Employing a New Catalytic Ozonation (O₃/MnO₂/CP) for Degradation of Nitro Toluene in Aqueous Environment Using Box-Behnken Experimental Design

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ABSTRACT: *In this work, the degradation of Nitro toluene (NT) which is one of the constituents of petrochemical wastewater was explored by MnO₂/Clinoptilolite/O₃ process. The Box-Behnken experimental design was used and the effect of some operating parameters such as concentration of pollutant, initial pH, and amount of MnO₂/CP was inspected. A radical mechanism with the formation of an anion radical ($O_2^{\bullet-}$) before hydroxyl radical is proposed for describing the interaction between ozone and MnO₂/CP. The optimum conditions predicted by the model were as the following: [MnO₂/CP] = 0.45 mg/L, pH at 8.5, ozonation time at 48 min and [NT] = 30 mg/L. In optimum condition, the removal of NT and Chemical Oxygen Demand (COD) was 99.8, and 74% respectively. The removal of NT in the ozone along with MnO₂/CP was higher than the sum of the separate processes of single adsorption of catalyst (6%) at 0.6 mg/L and single ozonation(79%).*

KEYWORDS: *MnO₂/CP nanocatalyst, Clinoptilolite Zeolite, Degradation, Nitro toluene (NT), Catalytic ozonation, Petrochemical wastewater.*

INTRODUCTION

The wastewater generated from Bandar Imam petrochemical company in Iran contains some Aliphatic and aromatic derivatives. Certain amounts of aromatic components are wasted during a process that contains a wide range of non-biodegradable pollutants that cause environmental problems [1]. Nitro toluene is probably considered carcinogenic to humans, based on the international agency for research on cancer [2]. The classical treatment methods have high operational costs, long reaction time, and secondary pollution [3], so the use of Advanced Oxidation Processes (AOPs) is essential[4-6].

AOPs such as UV/H₂O₂, UV/O₃, MnO₂/CP/UV, Fenton's reagents and catalytic ozonation include the production of non-selective oxidizing agents such as hydroxyl radicals, for degradation of toxic and refractory pollutants in different wastewaters [7]. Ozone is a powerful oxidant and is used greatly in the water treatment process [8–9]. But in most cases, it has been reported that ozone cannot degrade organic pollutants completely and sometimes generates toxic intermediates [10].

In these conditions, catalytic Ozonation has been fascinating the increasing notice as a result of its higher efficiency in the degradation and mineralization of organic pollutants and lower negative effect on water nature [11].

Unsupported and supported metals and metal oxides are the most ordinarily used catalysts for the Ozonation of organic contaminants in water. They can accelerate the Ozonation process for degradation of a wide range of different contaminants [11–14]. MnO_2/CP-catalyzed ozonation was more effective for the removal of some pollutant than ozone alone. The comprehensive mechanism of catalytic ozonation is not clear up to this time and many readings have been prepared so far but it is not absolutely clear and this object is one of the gaps in catalytic ozonation. The effect of MnO_2/CP on ozone decomposition to yield hydroxyl radicals was not clear. Some investigator suggested mechanisms based on non-radical pathway that form hydroxyl radical. A number of mechanisms are offered, but the direct creation of hydroxyl radicals from ozone disintegration on the surface of MnO_2/CP or indirect production as a result of secondary reactions were still unfamiliar [15]. *Rosal et al.* [16-17] inspected the degradation of Clofibric acid by catalytic ozonation on titania. It was suggested that the adsorption and the subsequent reaction of pollutants on catalyst sites are responsible for the progress of catalytic ozonation.

Moreover, heterogeneous Catalytic Ozonation Process (COP) is an exciting technique for treatment of various wastewaters because of its minimum cost, probable recovery of solid catalyst, and also lowest production of secondary pollution. In fact, this method combines the molecules of ozone with the adsorptive and oxidative properties of metal oxide catalysts to get mineralization of different organic contaminants at ambient temperature [18]. Catalytic mechanisms are approved for the COP, comprising acceleration of the production of hydroxyl radicals, complex catalysis, and the sorption of organic pollutant and ozone molecules on the surface of catalyst [19-20].

