Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23949

152 (2019) 108–115
June

Catalytic ozonation for the treatment of municipal wastewater by iron loaded zeolite A

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Received 12 September 2018; Accepted 11 February 2019

ABSTRACT

The work evaluates the performance of catalytic ozonation process on iron-loaded zeolite 4A (Fe-Z4A) for the chemical oxygen demand (COD) reduction of municipal wastewater. The effectiveness of adsorption (Fe-Z4A), ozonation (O_3), and catalytic (Fe-Z4A/O_3) ozonation processes were compared at wastewater pH. Furthermore, the removal of total Kjeldahl nitrogen (TKN), the effect of catalyst dose, the effect of tertiary butyl alcohol (TBA), reuse performance, and kinetic studies were conducted to understand the application of Fe-Z4A for municipal wastewater treatment. The results revealed that Fe-Z4A/O_3 process significantly remove COD and TKN in comparison with single processes. The results further reveal that Fe-Z4A show reasonably better reuse performance after three successive runs. The TBA effect indicates that Fe-Z4A/O_3 process follow radical mechanism. The kinetic studies revealed that Fe-Z4A/O_3 process follow pseudo-first-order kinetics for the treatment of COD. Moreover, the rate constant value was found significantly larger for the catalytic ozonation process in comparison with ozonation and adsorption. The experimental results reveal that Fe-Z4A catalyze the COD reduction from municipal wastewater.

Keywords: Catalytic ozonation process; Municipal wastewater; Fe-zeolite 4A; Chemical oxygen demand

1. Introduction

Chemical pollution is one of the major threats to the environment these days, which is due to its persistent and hazardous nature to aquatic organisms and humans [1–3]. The industrial waste discharge is one of the most important sources of contamination of wastewater [2]. The persistent organic pollutants were found even in biologically treated wastewaters [1]. Therefore, recently advanced oxidations have been proposed in combination with biological treatment processes for effective wastewater treatment [1,4,5]. Among the advanced oxidation processes, catalytic ozonation has shown superior removal efficiencies in comparison with ozonation alone for wastewater treatment [6,7]. Many materials have been used as catalysts in such studies, for example, activated carbon [8,9], TiO_2 [10,11], zeolites [12–14], reduced graphene oxide, etc. [15,16]. Fe-based catalysts have shown eminent catalytic activity in the catalyzed ozonation processes for the treatment of pollutants [17,18].

Zeolites are proven to be efficient catalysts for the abatement of various pollutants by catalytic ozonation processes

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[7,13,19–21]. However, most of these studies involve the applications of zeolites in aqueous solutions. This study is the continuation of author's previous work in which zeolite 4A was successfully applied as a catalyst for the removal of paracetamol in aqueous solutions [22]. In the current study, iron-loaded zeolite 4A (Z4A) was used for the treatment of domestic wastewater. Since wastewater is a complex matrix composed of various types of organic and inorganic species [1–3], it is indeed important to test a catalyst in actual conditions. It was reported that modified zeolites boost the aqueous ozone decomposition causing the production of hydroxyl radicals, which may degrade pollutants at much higher rates as compared with single ozonation [23]. Therefore, in the current investigation iron-loaded Z4A was implied as a heterogeneous catalyst.

To the authors' knowledge, current research is the first report using iron-loaded zeolite A catalyst for the treatment of municipal wastewater. It is a first study on the application of iron-loaded zeolite Fe-Z4A as a catalyst for the treatment of real municipal wastewater matrix by catalytic ozonation (Fe-Z4A/O_3) process. Since the real wastewater is a complex matrix composed of various types of organic and inorganic species, it is indeed important to test a catalyst in real wastewater applications. The current research study investigates the removal of COD (chemical oxygen demand) from municipal wastewater in both catalytic (Fe-Z4A/O_3) ozonation and single ozonation. In addition to this, the effect of catalyst dose, reuse performance of catalyst and COD removal rates were compared for catalytic (Fe-Z4A/O_3) ozonation and ozonation to study the effectiveness of Fe-Z4A.

2. Experimental procedure

2.1. Materials and reagents

The catalysts (Z4A zeolites) were procured from Sigma-Aldrich (USA). All the chemicals and reagents such as potassium dichromate ($K_2Cr_2O_7$), ferrous ammonium sulphate, ferroin indicator, mercuric sulphate ($HgSO_4$), silver sulphate (Ag_2SO_4), and concentrated sulphuric acid (H_2SO_4) were obtained from Sigma-Aldrich (USA) and were used to measure the COD.

