANOVA analysis of the first response i.e. percentage of COD removal. Due to low *P* value, high *F* value and sum of square the analysis suggests that the quadratic equation [Eq. (15)] describing the COD removal model is highly dependent on the square of the concentration of H_2O_2 and square of initial pH of wastewater [30,38]. It is also evident that the reaction time is not effective in the quadratic equation describing the model. The Model *F*-value of 39.58 implies the model is significant [39]. There is only a 0.01% chance that an *F*-value which is this big can occur due to noise.

In a similar way the ANOVA analysis for the response – ozone consumption [Eq. (16)] was done. The analysis of variance is given in Table 6. Thus it is clear that ozone con-

Table 5
Analysis of variance (ANOVA) for percentage COD removal

Source	Sum of Squares	d_f	Mean Square	*F* Value	*p*-value Prob > *F*
Model	1972.824	9	219.202	39.583	1.2×10^{-6}
A-pH	5.449	1	5.449	0.984	0.344
B- H_2O_2	6.664	1	6.664	1.203	0.298
C-Time	11.099	1	11.099	2.004	0.187
AB	22.351	1	22.351	4.036	0.072
AC	0.326	1	0.326	0.058	0.813
BC	5.751	1	5.751	1.038	0.332
A^2	1841.692	1	1841.692	332.574	5.28×10^{-9}
B^2	172.458	1	172.458	31.142	0.001
C^2	26.580	1	26.580	4.799	0.053

*A: pH, B: H_2O_2 (g/L), C: time (min)

Table 6
Analysis of variance (ANOVA) for ozone consumption

Source	Sum of Squares	D_f	Mean Square	*F* Value	*p*-value Prob > *F*
Model	4.994	9	0.554	160.207	1.3×10^{-9}
A-pH	0.002	1	0.002	0.521	0.486
B-H_2O_2	0.002	1	0.002	0.531	0.482
C-Time	4.119	1	4.119	1189.138	9.96×10^{-12}
AB	0.005	1	0.005	1.520	0.245
AC	8.97×10^{-5}	1	8.97×10^{-5}	0.025	0.875
BC	0.001	1	0.001	0.422	0.530
A^2	0.498	1	0.498	144.015	2.92×10^{-7}
B^2	0.037	1	0.037	10.759	0.008
C^2	0.255	1	0.255	73.845	6.26×10^{-6}

*A: pH, B: H_2O_2 (g/L), C: time (min) sumption is highly depends on the time and its square term, square of pH of the wastewater and square of H_2O_2 concentration. High *F* value, sum of square and low *P* value indicates that the model is effective in establishing a relation between the responses and the independent factors [39].

3.2.2. *Effect of independent factors on COD degradation using ozone and H_2O_2*

Response surface generated are examined to evaluate the variation of the three independent factor – pH, time and H_2O_2 concentration. Fig. 4a shows the variation of COD degradation with pH and H_2O_2 concentration. It can be seen that the COD degradation is maximum of 75.8% when the pH of the system is 9.5 and the H_2O_2 concentration is 3.5 g/L. From Fig. 4b which depicts the variation of COD removal with H_2O_2 concentration and time, it can be seen that the maximum COD removal was achieved at H_2O_2 concentration 3.5 g/L and reaction time 27.5 min. Fig. 4c shows the variation of COD degradation with reaction time and pH of the system. It is evident that the maximum degradation is achieved at pH 9.5 and reaction time of 27.5 min. The surface generated is clearly consistent with the ANOVA analysis which indicated that COD removal is not highly influenced by the reaction time, but the H_2O_2 concentration and the pH is the influencing factor. In all the three response surface that were generated, it can be seen that the COD removal increases up to 3.5 g/L of ozone dosage but beyond that the COD removal decreased. The increase in COD removal as H_2O_2 concentration increases can be attributed to the fact that presence of H_2O_2can initiate faster decomposition of ozone which causes better oxidation of organics [45]. COD removal is lower at higher H_2O_2 concentration because H_2O_2 acts as scavengers to highly reactive hydroxyl radical to produce hydro-peroxyl ions which have a lesser oxidation potential than hydroxyl radicals [46]. As for pH, the COD removal increases with pH of the wastewater up to a pH of 9.5 and after that, there is a decrease of COD removal. The O_3/H_2O_2 process operates via formation of hydroxyl ions which has a high oxidation potential and the rapid formation of this ions are initiated by the presence of H_2O_2. Not only low pH are known to suppress the formation of hydroxyl ions, but acids are scavengers of hydroxyl ions and they slow down the oxidation, hence COD degradation is higher at higher pH [47,48].