Magnesium Oxide, as a heterogeneous catalyst, has very good ability for destruction of different organic pollutants. It is cost-effective, harmless and also environment-friendly compound.

The novelty of this project is that, no study has been done on degradation of Nitro toluene by catalytic ozonation with MnO_2/CP up to this time. In this work, degradation of NT as an aromatic pollutant was studied by O_3/MnO$_2$/CP process and the effect of pH, initial concentration of NT, and amount of MnO2/CP for higher degradation of NT was investigated.

EXPERIMENTAL SECTION
Materials

Nitro toluene (NT), HCl and NaOH, potassium iodide and sodium thiosulphate were of reagent grades and provided from Merck. Nano sized MnO2/CP was lower than 50 nm and synthesized previously. Ozone was manufactured in an Ozone generator fed by dry oxygen and all components were used as received without additional purification. Distilled water was used during this study.

Apparatus

The experiments were performed in a semi batch (batch for MnO2/CP and NT and continuous for ozone) reactor. The pure oxygen, from a pressurized capsule, was entered into Ozone Generator (214V and 0.39A) from ARDA companies of Iran. The reactor was prepared with a water-flow jacket coupled to a thermostat (BW20G model from Korean Company) for regulating temperature fixed at 25ºC which is presented in Fig.1. The pH was measured by pH Meter PT-10P Sartorius Instrument Germany. The advancement in the degradation of the NT was recorded by a high performance liquid chromatography (Knauer, Germany) equipped with Spectrophotometer (Platm blue Germany). A reverse phase column filled with 3 μm Separon C_{18} and it was 150 mm in length and 4.6 mm in diameter. The Isocratic technique with accustomed pH to 2.5, using orthophosphoric acid and a solvent mixture of acetonitrile and deionized water (60:40% v/v) at room temperature at a flow rate of 1 ml/min was employed. In all experiments, the suspension was centrifuged and filtered to separate the catalyst particles.

Catalytic Ozonation tests

About 2 L of aqueous solution holding identified concentration of NT and nano MnO2/CP were mixed absolutely in the reactor. A combination of O_3/O_2 was made by Ozone generator and entered to the bottom of the reactor by a porous diffuser for saturating solution with O_3 and better reaction between ozone, MnO_2/CP and the contaminant. The concentration of gaseous ozone was measured by the iodometric method using 2% neutral buffered potassium iodide for ozone trapping and sodium thiosulfate as a titrant [21]. In all runs, the flow rate of O_3/O_2 mixture was kept constant at 0.5 L/min with the concentration of ozone at about 20 mg/ L. For measuring
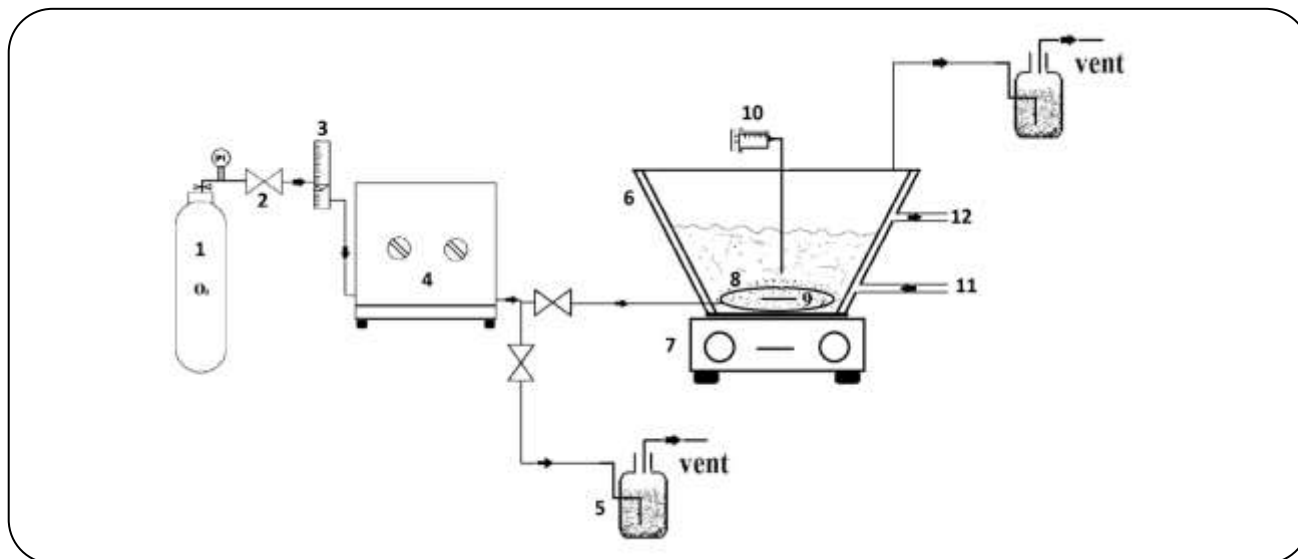
Fig. 1: Schematic diagram of the experimental set up. Notes: 1-Pure oxygen, 2- Shut off valve, 3-Gas flow meter, 4-Ozone generator, 5-Washing bottle, 6-Reactor, 7- Magnetic stirrer, 8- Ozone diffuser, 9- Magnetic bar, 10- Sampling port, 11-Cooling water supply from thermostat 12- Cooling water return to thermostat.