2.2. Catalyst preparation

The Z4A was washed with ultra-pure de-ionized water and was then filtered. The filtered Z4A was dried in air for 48 h. The dry zeolite was rinsed in 0.1 M nitric acid for 1 d. Then, washing with distilled water and drying at 110°C was done. To prepare 0.176 M solution of $FeSO_4.7H_2O$, 4.89 g of $FeSO_4.7H_2O$ were taken and was dissolved into 100 mL of distilled water.

The iron-loaded zeolite catalyst was prepared by adding 6 g of zeolites to 30 mL of a 0.176 M $FeSO_4 \cdot 7H_2O$ solution with reflux at 60°C [24]. The zeolites were filtered, washed with and then dried overnight at 110°C [24].

2.3. Catalyst characterization

The surface characterization of the catalyst was studied by the BET method using Micromeritics (USA) ASAP 2020 analyzer. The functional groups at the catalyst surface were characterized by fourier transform infrared spectroscopy (FTIR) using PerkinElmer (USA) spectrum 400 analyzer. The catalyst surface morphology and elemental analysis were characterized by SEM–EDX using Tescan, UK, Vega LMU.

2.4. Experiments of ozonation

The experiments (ozonation and catalytic [Fe-Z4A/O_3] ozonation) were performed in a reactor (Fig. 1). In this study, 450 mL of municipal wastewater (MWW) was taken and 0.5 g of (Fe-Z4A) catalyst was added. Then, ozone was produced through an ozone production unit (AZCO Canada, Model: HTU-5000GE-120) and injected into the reactor for 120 min. Samples were taken every 20 min [7]. Finally, the COD was determined by open reflux titrimetric method [25].

2.5. Analytical procedures

2.5.1. Ozone dose

The ozone dose assessment was done by the iodometric technique [25]. In this method, ozone was trapped using two sets of 200 mL of the 2% KI solution traps (2% KI). After ozonation, the quenching was done using 2 M H_2SO_4. Then, the titration was done with 0.005 M sodium thiosulfate using starch as an indicator [25].

2.5.2. Analysis of chemical oxygen demand

The open reflux titrimetric method was implied to measure the COD of wastewater. The method determines the COD by evaluating the excess oxidizing agent such as dichromate or permanganate left over in the sample [25].

2.5.3. Analysis of total Kjeldahl nitrogen

The samples after collection were quenched using Na_2CO_3 (0.025 M) to eliminate left over ozone. The TKN was assessed by the Kjeldahl method (Behrotest inkjet nitrogen digestion system, Behr Technik, Germany) [25].

2.6. Municipal wastewater studies

2.6.1. Baseline study of the catchment area of main outfall pumping station

The main outfall pumping station in Lahore, Pakistan, is receiving the wastewater from Bilal Gunj and Sanat Nagar

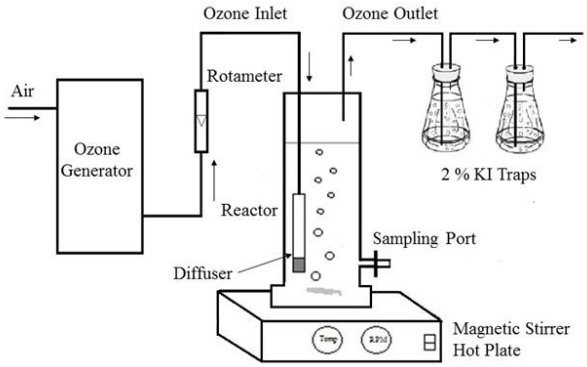

Fig. 1. Reactor setup.

Lahore, Pakistan, etc., with an average discharge of 127.56 cusecs. The Bilal Gunj and Sanat Nagar areas are highly populated areas of Lahore. These areas are famous due to auto bikes workshops, small-scale electronics markets, small-scale tannery, many educational institutions, and health care centers/hospitals. Thus, these features make the selected study area a representative sample of Lahore's typical municipal wastewater.

2.6.2. Sampling and characterization of municipal wastewater

The samples were taken from the main sewage outfall near Saggian Bridge, Lahore. After collection, both samples were taken to the laboratory for necessary analysis. The pH of the wastewater samples was measured, and they were poured into Imhoff cone for pre-setting. After 45 min, the supernatant was removed from the apparatus and was kept at 4°C until analysis or experiments. Finally, the samples were analyzed for the following parameters: chemical oxygen demand (COD), turbidity, total suspended solids (TSS), chlorides, alkalinity, total hardness, phosphate, sulphates, total Kjeldahl nitrogen, and ammonia nitrogen. All the tests on MWW have been performed according to the procedures as mentioned in "Standard Methods for the Examination of Water and Wastewater" [25].