3.2.3. *Effect of independent factors on ozone consumption for ozone and H_2O_2 process*

Response surface generated were analyzed to delineate the variation of the independent factors on ozone consumption. The change in ozone consumption with the variation of H_2O_2 concentration and pH (shown in Fig. 5a), with the variation of reaction time and H_2O_2 concentration (shown in Fig. 5b) and with the variation of reaction time and pH (shown in Fig. 5c) has been examined. The observations from the response surface are consistent with the ANOVA

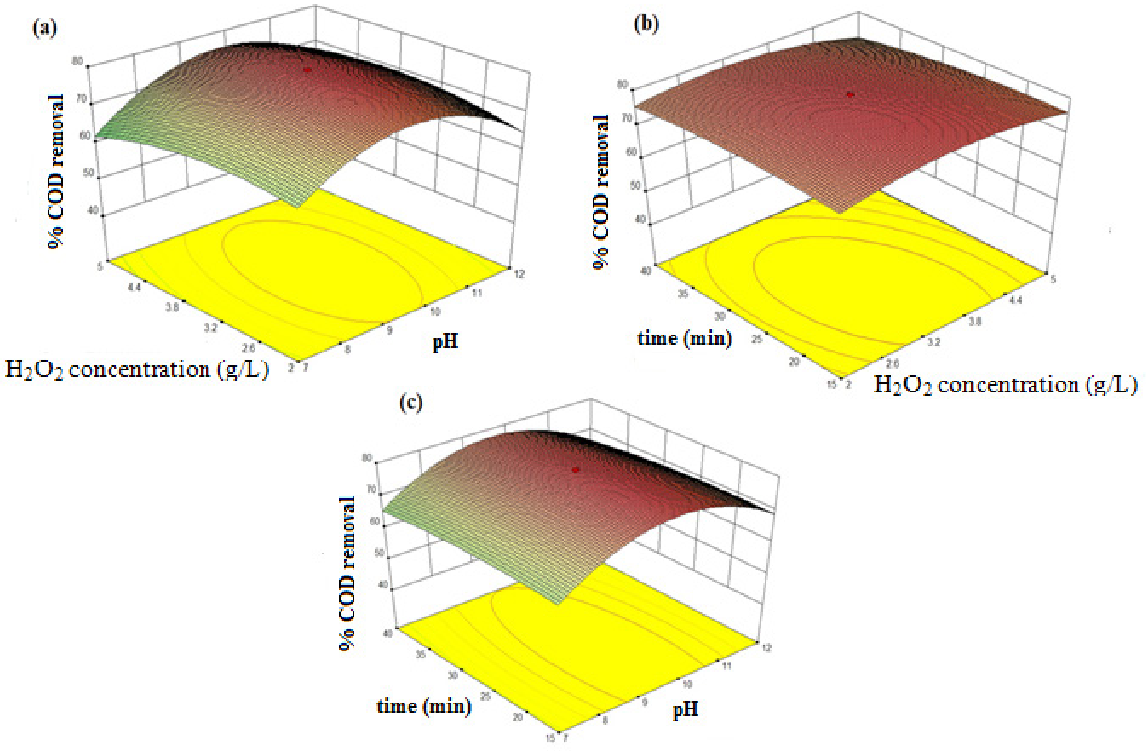

Fig. 4. Response surface for the degradation of COD and its variation with (a) H_2O_2 concentration and pH (b) H_2O_2 concentration and time and (c) time and pH.