the consumed ozone, the outlet gas of reactor was bubbled through a KI (2%w) tamponed solution for determining not reacted ozone, where the excess ozone reacted with potassium iodide solution based on the following equation (Eq. (1)):

$$O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2 \quad (1)$$

The formed iodine was titrated by standard Sodium thiosulphate in the presence of starch as an indicator. The amounts of not reacted and reacted ozone were determined and the value of ozone in tail gas was gained, respectively. The residual of ozone in aqueous solution was valued by a spectrophotometer using the Indigo method [22].

Samples were taken at different intervals and filtered to remove MnO_2/CP particles. The concentration of NT was determined by Spectrophotometric at 273 nm. The HPLC and spectrophotometry methods gave parallel results and the difference between them was little that is corrected. The experiments were performed at the pH range of 4-10. The pH was adjusted only at the start of reaction by adding HCl (0.1 M) or NaOH(0.1 M). A minor decrease in pH was happened based on the production of intermediated acids.

COD was measured by Colorimetric and the standard closed reflux method [23] and the absorbance of samples for COD was measured by spectrophotometer at 600 nm.

The removal percent of NT and COD is given by the following equations (Eq.2-3):

$$Removal\ of\ NT\ (\%) = \left(\frac{[NT]_0 - [NT]_t}{[NT]_0} \right) \times 100 \quad (2)$$

$$Removal\ of\ COD\ (\%) = \left(\frac{[COD]_0 - [COD]}{[COD]_0} \right) \times 100 \quad (3)$$

Where $[COD]_0$ and $[NT]_0$ are the initial concentrations of COD and NT at the start of the reaction, and $[COD]$ and $[NT]$ are the amount of COD and concentration of NT at time t, respectively.

RESULT AND DISCUSSIONS
Experimental design and statistical analysis

The Box-Behnken experimental design method was used to optimize the percentage of NT removal from the typical industrial wastewater. The effects of Manganese oxide concentration (C_{Cat}), Ozonation time (t), Nitro toluene concentration and acidity (pH) on NT removal were investigated to optimize the process. The input variables and their values were presented in Table 1.