3. Results and discussion

3.1. Catalyst characterization

The catalyst characteristics (iron-loaded Z4A) are given in Table 1. The determined pore size and surface area of the catalyst were 4 Å and 90.55 $m^2\ g^{-1}$, respectively. The thermal decomposition temperature of the catalyst was 700°C. The point of zero charge was 6.5 ± 0.3 by using mass titration method. [14].

The FTIR spectrum of Z4A and Fe-Z4A are shown in Figs. 2(a) and (b), respectively. A sharp peak observed at 970.64 cm^{-1} corresponds to the stretching vibrations of Si–O and Al–OH [26,27] and drifted to 973.36 cm^{-1} after iron loading. The peaks at 669.21 cm^{-1}, 1,635.82 cm^{-1}, and 3,115.64 cm^{-1} indicate vibration of the Si–O–Si stretch, O–H bending vibrations and O–H stretching and deformation [26,27]. A new peak at 1,442.34 cm^{-1} was observed due to iron loading that corresponds to Fe–OH stretching vibrations [26,27]. The SEM image of Fe-Z4A (Fig. 3) shows a highly porous surface texture of the catalyst.

3.2. Characteristics of municipal wastewater

The municipal wastewater samples were collected from the main sewage outfall near Saggian Bridge, Lahore, Pakistan. Table 2 gives the characterization results of various parameters of wastewater. The testing for which has been performed as mentioned in "Standard Methods for the Examination of Water and Wastewater" [25].

Table 1
Properties of iron-loaded zeolite 4A

Pore size (Å)	4
Thermal decomposition (°C)	700
Surface area ($m^2\ g^{-1}$)	90.55
Point of zero charge (pH_{pzc})	6.5 ± 0.3
% wt. iron (EDX)	8.5

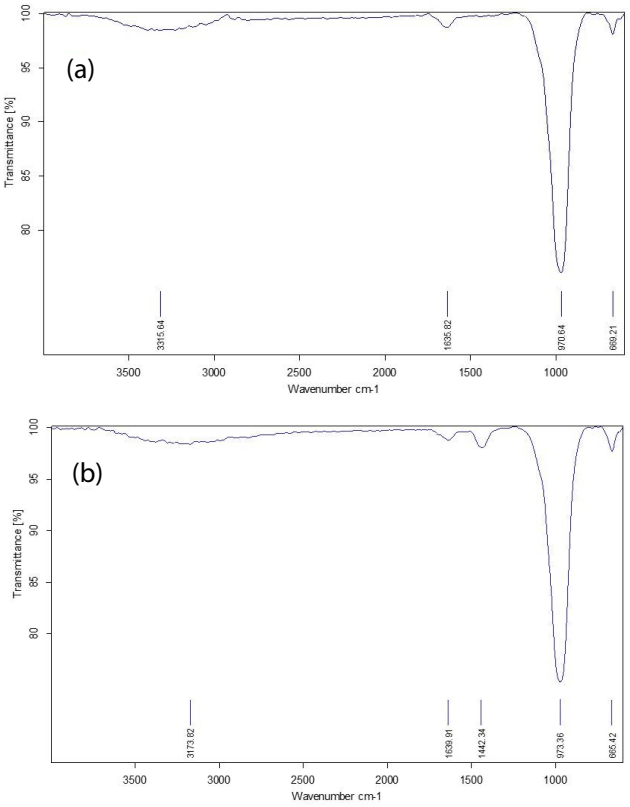

Fig. 2. FTIR spectrum of (a) Z4A and (b) Fe-Z4A.