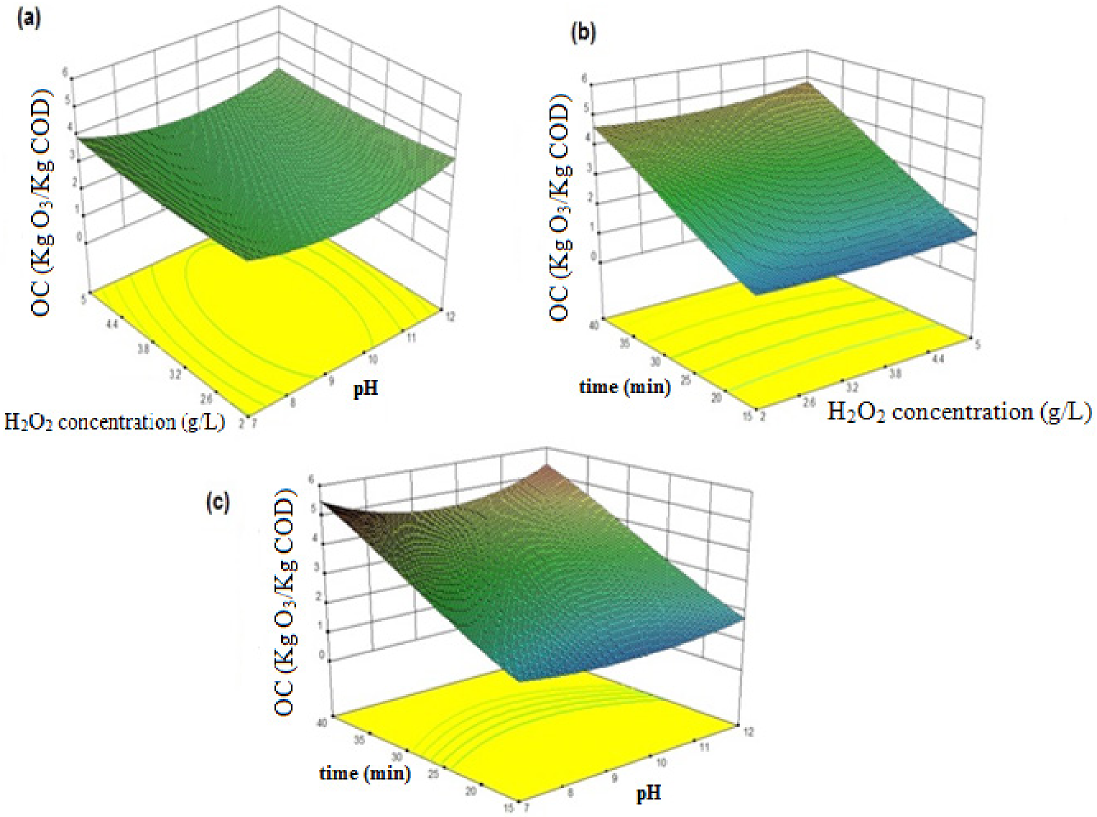

Fig. 5. Variation of ozone consumption on the various combinations of factors (a) variation with H_2O_2 concentration and pH (b) Variation with reaction time and H_2O_2 concentration (c) variation with reaction time and pH.

analysis which indicated that reaction time greatly influences ozone consumption, while the other factor's square term influences the response most. It is clear from Fig. 5a and Fig. 5b that ozone consumption increases as the reaction time increases. This is clearly consistent with Eq. (16) which indicates an increase in ozone consumption with time. The ozone consumption is minimum (2.7 kg O_3/kg COD removal) at pH 9.5 and H_2O_2 concentration of 3.5 g/L which can be attributed to the fact that maximum hydroxyl ions which are responsible for oxidation are generated rapidly at those conditions, thus lowering the ozone consumption as maximum ozone utilization takes place in this condition.

3.3. Kinetics of the O_3/AC and O_3/H_2O_2 processes and mechanism of oxidation

The determination of kinetic parameters is essential for the design of pilot plants and for further scale up of the newly designed process [49]. Kinetics of COD removal was investigated at the optimized conditions for both the processes i.e. at pH 5.0, 13.5 min reaction time and 2.0 g/L activated carbon for the O_3/AC process and pH 9.5, 3.5 g/L H_2O_2 concentration and 27.5 min reaction time for O_3/H_2O_2 process. Table 7 lists the kinetic parameters of the two processes along with the R^2 value of each of the kinetic models. An R^2 value of unity indicates the best fit. An R^2 value close to unity as evident in the case of Pseudo second order kinetic model indicates that Pseudo second order model best describes the processes. The pseudo second order kinetic constants are 16.10 × 10^{-5} L/mg·min and 7.04 × 10^{-5} L/mg·min for O_3/AC and O_3/H_2O_2 process respectively. AC not only act as a catalyst surface for O_3 decomposition but it also acts as an adsorbent [43]. In such cases, the containments are carried from the bulk liquid to through the solid-liquid interface into the active sites of the adsorbents by intra-particle diffusion [50]. AC acts as catalyst to form hydroxyl radicals because of the functional groups present on the surface of AC which contains oxygen and delocalized ϖ-electrons of the graphite layer of the AC which acts as a Lewis base and eventually form electron accepter-donor complex with H_2O molecule as shown in the following equations [51]:

Table 7
Kinetic parameters of the two processes

System	Pseudo first order		Pseudo second order	
	K_1 (1/min)	R^2	K_2 (L/mg.min)	R^2
Ozone/AC	0.078	0.88	16.10 × 10^{-5}	0.98
Ozone/H_2O_2	0.056	0.75	7.04 × 10^{-5}	0.91

$$C = C\ (\text{Graphite}) + H_3O^+ \leftrightarrow C^+\text{—}CH(\text{Graphite}) + H_2O \quad (17)$$

$$2H_2O \leftrightarrow H_3O^+ + OH^- \tag{18}$$

The hydroxyl ion is thus released and this initiates the oxidation by ozonation as shown in Eq. (19) [51].

$$O_3 + OH^- \; OH^{\cdot} + O_2^{\cdot} \tag{19}$$

Under the influence of H_2O_2 the O_3 molecule forms hydroxyl radical which participates in oxidation of the contaminants as depicted in Eq. (20).

$$H_2O_2 + 2O_3 \rightarrow 2OH^{\cdot} + 3O_2 \tag{20}$$

3.4. Characterization of AC used in the O_3/AC process

SEM micrographs in Fig. 7a and Fig. 7b show that there are significant changes in the surface morphology of the AC before and after the treatment of wastewater. The surface morphology of the unused AC is more porous and have a rough and corrugated compared to the surface morphology of AC after the treatment. This is caused by the contaminant particles which gets attached to the pores of AC during the wastewater treatment process, making the surface of AC less porous and smoother as seen in Fig. 7b. Fig. 8a shows the FTIR spectra of AC before the treatment while Fig. 8b delineates the FTIR spectra of AC which has already been used for the treatment of coke oven wastewater in the O_3/AC process. The shifting of the peaks in the spectra indicates the active participation of AC in COD degradation in the O_3/AC process and confirms that AC not merely acts as a catalyst but participates in active adsorption too [52]. The XRD spectra of AC before (shown in blue) and after (shown in orange) the treatment of coke oven wastewater is given by Fig. 9. The presence of sharp peak indicates that the AC is amorphous in nature [53,54].

3.5. Cost analysis

Economics of a process is also an integral part of while considering the process for commercial application on a large scale. The cost of the process depends on the various material and energy requirement to run the process. Electricity and chemical ingredients like H_2O_2 and AC are the major requirements for the process. The costs of these