The Box-Behnken experimental design needs a smaller number of tests compared to all the response surface methodologies (RSM) [24]. The following model (Eq. (2)) was proposed for the response variable (Y) as a polynomial equation of independent variables.

$$Y = b_0 + \sum b_i x_i + \sum b_{ij} x_i x_j + \sum \sum b_{ii} i x_i^2 + \varepsilon \quad (2)$$

Table 1: The range and levels of the variables.

variables	Symbol	Range and levels		
		-1	0	+1
pH	C_{pH}	4	7	10
MnO2/CP (Mg/L)	C_{Cat}	0.2	0.4	0.6
Ozonation time(min)	t	10	30	50
Nitro toluene(mg/L)	NT	25	75	125

Where b_0 is a constant number, ε is the remainder of the equation, , b_i is the slope of the variable, b_{ii} is the quadratic coefficient (i = 1,2,3,4) b_{ij} is a linear interaction between the input variables of x_i and x_j (I = 1,2 and j = 1,2,3). Analysis of variance (ANOVA) was used to consider the significance of each variable in the polynomial equation (Eq. (2)) [25]. In the ANOVA, the level of significance or *p*-value was set at 0.05. The statistical significance of the second-order models was defined by *F*-value. When the calculated *F*-value is higher than the *F*-value in the table, the *p*-value will be much smaller; it designates the significance of the statistical model. The calculated *F*-value is obtained through dividing the mean squares of regression (involving linear, square, and interaction) by the mean squares of residual as follows (Eq.4)[26]:

$$F-value = \frac{MS_{Reg.}}{MS_{Res.}} = \frac{SS_{Reg.} / DF_{Reg.}}{SS_{Res.} / DF_{Res.}} \qquad (4)$$

The residual degrees of freedom ($DF_{Res.}$) is the total degrees of freedom minus the regression degree of freedom and regression degree of freedom ($DF_{Reg.}$) is the number of terms minus one [27]. The design of the experiments involves 27 tests; Table 2 shows the percentages of NT removal as well as the value predicted by the model.

Modeling and optimization of NT removal in O₃/MnO₂/CP process

In this study, the effect of three independent variables on the response function was inspected using the BBD and RSM, to get the optimal conditions. The mathematical relation between the response and three significant variables is considered by a quadratic polynomial equation. The equation for the degradation of COD is presented as the following (Eq. 5):

$$\text{Re moval of NT}(\%) = -107 + 25.29X_{pH} + \qquad (5)$$
$$90.9X_{cat} + 3.329X_{time} + 0.093X_{NT} - 1.442X_{C_{pH}}^2 -$$
$$79.8X_{C_{Cat}}^2 - 0.03379X_{C_{time}}{}^2 - 0.001752X_{C_{NT}}^2 -$$
$$2.29X_{pH}X_{cat} - 0.0050X_{pH}X_{time} +$$
$$0.01833X_{pH}X_{NT} + 0.062X_{time}X_{cat} -$$
$$0.063X_{cat}X_{NT} - 0.00240X_{time}X_{NT}$$

The attained results from the BBD, with residuals for all runs are shown in Table 3. The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be stated in the original units for each factor.

The significance of the coefficients was shown in Table 3. The Model F-value of 103.9 suggests that the model is significant. P-values less than 0.0500 designate model terms are significant. Values greater than 0.1000 indicate the model terms are not significant. The linear terms; $C_{PH}, C_{Cat}, C_{time}, C_{NT}$ and their quadratic terms have a *p*-value of less than 0.01, thus they are very significant. However, the term of the binary interaction between the variables has a *p*-value of more than 0.05, which means that the interaction of variables is insignificant [28,29]. In order to improve the model, the insignificant terms were eliminated as shown in Table 3.

The "Lack of Fit Tests" pane matches residual error with "Pure Error" from replicated design points. If there is significant lack of fit, as depicted by a low probability value ("Prob > F"). As signified in the Table, the lack of fit was significant compared to the pure error since its p-value (0.013) was lower than 0.05, revealing that the model was suitable for predicting NT removal efficiencies within the mentioned ranges of the process factors.