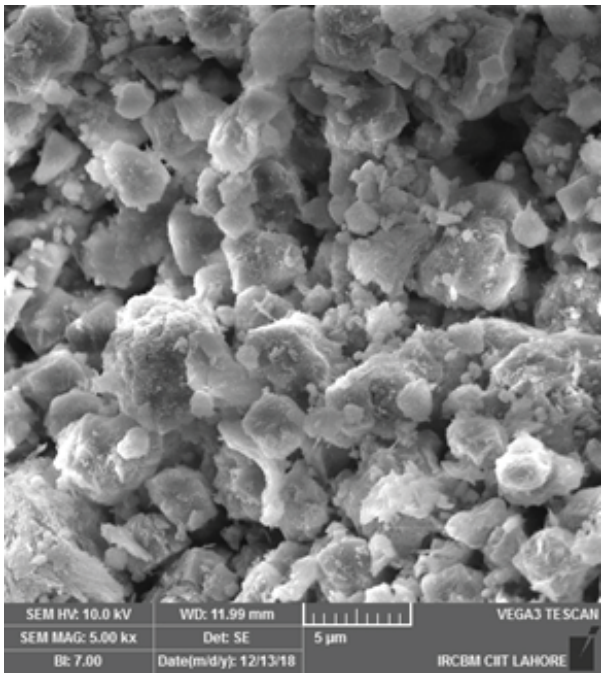

Fig. 3. SEM image of Fe-Z4A.

3.3. Municipal wastewater treatment by ozonation, adsorption, and the catalytic (Fe-Z4A/O_3) ozonation

The results (Fig. 4) reveal that catalytic ozonation (Fe-Z4A) has the highest COD removal efficiency in comparison with adsorption and single ozonation process at pH 6.98 ± 0.8. The ratio of COD at 40 min and initial COD was found to be 0.97, 0.57, and 0.33 for adsorption, ozonation, and the catalytic ozonation, respectively, which shows that Fe-Z4A catalyze the pollutants degradation in studied municipal wastewater leading to the decrease in COD values (Fig. 4). The COD removal in the first 40 min of catalytic ozonation process was found quite fast; afterwards the COD removal was found to be slow down (Fig. 4). This may be due to the pollutants degradation causing the generation of by-products deactivating the sites. Xu et al. [28] reported that the intermediates formed during catalytic ozonation process lay the main role in the case of phenacetin removal on the manganese ferrite and the nickel ferrite and may cause a reduction in catalytic activity of the former catalyst. This further supports our above-mentioned hypothesis [20,29]. In this study, the experiments were performed at municipal wastewater pH, which was near to the point of zero charge of the studied catalyst (Table 1). Therefore, under studied conditions, the Fe-Z4A may have its maximum activity [19,29].

Table 2
Characterization of wastewater from Lahore Main out fall

Parameters	Value
pH	6.98 ± 0.5
Turbidity (NTU)	99 ± 5
BOD (mg L^{-1})	132 ± 7
COD (mg L^{-1})	180 ± 10
Chlorides (mg L^{-1})	160 ± 11
Alkalinity (mg L^{-1})	270 ± 15
Total hardness (mg L^{-1})	288 ± 10
Phosphate (mg L^{-1})	1 ± 0.4
Sulphate (mg L^{-1})	15 ± 4
TDS (mg L^{-1})	641 ± 30
TSS (mg L^{-1})	184 ± 16
Total Kjeldahl nitrogen (mg L^{-1})	42.6 ± 16
Ammonia nitrogen (mg L^{-1})	22.8 ± 12

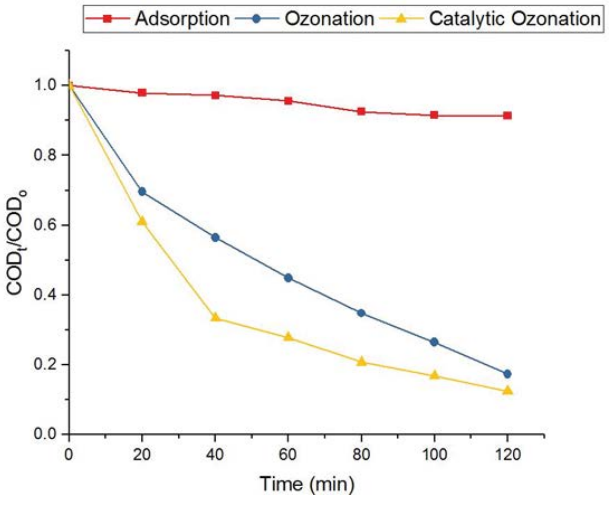

Fig. 4. COD removal of municipal wastewater in adsorption, ozonation, and catalytic ozonation (COD_o = 90 ± 10 mg L^{-1}; O_3 = 0.9 mg min^{-1}; amount of catalyst = 0.5 g; T = 120 min; temperature = 25°C ± 2°C; pH = 6.98 ± 0.8; V = 450 mL).