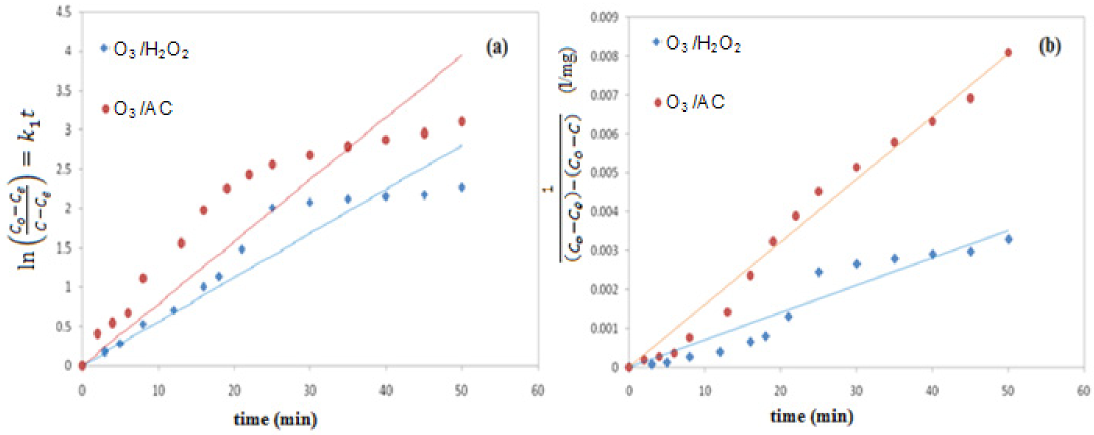

Fig. 6. Kinetics of treatment with ozone along with activated carbon (shown in red) and ozone along with H_2O_2 (shown in blue) for (a) pseudo first order kinetics and (b) for pseudo second order.

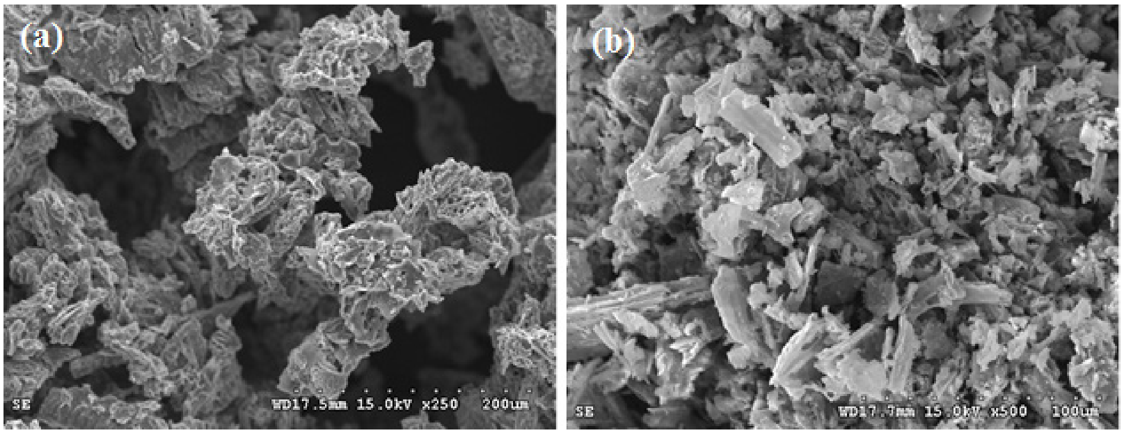

Fig. 7. SEM micrographs of AC (a) before and (b) after treatment of coke oven wastewater in the O_3/AC process.

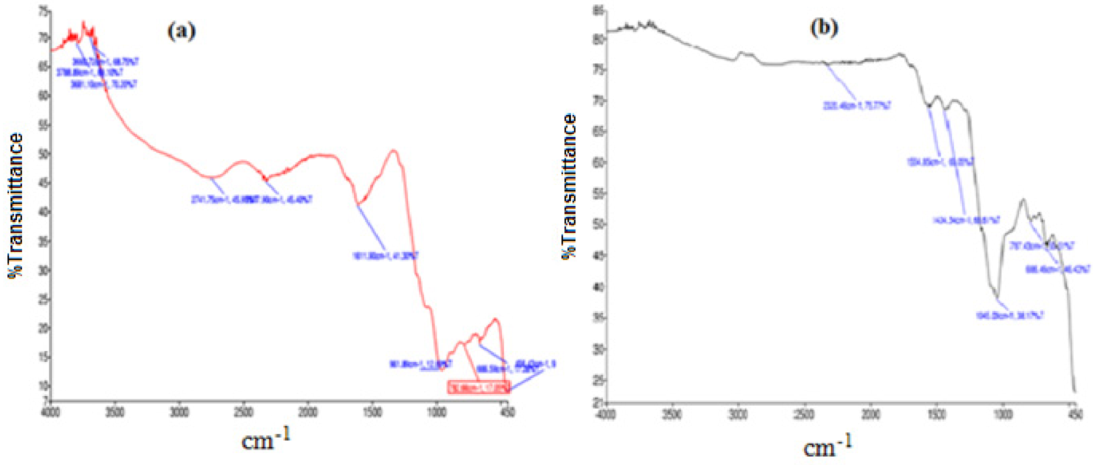

Fig. 8. FTIR spectra of (a) AC before treatment and (b) AC after treatment of coke oven wastewater in the O_3/AC process.