The Predicted R² of 0.9918 is in realistic agreement with the adjusted R² of 0.9823; i.e. the difference is less

Table 2: Experimental design for three independent variables and their response.

Run no.	X_{pH}	X_{cat}	X_{time}	X_{NT}	Exp.	Pred.
1	7	0.6	50	75	91.3	92.60
2	7	0.4	50	125	78	80.21
3	4	0.2	30	75	49.5	49.79
4	10	0.4	30	125	80.0	79.89
5	4	0.4	50	75	68	65.01
6	7	0.6	10	75	47.3	47.64
7	4	0.4	10	75	18.3	19.94
8	4	0.6	30	75	58	55.81
9	7	0.4	10	25	54	49.59
10	10	0.4	10	75	49	52.99
11	7	0.6	30	25	83.5	86.81
12	7	0.4	10	125	42.0	40.54
13	10	0.4	50	75	97.5	96.86
14	7	0.4	30	75	85	85.2
15	7	0.2	30	25	81	82.29
16	7	0.4	50	25	99.6	98.86
17	10	0.2	30	75	85	85.2
18	7	0.2	10	75	45	44.87
19	4	0.4	30	25	60	61.29
20	7	0.2	30	125	72	71.71
21	10	0.6	30	75	88	88.84
22	7	0.4	30	75	85	84.99
23	10	0.4	30	25	89	88.24
24	7	0.4	30	75	85.6	85.2
25	4	0.4	30	125	40.0	41.94
26	7	0.2	50	75	88	88.84
27	7	0.6	30	125	72	71.71

Table 3: ANOVA tests for quadratic models in the removal of NT by O_3/MnO_2/CP process (Continued).

Model	DF	Adj SS	Adj MS	F-Value	P-Value
Linear	14	11258.2	804.15	103.9	0.00
$X_{C_{PH}}$	4	9698.3	2424.59	313.26	0.00
$X_{C_{Cat}}$	1	3159.0	3159.01	408.14	0.00
$X_{C_{time}}$	1	32.0	32.01	4.14	0.065
$X_{C_{NT}}$	1	5931.9	5931.85	766.4	0.00
Square	1	575.5	575.47	74.35	0.00
$X_{C_{pH}}^2$	4	1496.8	374.2	48.35	0.00
$X_{C_{cat}}^2$	1	898.4	898.45	116.08	0.00
$X_{C_{time}}^2$	1	54.3	54.33	7.02	0.021
$X_{C_{NT}}^2$	1	974.4	974.4	125.89	0.0
Model	1	102.3	102.28	13.21	0.003
2-Way Interaction	6	63.0	10.50	1.36	0.307
$X_{C_{PH}}X_{C_{Cat}}$	1	7.6	7.56	0.98	0.342
$X_{C_{time}}X_{C_{pH}}$	1	0.4	0.36	0.05	0.833
$X_{C_{NT}}X_{C_{PH}}$	1	30.2	30.25	3.91	0.071
$X_{C_{Cat}}X_{C_{time}}$	1	0.3	0.25	0.03	0.86
$X_{C_{NT}}X_{C_{Cat}}$	1	1.6	1.56	0.2	0.661
$X_{C_{NT}}X_{C_{time}}$	1	23	23.04	2.98	0.11
Error	12	92.9	7.74		
Lack of fit	10	92.6	9.26	77.2	0.013
Pure error	2	0.2	0.12		
Total	26.0	11351.0			
Model Summary	S	R^2	R_{adj}^2	R_{pred}^2	
	2.78207	0.9918	0.9823	0.9523	

than 0.2. Adequate Precision calculates the signal to noise ratio. A ratio greater than 4 is required.

The correctness of the model as illustrated in Fig. 2, compares the experimental values versus the predicted responses by the model in degradation of NT. It was observed that the predicted responses from the model are in agreement with the experimental data.