Fig. 5 shows the SEM images of Fe-Z4A catalyst before and after the treatment. No significant change in surface morphology was observed, so even after the treatment with municipal wastewater, the catalyst may retain its surface morphology and significant pores may be seen on the surface (Fig. 5) which may indicate that organic pollutants adsorbed on the surface of the zeolite may be degraded by the radicals and adsorbed ozone.

3.4. Total Kjeldahl nitrogen removal

The removal efficiencies of both the ozonation and catalytic ozonation processes were investigated in terms of total Kjeldahl removal [13,30]. The results (Fig. 6) reveal

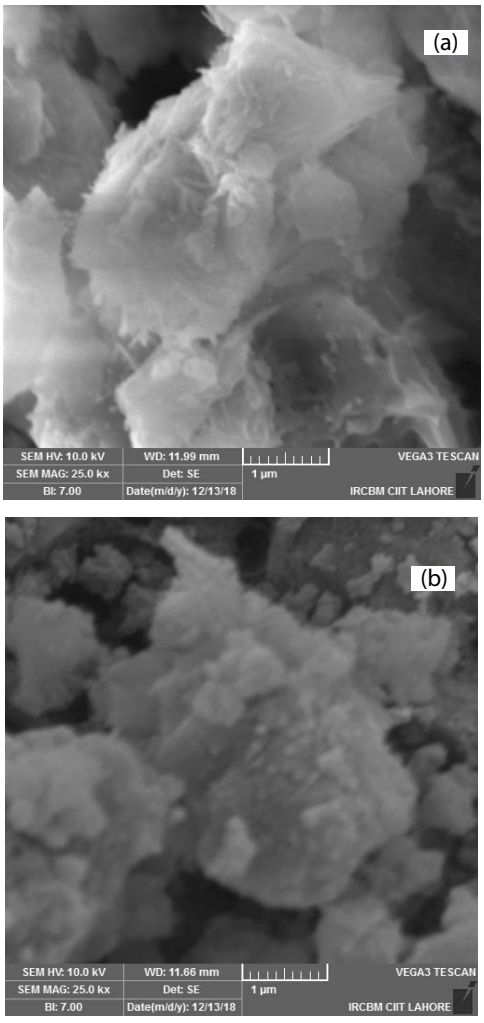

Fig. 5. SEM image of Z4A (a) before treatment and (b) after treatment.

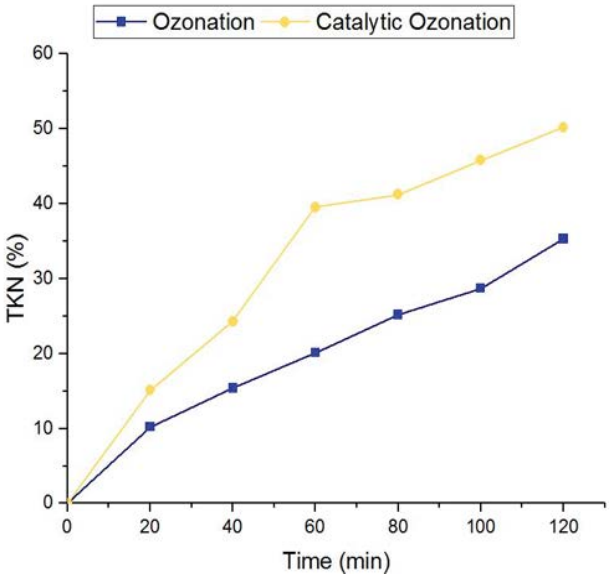

Fig. 6. Total Kjeldahl nitrogen removal of domestic wastewater in ozonation and catalytic ozonation (TKN_o = 42.6 mg L^{-1}; O_3 = 0.9 mg min^{-1}; amount of catalyst = 0.5 g; T = 120 min; temperature = 25°C ± 2°C; pH = 6.98 ± 0.8; V = 450 mL).

that Fe-Z4A/O_3 process show high removal efficiency with respect to single ozonation process. For example, 50% and 35% TKN was removed for catalytic ozonation process and single ozonation process (Fig. 6). The results suggested that Fe-loaded zeolite 4A may be a good catalyst for the treatment of municipal wastewater.

3.5. Catalyst dose effect

The Fe-Z4A catalyst dose effect in the catalytic ozonation process on COD removal of municipal wastewater was studied at various doses of 0.1, 0.5, and 1 g of catalyst in a semi-batch reactor. Results (Fig. 7) reveal that the rise in the amount of catalyst in the system increases the COD removal; this may be due to the enhanced active sites and adsorption of pollutants with the increase in catalyst amount [21].

