



# Application of green and red local soils as a catalyst for catalytic ozonation of fulvic acid: experimental parameters and kinetic

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## Abstract

The chlorination of surface waters leads to the formation of trihalomethans (THMs) and haloaceticacids (HAAs) due to the presence of natural organic matters. Thus, the removal of fulvic acid (FA) as one of the most prominent natural organic matters in water is necessary. Therefore, this study was aimed to evaluate the efficiency of catalytic ozonation of FA in the presence of the local montmorillonite (Mnt). The soils were collected from the Ardabil Sarcham area and used as a catalyst, after the required preparation. The variables in this study including initial solution pH, catalyst dosage, reaction time, and initial pollutant concentration were examined. For the ozonation of the samples, an ozone generator with a capacity of 5 g/h was used. It was found that, with increasing contact time, pH, and catalysts dosage, as well as decreasing initial FA concentration, the performance of the catalytic ozonation process increased significantly. The results demonstrated that radical scavengers like nitrate, chloride, sulfate, and carbonate a high concentration had very low effect on the efficiency of this process compared to conventional ozonation. The kinetic data was found to fit into the pseudo-first-order kinetic model ( $R^2 = 0.98$ ) than the zero and pseudo-second-order model. The Green Mnt was more effectual than the Red Mnt at pH: pH = 7, FA concentration = 25 mg/L, time = 30 min, catalyst dosage = 1.25 g/L, inlet ozone concentration = 2.2 mg/L-min; which gave COD removals of 84.68 and 78.25%, respectively. As a whole, green and red soils increase highly the efficiency of FA removal in the catalytic ozonation process, because of low costs and availability of these soils.

**Keywords** Advanced oxidation process · Catalytic ozonation process · Fulvic acid · Green soil · Red soil

## 1 Introduction

Natural organic matters (NOMs) are divided into two categories, one of which is autochthonous natural organic matters created by microorganisms, coarse macromolecules in water and carbon fixation by water plants and algae. The second class is allochthonous natural organic matters resulting from the disintegration of plant and animal residuals in the water, which actually refers to humic substances [1, 2]. However, the exact chemical structure of humic substances is unknown. These substances in surface waters are mainly divided into two classes: fulvic acids with a molecular weight of 2000–5000 gr/mole, and FA with a molecular weight of 500–2000 g/mole [3, 4]. Chlorination of waters containing NOMs causes the creation of disinfection by-products (DBPs) including trihalomethanes (THMs) and haloacetic acids (HAAs) [5]. In recent years, much attention has been paid to health risks potential of these compounds [6]. It should be pointed that conventional water treatment

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processes are only able to remove 10–30% of NOMs. Since removal of THMs and HAAs is more expensive, thus, the selection of a method having high efficiency in removing the precursor of THMs and HAAs is fully necessary [7]. Accordingly, various methods such as coagulation process, adsorption, ion exchange, and advanced oxidation processes (AOPs) have been utilized to remove humic substances [8]. The high performance of AOPs can be regarded as a major advantage [9–11]. Ozone is known as a strong oxidizing agent through direct reaction of the molecular ozone or indirectly reactions of hydroxyl radicals that are produced by ozone decomposition [12]. However, there are many obstacles to using the simple ozonation process in industrial scale including high installation and operation costs and weak ozone mass transfer rate [13]. Fortunately, the catalytic ozonation process (COP) raises the mineralization power of ozone by converting ozone molecules to more active forms leading to the higher efficiency and economic feasibility than the simple ozonation process [14]. The COP process has successfully been used for the decomposition of organic matters such as aromatic hydrocarbons, pharmaceuticals, pesticides, dyes and organic acids [15, 16]. Many materials like active carbon,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  have been applied as a catalyst in COP [17–20]. Also, the application of bone char in COP leads to an increase in the speed of the FA decomposition [21]. Hence, the performance of ozonation processes in the decomposition of NOMs can be enhanced dramatically through catalysts. However, few catalysts have been assessed in this regard. Thus, it is essential that affordable and accessible catalysts be investigated [19]. Therefore, this research provided an opportunity for further study on alternative catalysts in COP. In this study, green and red local soils were evaluated as a catalyst in catalytic ozonation for the degradation of FA in synthetic water solutions.

## 2 Materials and methods

### 2.1 Reagents, materials, and solutions

FA was provided from Sigma–Aldrich (OH, USA). Other chemicals used in this study were of analytical grade and obtained from Merck Company (Darmstadt, Germany). Green and red soils were collected from the Ardabil Sarcham area (Ardabil, Iran).