Effect of catalyst amount on MnO_2/CP/O_3 process

The influence of catalyst dose on the degradation of NT is showed in Fig. 3. In the non-catalytic ozonation process, the ordinary conversion of the NT was attained because the action of free radicals produced from self-decomposition of ozone was poor. It is satisfactory that ozonation of water also leads to the production of hydroxyl radicals over ozone breakdown [30]. The degradation proficiency of the NT was meaningfully increased in the presence of both ozone and catalyst. An exceptional feature of nano MnO_2/CP is its extremely high surface area. It is clear that, the degradation of the NT was based on the action of some ozone absorbed species or free radicals shaped perhaps on the catalyst surface or in the aqueous solution. Catalyst amounts had a positive effect on NT removal in MnO_2/CP/O_3 process. But as showed in Fig. 3,
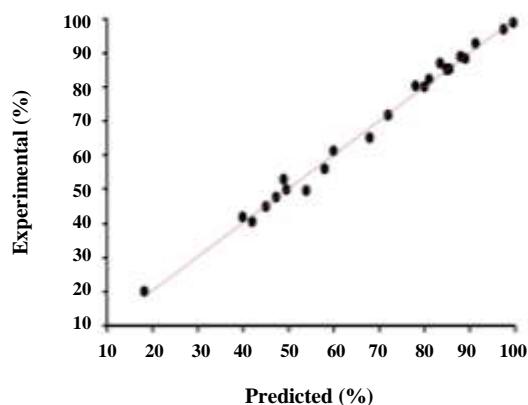
Fig. 2: Comparing the experimental and predicted value for the removal of NT in $O_3/MnO_2/CP$ process.

the removal efficiency was increased by an increase in catalyst dose from 0.2 to 0.4 mg/L. A further increase in catalyst amounts to 0.6 g/ L did not yield any significant increase in the degradation rate. Therefore 1.2 g/L of catalyst was gained as an optimum concentration of MnO2/CP.

Effect of pH on $MnO_2/CP/O_3$ process

In $MnO_2/CP/O_3$ method, pH had two direct effects, one is ozone decomposition and another is surface charge and characteristic of MnO_2/CP nano catalyst which has a direct effect on the adsorption of pollutant molecules [31]. The point of zero charge (PZC) of the MnO2/CP is reported at 7.0 [32] and this factor affects the absorption of pollutant on catalyst and it was determined by Potentiometric titration as explained by *Halter* [33]. Organic pollutants in neutral state may be adsorbed on the surface of catalyst if the surface is not charged near the pH_{PZC} of the catalyst [34].

The effect of pH on $MnO_2/CP/O_3$ process is shown in Fig.4. From the experimental results, it was obvious that during treatment, the best results were gained at a neutral pH. The influence of catalyst concentration on the removal of NT was sharp at neutral pH rather than acidic and alkaline pH. In neutral pH the catalytic ozonation is predominant, but in alkaline pH the only ozonation reactions is predominant. The surface properties and the electrostatic interactions between MnO_2/CP and hydroxide ions in the solution were the main factors affecting the degradation of NT.

Effect of initial concentration of NT on the removal efficiency

The effect of initial concentration of NT on the efficiency of degradation in $MnO_2/CP/O_3$ was investigated over the concentration range from 25 to 125 mg/L and results showed in Fig.5.

Results showed that the percent of removal was decreased slightly with an increase in NT dosage from 25 to 125 mg/L. When the initial dosage of the pollutant was high (125 mg/L), the number of available active sites were reduced and the production of hydroxyl radicals were decreased by NT molecules, because of their competitive adsorption on MnO2/CP surface.

With an increase in the initial concentration of NT, active agents such as hydroxyl radicals produced from the process were reduced because they react with a large number of pollutant molecules [35]. When the concentration of NT increased, the surface of MnO_2/CP was covered by pollutant molecules instead of ozone and subsequent production of active agents for destroying pollutant was reduced. But, when the number of pollutant molecules was very low, their collisions with active sites were reduced and degradation efficiency decreased [36].