3.6. Catalyst reuse performance

To study the long-term performance efficiency of iron-loaded zeolite 4A, continuous series of experiments of catalytic ozonation were performed. The results presented in Fig. 8 revealed that the catalytic performance of Fe-Z4A does not alter significantly even after three successive runs (360 min ozonation time). For example, at 120 and 360 min, the ratio of COD_t and initial COD was 0.13 and 0.27, respectively. Some decrease in COD removal after the third run may be because of the unwanted reaction intermediates adsorption on the catalyst that may deactivate the active sites [28].

3.7. TBA effect

TBA (tert-butyl) was used to study the radical's performance in both processes (ozonation and catalytic [Fe-Z4A/O_3] ozonation). TBA being a radical scavenger

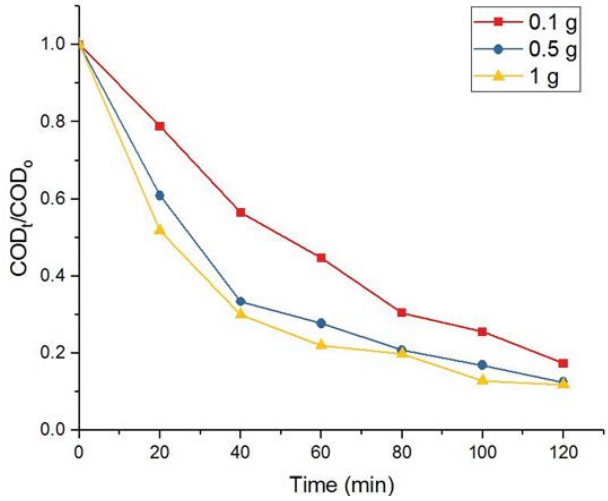

Fig. 7. Catalyst dose effect on the removal of COD of municipal wastewater during the catalytic ozonation (COD_o = 90 ± 10 mg L^{-1}; amount of catalyst = 0.1, 0.5, and 1.0 g; T = 120 min; temperature = 25°C ± 2°C; O_3 = 0.9 mg min^{-1}; pH = 6.98 ± 0.8; V = 450 mL).

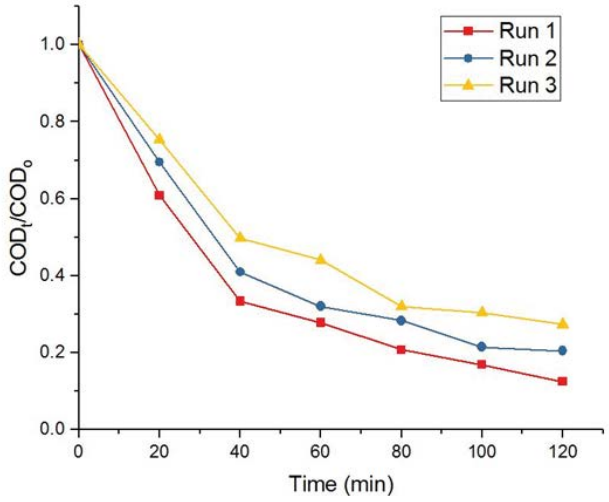

Fig. 8. Catalyst reuse performance effect for COD removal of municipal wastewater during the catalytic ozonation process in three successive runs (COD_o = 90 ± 10 mg L^{-1} O_3 =0.9 mg min^{-1}; amount of catalyst = 0.5 g; T = 120 min; temperature = 25°C ± 2°C; pH = 6.98 ± 0.8; V = 450 mL).

having a lower reaction rate with O_3 ($k_{TBA/O_3} = 3 \times 10^{-3}$ M^{-1} s^{-1}) and higher reactivity with •OH radicals ($k'_{TBA/OH} = 6 \times 10^8$ M^{-1} s^{-1}). Fig. 9 shows the effect of TBA on COD removal efficiency for ozonation and catalytic (Fe-Z4A/O_3) ozonation process. The COD_t/COD_o ratio was 0.57 at 40 min in the ozonation process (without using TBA) while using TBA the COD_t/COD_o ratio increased to 0.64 at 40 min. Similarly, for the catalytic (Fe-Z4A) ozonation process, by using TBA, the COD_t/COD_o ratio increased from 0.33 to 0.53 at 40 min. To find out whether the process follows a radical mechanism or non-radical mechanism, it is necessary to compare the COD removal efficiency in both processes (O_3-O_{3TBA} and