### 2.2 Preparation of catalyst

In the present study, we used a green local montmorillonite collected from Sarcham Region in Ardabil, Iran. They were first washed several times with deionized water to remove color and impurities. Then, they were dried at 60 °C for 24 h. Afterwards, the soil granules were sieved through 100

mesh and kept in a special repository away from moisture for further use.

### 2.3 Characterization of catalyst

Different analytical techniques were used to determine the properties of the prepared catalyst.  $\text{N}_2$  adsorption for determining the specific surface areas (Brunauer–Emmett–Teller) and pore volumes. Chemical compounds of catalyst were performed by using X-ray spectroscopy (XRF) (Philips–Magix Pro., Philips Electronics Co., Netherlands). Finally, for characterization of the functional groups on the surface of the samples using Fourier transform infrared spectroscopy (FT-IR) (PerkinElmer, USA) under a dry air at room temperature by the KBr pellets method. The infrared spectra were measured within a range of 450–4000  $\text{cm}^{-1}$ .

### 2.4 Determination of point of zero charge ( $\text{pH}_{\text{zpc}}$ )

The determination of  $\text{pH}_{\text{zpc}}$  of the samples was carried out as follows: initial pH a value of 50 mL of 0.1 M NaCl was used as an electrolyte; the pH was adjusted to a value between 2 and 12 by adding 0.1 M NaOH and/or  $\text{H}_2\text{SO}_4$ . Then, 0.1 g of sample added into each solution and has been shaken for 48 h under agitation at room temperature. After this period of agitation, the adsorbent was filtered and the final pH of the solution ( $\text{pH}_f$ ) was also determined. At the final step, the value of  $\text{pH}_{\text{zpc}}$  of adsorbent was found from the intersection of the curve of the initial pH and the final pH [22, 23].

### 2.5 Experimental procedure and analysis

Ozonation was done in a batch glass reactor with  $0.2 \times 0.2 \times 0.3$  meter dimensions; Fig. 1 shows a schematic diagram of the reactor. First, the reactor was filled with 7-liters sample, and then the ozonation was performed after providing the requirement variables. An ozone generator (ARDA-MOG) with 5 g/h capacity was used to produce ozone. A 20-L high

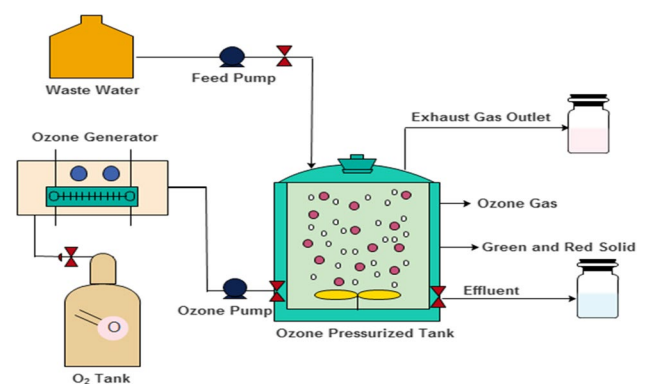


Fig. 1 Schematic of the ozonation pilot

purity oxygen tank was applied as the fed source for the ozone generator. The concentration of injected ozone was measured according to the 2350–E procedure explained in the Standard method [24]. All of the experiments were performed at mixing rate of 300 rpm and room temperature. To determine the effect of initial pH on the efficiency of the process, the examination was continued by adding 0.5 g/L of the catalysts at the pH of 2–4–6–8–11. And, other trials were done at the natural water pH range (pH = 7). In order to determine the optimal dose of the catalyst, the concentrations of 0.25–0.5–0.75–1–1.25–1.5 and 2 g/L were added to the samples for 30 min. To observe the effects of initial concentration and time in the performance of the COP, FA in the concentration of 5–10–25–50–100 mg/L was prepared. In this study, the time periods of 5–10–15–20–25–30 minutes were tested at the optimal amount of the catalyst and the removal efficiencies were measured. Also, to ensure repeatable results, every step of the experiments was repeated twice, and the average results were reported. The colorimetric method at 254 nm wavelength by means of a Perkin Elmer-25 lambda spectrophotometer was used to measure FA content. Before the quantification of residual FA, the samples were centrifuged at 10000 rpm speed. The percentage of FA removal rates was calculated by Eq. (1) [25–27].

$$\text{Removal Percentage (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where  $C_0$  and  $C_e$  are the initial and final concentrations in mg/L, respectively.