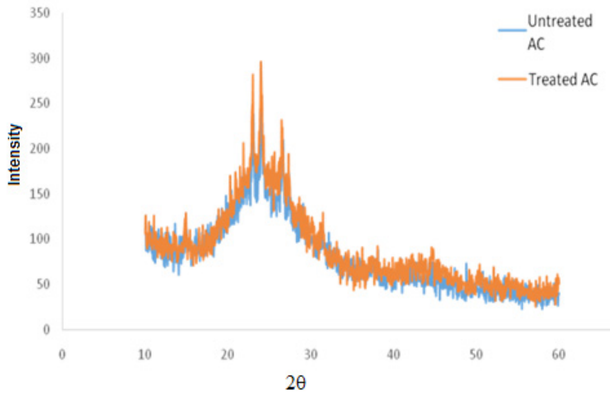

Fig. 9. XRD spectra of the AC used for the treatment of coke oven wastewater via O_3/AC process.

Table 8
Cost comparison of O_3/AC and O_3/H_2O_2 process

Process	O_3/AC process (Basis: 1 Kg COD removal)			
Ingredients	Amount	Rate	Cost	Total Cost
Electricity for O_3 production	5.9 kWh	INR 8/kWh	INR 47.2	INR 371.2
Activated carbon	0.81 Kg	INR 400/Kg	INR 324	
Process	O_3/H_2O_2 process (Basis: 1 Kg COD removal)			
Ingredients	Amount	Rate	Cost	Total Cost
Electricity for O_3 production	10.96 kWh	INR 8/ kWh	INR 87.68	INR 477.68
H_2O_2 (30% V/V)	0.65 L	INR 600/L	INR 390	

*Electricity required is 8 kWh per Kg of O_3 generated
*All costs are given in INR (1 INR = 0.015 USD)

are taken as par the maximum possible rate, while AC was prepared in the laboratory and costs around INR 400 for each Kg [27].The silica extracted in the process can also be sold in the market which would possibly reduce the overall AC cost. However, we have neglected this cost reduction during the economic analysis. The economic analysis was made with 1 Kg COD removal as the basis. The detailed analysis has been tabulated in Table 8. It can be clearly seen that the operational cost for using the O_3/AC is much lower compared to the O_3/H_2O_2 process. In studies by Mielczarek et al. [14], COD value was reduced from 3348.9 mg/L to 1279.2 mg/L, which is about 62.8%. In another study by Mielczarek et al. [16], COD value was decreased from 4519.6 mg O_2/dm^3 to 2707.6 mg O_2/dm^3, which is about 40.1%. When compared with these studies, both the system were at par in term of contamination degradation and removal.

4. Conclusion

The optimized condition for O_3/AC process was reaction time of 13.5 min, pH 5.0 and AC dose of 2.0 g/L while for the O_3/H_2O_2 process the condition was – reaction time 27.5 min, pH 9.5 and H_2O_2 dose of 3.5 g/L. The COD removals were 76.79% and 75.8% for the O_3/AC process and O_3/H_2O_2 process respectively. The results were promising and the percentage degradation was similar to what has been achieved in various studies, but this technique was superior on the ground of requirement of lesser reaction time. Ozone consumption was another response for the processes and for the O_3/AC process it was 2.6 kg O_3 for each kg of COD removal while for the O_3/H_2O_2 process it was 2.7 kg O_3 for each kg COD removal. COD removal for the O_3/AC process is highly influenced by pH and time while pH and H_2O_2 dosage was the primary influencing factor for the O_3/H_2O_2 process. Both the process followed pseudo second order kinetics with a kinetic constant of 16.10×10^{-5} L/mg·min and 7.04×10^{-5} L/mg·min for O_3/AC and O_3/H_2O_2 process respectively. The economic analysis reveals that the O_3/AC process is more economic compared to the O_3/H_2O_2process. Hence all data suggests that the O_3/AC process is more economical, requires less ozone, faster and is more effective in removing COD from the coke oven wastewater. Although both the process of using ozone are feasible in removing COD from coke oven wastewater, the O_3/AC process proves to be a better option among the two. These revelations could help industries to design a better wastewater treatment system which would help them to mitigate environmental pollution.

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