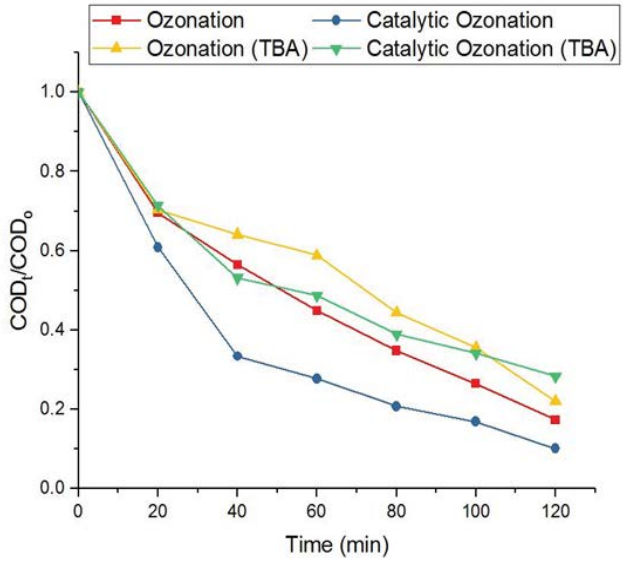

Fig. 9. Effect of TBA on COD removal of municipal wastewater in adsorption, ozonation, and catalytic ozonation (COD$_o$ = 90 ± 10 mg L^{-1}; TBA = 100 mg L^{-1}; O_3 = 0.9 mg min^{-1}; amount of catalyst = 0.5 g; T = 120 min; temperature = 25°C ± 2°C; pH = 6.98 ± 0.8; V = 450 mL).

Cat/O_3-Cat/O_{3TBA}). The catalytic (Fe-Z4A) ozonation process has more % decrease than ozonation processes showing the vital role of the radical-based mechanism of the removal of COD. It is important to mention here that the authors' previous finding indicates that Z4A follows non-radical mechanism and adsorption aids the catalytic ozonation process [22]. In current investigation, Z4A was modified by iron loading, that may be the active site for the hydroxyl radicals production, which is in agreement with some previous findings using iron-loaded catalysts [31].

TBA inhibits the pollutants degradation in catalytic ozonation process by decelerating the generation of •OH radicals which readily attack organic pollutants. Due to the chemical and physical properties of TBA, it cannot be directly adsorbed on catalyst surface [17]. The pollutants degradation may take place at both inside the solution by homogeneous liquid phase reactions or on the surface of Fe-Z4A catalyst by heterogeneous reactions. The TBA breaks the chain reaction between organic pollutants and •OH radicals [17]. The pollutants degradation is mainly due to the homogeneous liquid phase reactions of molecular ozone inside the solution and heterogeneous reactions occurring by adsorbed ozone on the Fe-Z4A surface. The results show the •OH radicals predominant effect in the Fe-Z4A catalytic ozonation process.

3.8. Ozone dose effect

The effect of ozone dose in catalytic ozonation process on the COD removal of municipal wastewater was studied at various ozone doses and the results are shown in Fig. 10. A significant rise in the COD removal was observed by an increase in the ozone dose. The enhanced COD removal at high ozone doses may be due to the prompt availability of

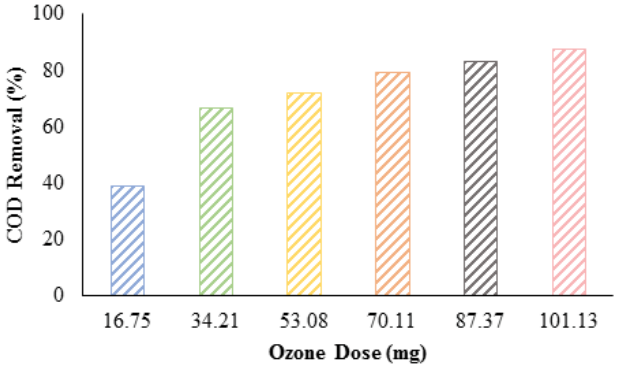

Fig. 10. Ozone dose effect on COD removal of municipal wastewater during the catalytic ozonation process (COD$_o$ = 90 ± 10 mg L^{-1}; amount of catalyst = 0.5 g; temperature = 25°C ± 2°C; pH = 6.98 ± 0.8; V = 450 mL).

ozone in the liquid phase thereby increasing the gas–liquid mass transfer rates and accelerating the rates of chemical reactions at the surface of the catalyst [32,33]. However, according to some reports, the actual ozone concentration in catalytic ozonation process depends on the nature of pollutants and the by-products generated by ozone oxidation [17].