Kinetics studies are consequential key-factor for determination of the order and rate constant which is so significant for designing an adsorption process. For kinetics studies, 1.25 g/L of the catalyst was contacted with 1000 mL of FA solutions with the initial concentration of 25 mg/L of FA.

## 3 Results and discussion

### 3.1 Catalyst characterization

#### 3.1.1 XRF analysis

According to the X-ray fluorescence (XRF) results (Table 1), the chemical composition of green and red soils included silica, magnesium, aluminum, sodium, calcium, titanium and potassium. Researchers have clarified the role of these metals in the conversion of ozone into active

radicals [8]. Active sites on these metals are important in decomposition of ozone; they also play a role in the formation of functional groups on the surface of the soils. When the soils are added to water, these metals are covered with water molecules that are being decomposed and this then leads to the formation of metallic functional groups on the surface of catalysts.

#### 3.1.2 FTIR analysis

The FTIR results in 400–4000  $\text{cm}^{-1}$  indicated the presence of active functional groups on the surfaces of the catalyst (Fig. 2). The existences of these functional groups cause the catalyst to act as a Lewis acid-base and convert ozone into active radicals. It is worth noting that soils' functional groups including carboxylic acid groups, ethers, esters, aldehydes, ketones, amines, and hydroxyl are main factors in the conversion of ozone to more active forms [28]. Some researchers believe only the surface neutral hydroxyl functional groups have a high catalytic activity and expedite the decomposition of ozone and production of hydroxyl radicals [29]. Yuan et al. reported that, in the presence of a catalyst, the production of hydroxyl radicals increased significantly. Also, they stated that hydroxyl functional groups have the main cause in the catalytic decomposition of ozone [30].

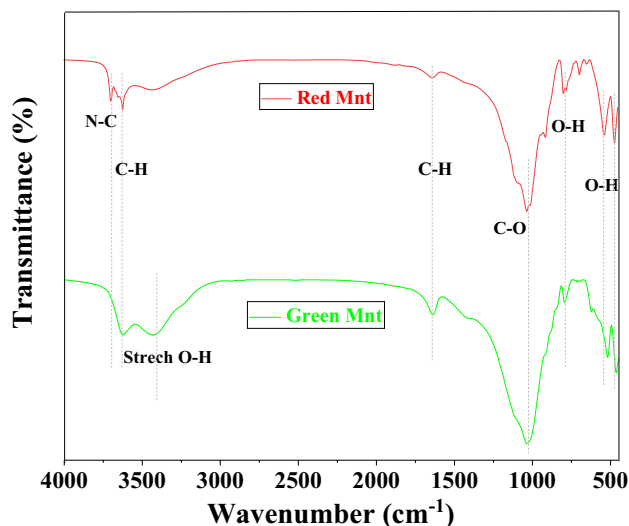


Fig. 2 FTIR analysis of green and red Mnt

**Table 1** XRF results of green and red soils

Metal oxides	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>
Green Mnt(Wt%)	56.9	13.5	9.7	9.6	2.6	2.1	1.6	1.3
Red Mnt(Wt%)	58.3	17.7	2.8	11	1.4	3.9	1.2	1.4

### 3.1.3 BET analysis

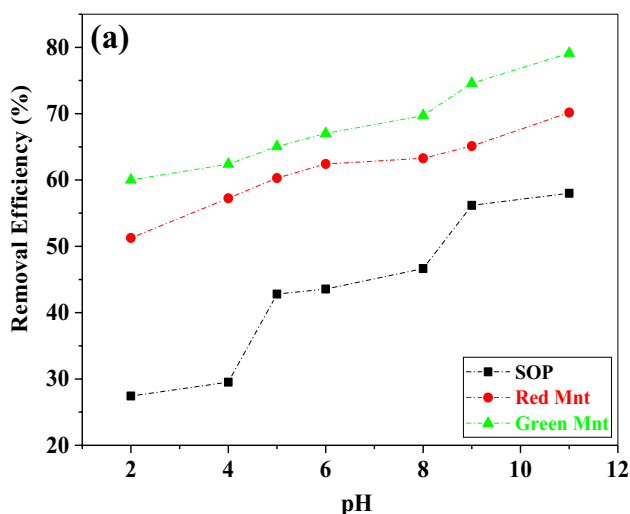
BET analysis based on the measurement of absorbed and desorbed nitrogen gas by the substance surface at the constant temperature of liquid nitrogen (77 K) to calculate the volume of pores and area of surface. Table 2 shows the nitrogen adsorption/desorption isotherms of the green and red soil. By comparing Table 2 can be found that the porosity of the green soil is more than red soil. The area of specific surface of green and red soil is respectively calculated 13.02 and 2.88 m<sup>2</sup>/g. Also, the total volume pores in green and red soil has respectively been 7.38 and 6.9 cm<sup>3</sup>/g and is indicator the amount of volume of pores in composite. The BET results show that the special area of the green soil was higher than that of the red soil; also, the green soil had extended area for the decomposition of ozone to active species. This illustrated that the green soil had a better performance than the red soil.