Degradation of NT by MnO2/CP/O₃ processes

Ernst et al. [37] are offered that the dissolved ozone is adsorbed first on the catalyst surface during the catalytic ozonation with Al_2O_3, and then degraded rapidly, based on the existence of hydroxyl surface groups, the $O_2^{\bullet-}$ was formed and it would result in the production of hydroxyl radicals by a series of reactions. Also *Zhang et al.* [38] suggested that $O_2^{\bullet-}$ and hydroxyl radicals were created by ozone molecule with the hydroxyl group of catalyst. In this study, the dissolved molecular ozone was adsorbed on the MnO_2/CP surface at first and then decomposed into $O_2^{\bullet-}$ and $OH^{\bullet}$ quickly due to the presence of hydroxyl surface groups on the catalyst (Eqs.6, 7). Additionally, the shaped $O_2^{\bullet-}$ could support molecular ozone to decompose into hydroxyl radicals. Then the NT adsorbed on the surface of the MnO2/CP would be degraded by $OH^{\bullet}$ and molecular ozone (Eqs. 6, 7). As ozonation along with MnO_2/CP can happen through either direct reaction with molecular ozone or indirect reaction with the produced hydroxyl radicals, the removal of the NT can be represented by the following simple reactions (Eqs.6-11) [39]:
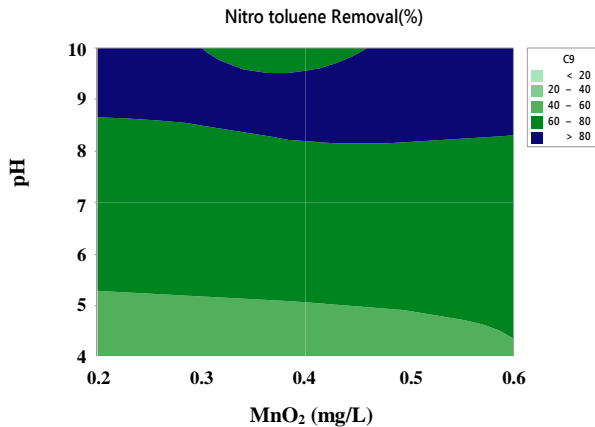
Nitro toluene Removal(%)

Fig. 3: The counter plot of the interaction between catalyst concentration and pH on the removal of Nitro toluene.
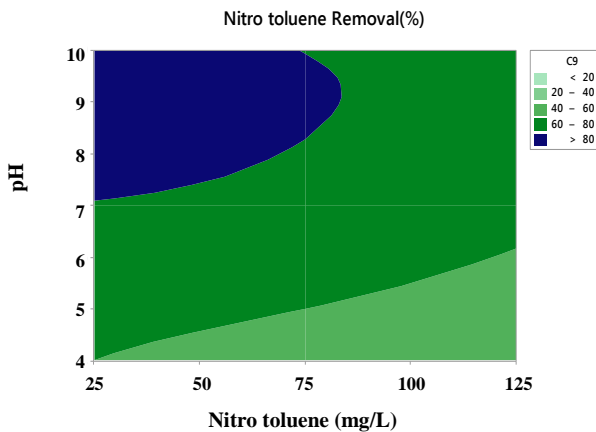
Nitro toluene Removal(%)

Fig. 4: The counter plot of the interaction between catalyst and Nitro toluene concentration on the removal of Nitro toluene.
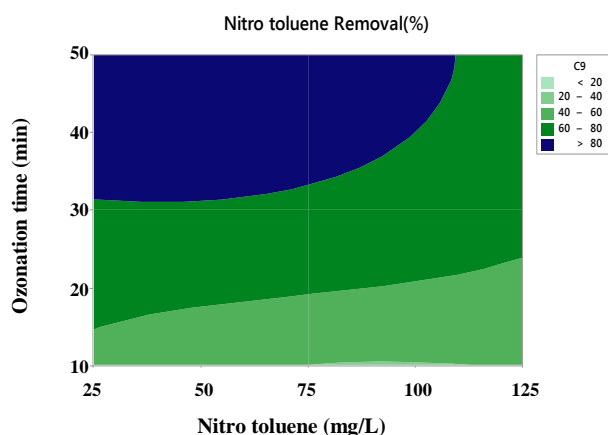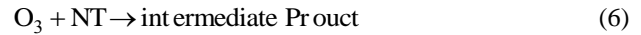
Nitro toluene Removal(%)