3.9. Kinetic study

The kinetics for the catalytic ozonation of municipal wastewater on Fe-Z4A zeolites were studied at wastewater pH (Table 3). The processes followed the pseudo-first-order kinetics (Fig. 11) as shown by the R^2 values in (Table 3). The determined values of rate constants for the treatment of COD are shown in Table 3. The experimental results revealed that the COD removal rates were at the higher side for the case of catalytic ozonation (Fe-Z4A/O_3) in comparison with single ozonation (Table 3). The rate constant for COD removal on Fe-Z4A/O_3 was 18.8 × 10^{-3} min^{-1}, on single ozonation was 13.9 × 10^{-3} min^{-1} and on adsorption was 0.8 × 10^{-3} min^{-1}, respectively (Table 3).

The maximum COD degradation achieved in the (Fe-Z4A/O_3) catalytic ozonation process (Fig. 4) and highest rate constant (Table 3) lies in the synergetic effect of adsorption, ozonation, and catalytic ozonation. The single adsorption was the least effective process for COD degradation due to the absence of •OH radicals and only the Fe-Z4A surface characteristics play the active role in

Table 3
Pseudo-first-order kinetic rate constants for COD removal of domestic wastewater (a) ozonation and (b) catalytic ozonation (COD$_o$ = 90 ± 10 mg L^{-1}; amount of catalyst = 0.5 g; O_3 = 0.9 mg min^{-1}; T = 120 min; temperature = 25°C ± 2°C; pH = 6.98 ± 0.8; V = 450 mL)

Process	K × 10^{-3}(min^{-1})	R^2
Adsorption	0.8	0.990
Ozonation	13.9	0.9899
Catalytic ozonation	18.8	0.9617

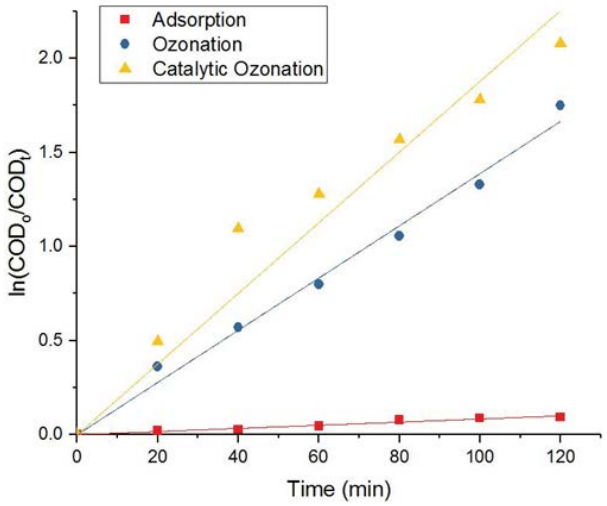

Fig. 11. Linear pseudo-first-order kinetic plots for COD removal of domestic wastewater (a) ozonation and (b) catalytic ozonation (COD_o = 90 ± 10 mg L^{-1}; O_3 = 0.9 mg min^{-1}; amount of catalyst = 0.5 g; T = 120 min; temperature = 25°C ± 2°C; pH = 6.98 ± 0.8; V = 450 mL).

pollutant degradation. In single ozonation process, the direct oxidation by molecular ozone or indirect oxidation by •OH radicals is the main mechanism for pollutant degradation. In (Fe-Z4A/O_3) catalytic ozonation process, the metal-loaded catalyst active sites provide a platform for the fast generation of •OH radicals that significantly enhances the pollutant degradation by synergetic effect as revealed by some studies [17,21].

4. Conclusions

The current research work implies the conclusions:

- Fe-Z4A zeolites are the efficient catalysts for the municipal wastewater degradation by ozonation at almost wastewater pH.
- Fe-Z4A zeolites show reasonably good reuse performance in catalytic ozonation of municipal wastewater.
- The removal of chemical oxygen demand of municipal wastewater on Fe-Z4A catalyst follows pseudo-first-order kinetics, with the highest rate of degradation achieved in catalytic ozonation process.

Acknowledgements

The authors gratefully acknowledge the Institute of Environmental Engineering and Research, University of Engineering and Technology, Lahore (Pakistan) for their support.

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