### 3.2 Effect of initial pH on the performance of COP process

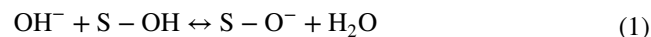
The  $pH_{zpc}$  is another important parameter when a catalyst is applied. This characteristic shows the properties of catalyst surface [31, 32]. The  $pH_{zpc}$  values of red and green soils were obtained 7.4 and 6.4, respectively (Fig. 3). The  $pH_{zpc}$  is

**Table 2** BET characteristics of green and red soils

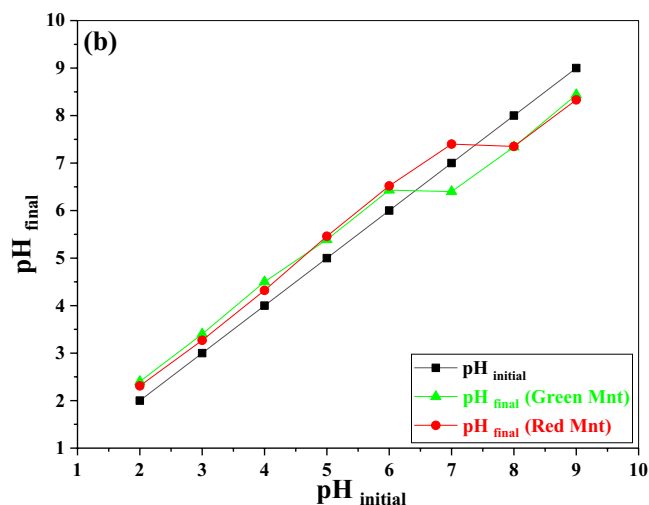
Characteristics	Green soil	Red soil
Specific area(m <sup>2</sup> /gr)	13.02	2.88
Mean pore diameter	22.7	9.57
Total pore volume(cm <sup>3</sup> /gr)	7.38	6.9



important for the perception and evaluation of catalytic ozonation mechanism; when pH is higher than  $pH_{zpc}$ , the functional groups are deprotonated (Eq. 1) and, in the pH level lower than  $pH_{zpc}$ , the surface functional groups are protonated (Eq. 2) [33].



Deprotonating and protonation of functional groups cause catalysts to act as a Lewis acid-base and this phenomenon plays a basic role in the performance of soil used as a catalyst [34, 35]. Therefore, based on the results of this study and other related studies, it can be concluded that these properties must be examined separately, due to the importance of the chemical properties of the catalyst [19]. The results show that FA removal increased with raising initial pH values in both simple and catalytic ozonation processes (Fig. 3). In the simple ozonation process, due to the initial pH, ozone reacts with pollutants through two different ways, direct oxidation, which is a major factor in the decomposition of FA in acidic conditions and indirect oxidation, in which hydroxyl radicals are major oxidizing agents, in alkaline conditions. With increasing the pH value, the number of generated radicals increased, leading to further degradation of FA [36]. It was found that in the catalytic ozonation process, the removal efficiency of FA at all pH values was higher than that of the conventional ozonation process. In acidic conditions, ozone is absorbed on soil surface. The following equations show absorbing compounds react with absorbed ozone [37].



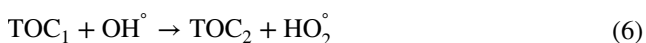
**Fig. 3** Effect of initial pH on SOP and COP processes (inlet ozone concentration = 2.2 mg/L-min, catalysts dosage = 0.5 g/L) (a) and  $pH_{zpc}$  (b)



Where  $TOC_1$  indicates total organic carbon that is adsorbed on the surface of soil and  $TOC_2$  represents oxidized organic carbon. Hydrogen peroxide is formed through the decomposition of ozone on the surface of soil. But the effect of the generated hydrogen peroxide in this way is low in the efficiency of the process. The reaction of adsorbed ozone on the surface with hydrogen peroxide leads to the formation of radicals species [17].



suspended organic compounds react with the produced radicals via the following equation [38].