Fig. 4: The counter plot of the interaction between the time of ozonation and Nitro toluene concentration on the removal of Nitro toluene.

$$O_3 + NT \rightarrow intermediate\ Prouct \qquad (6)$$

$$OH^{\bullet} + NNT \rightarrow intermediate\ Prouct \qquad (7)$$

$$O_3 + OH^- \rightarrow HO_2^{\bullet} + O_2^{\bullet-} \qquad (8)$$

$$O_3 + HO_2^{\bullet} \rightarrow OH^{\bullet} + 2O_2 \qquad (9)$$

$$O_3 + OH^{\bullet} \rightarrow HO_2^{\bullet} + O_2 \qquad (10)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (11)$$

It has been proposed that ozone can be adsorbed on a catalyst surface to produce various oxidizing species [40]. The proposed mechanism mentioned that ozone and organic molecules adsorbed on the catalyst surface simultaneously, ozone degrades on the metallic sites and produce the surface bond radical ($O_2^{\bullet-}$), that they are more reactive than ozone and result in the production of hydroxyl radicals. Oxidation lasts through some oxidized intermediates progressively, while $O_2^{\bullet-}$ radicals are continuously produced by dissolving ozone that is transferred to the catalyst surface. The attraction of the oxidation products to the surface of catalyst decreases and final degradation products repulse from the catalyst surface [41]. The NT removal rate in the ozone along with MnO₂/CP was higher than the sum of the separate influences of single adsorption of catalyst (6%) at 0.6 mg/L and ozonation(79%).

Optimization of operating conditions

The percentage of NT removal can be high in some conditions. Using the Minitab software, the values of different variables were selected to maximize the percentage of NT removal. These optimal values, along with the percentage of NT removal, are shown in Table 4.

The optimum conditions predicted by the model were as follows: the [MnO₂/CP] = 0.45 mg/L, pH at 8.5, ozonation time at 48 min and [NT] = 30 mg/L. Under the predicted optimum conditions the removal efficiency of NT recommended by the software was 99.8%.

CONCLUSIONS

The combination of ozone and MnO₂/CP catalyst has important effect on the removal of NT in aqueous solutions and based on the experimental results the following conclusions are obtained: In MnO₂/CP/O₃ technique,

Table 4. Optimal coditions of parameters and NT removal % .

Parameters	Unit	Value
pH		8.5
MnO2/CP concentration	mg/L	0.45
Ozonation time	min	48
Concentration of NT	mg/L	30
Predicted NT removal	%	102.6
Experimental NT removal	%	99.8

the pH has two direct effects on the process, one is ozone decomposition and the other one is surface charge and properties of MnO_2/CP nano catalyst. The removal of NT and COD were 99.8% and 74%, respectively at 48 min of reaction.

The NT removal rate in the ozone along with MnO_2/CP was higher than the sum of the separate influences of single adsorption of catalyst (6%) at 0.6 mg/L of catalyst and single ozonation(79%). These experimental results confirmed the hypothesis that the removal of NT by O_3/nano-MnO_2/CP process followed a radical-type mechanism. The suggested mechanism mentioned that ozone and organic molecules adsorbed on the catalyst surface concurrently, ozone degrades and produce the surface bond radical ($O_2^{\bullet-}$), that they are more reactive than ozone and lead to the production of hydroxyl radicals.

Acknowledgements

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