The formation of hydrogen peroxide in the reaction of ozone with the catalyst was reported by Alvarez et al. [39]. The chemical adsorption of ozone on the catalyst surface results in the formation of activated radicals reacting with suspended Fulvic acids [1]. Also, FA is removed through the direct reaction of molecular ozone and FA is chemically absorbed on the surface of the catalyst and then it reacts with molecular ozone. Therefore, in acidic conditions, the absorption of ozone and FA molecules in the same time on the catalyst surface and their reactions lead to FA removal, thereby enhancing catalytic ozonation compared to the conventional ozonation at the same situations [7, 40]. Faria et al. surveyed the performance of activated carbon as a catalyst in the removal of oxalic acids and oxamic acid; they reported that reactions that take place on the surface of the activated carbon in acidic conditions are the main factor increasing the performance of the catalytic ozonation [16].

Researchers have claimed that the dissociation of functional groups occurs at pH values higher than  $pH_{zpc}$ ; thus, the nucleophile properties of functional groups increase. Under these conditions, the dissociated functional groups on the surface of the catalyst tends to increase the reaction rate of ozone [41]. The loss of these electrons causes them to transfer to ozone molecules and promote ozone decomposition to very active radicals on the catalyst surface. Eventually, this electron transfer leads to the formation of ozonized anions, and this cycle of radical reactions continues [42]. In fact, an increase in pH and subsequent reactions on the catalyst surface has a synergistic effect on FA removal [43]. With raising pH, the concentration

of hydroxyl ions in the liquid phase increased. These ions trigger a reaction of ozone decomposition into radical agents.

### 3.3 Catalyst dosage

In order to evaluate the effect of catalysts dosage on the removal of FA, the catalyst was added to the sample in doses between 0.25 and 2 g/L. The results showed that, with increasing the dose of the red and green soil, the removal rates went up from 35.12 to 79.26% and 48.89 to 84.89%, respectively (Fig. 4). As can be seen in Fig. 4, increasing catalyst dosage more than 1.25 g/L a significant change did not happen. Therefore, the optimized dose in the COP process was 1.25 g/L.

One of main parameters in the designing of COP process is minimum required catalyst dose as an initiator or promoter of ozone decomposition reactions [19]. The following reactions happen in the presence of ozone and soil, which can be a cause for the high efficiency in the presence of green and red soil. In this reactions, soils act as an initiator for radical production and absorption of ozone on the soil surface leading to ozone destruction and active radicals production [9]. In other words, the Lewis acid site reacts with ozone and produce oxygen radicals. Also, in the presence of water, the oxygen radicals produce hydroxyl radicals and increase the process efficiency [44].

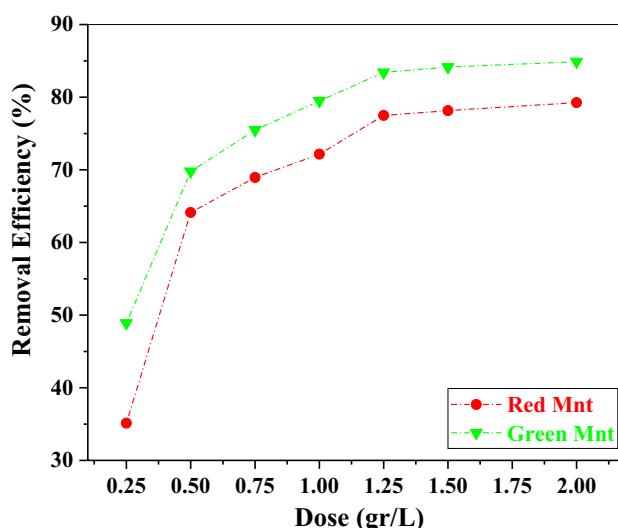
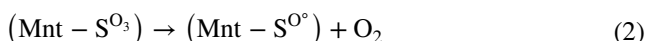
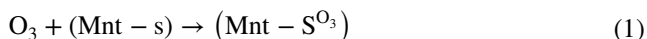
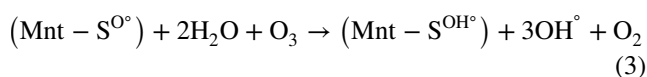


Fig. 4 Effect of catalyst dosage (pH = 7, inlet ozone concentration = 2.2 mg/L-min)



-S index indicates the Lewis acid on the surface of montmorillonite.

With a further increase in the catalyst dosage since 1.25 to 2 g/L, a significant improvement in the efficiency of the process was not observed. Therefore, a small amount of the catalyst was sufficient to catalyze and increase FA decomposition. Thus, in the catalytic ozonation process, the optimum catalyst dosage depends on the catalyst type, target compound, and the reaction conditions [45].

### 3.4 Effect of contact time and initial FA concentration

According to the results (Fig. 5), the removal efficiency of FA significantly decreased with increasing initial soil concentration, which can be compensated with increasing in inlet ozone injection [46]. Contact time is the time required to achieve the desired goals in a purification process and it is one of the most important designing and operating parameters in oxidation processes. High contact time means higher construction costs [47]. It was found that, with increasing retention time, the removal efficiency of FA increased. Interestingly, less reaction time is required in the case of catalytic ozonation in compared with conventional ozonation, thereby reducing the required reaction time; this is possibly due to the production of oxygen and hydroxyl radicals caused by the presence of the catalyst and molecular ozone resulting

in further power and decomposition speed in the catalytic ozonation process [48].

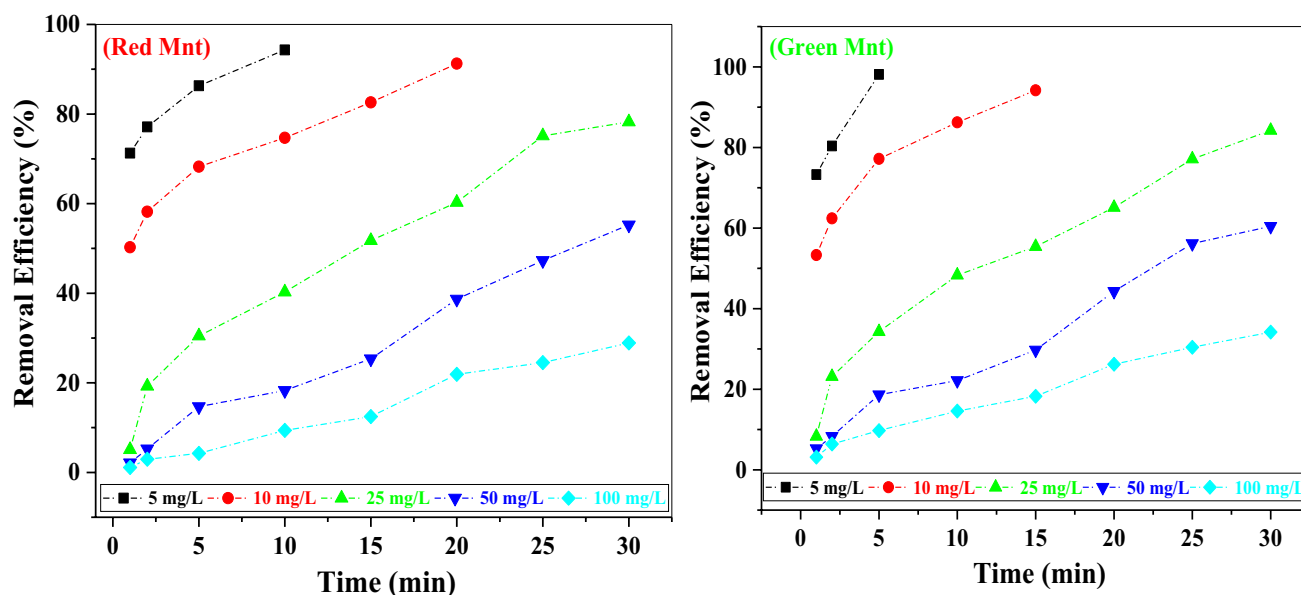
### 3.5 Kinetic study

To investigate the kinetic of FA disintegration using catalytic ozonation process, zero order, pseudo-first order and pseudo-second order kinetics, of different organic compounds, especially FA, were studied. The test was applied in optimum conditions to study the disintegration synthetic (dose 1.25 g/L, pH = 7, and concentration of 25 mg/L). The reduction of FA concentration was observed as a function of irradiation time and data were fitted to a first order rate [49, 50]. The amount of fixing coefficient for regression line is 0.98; hence, FA deleting reaction of pseudo-first-order model follows it (Table 3 and Fig. 6). Pseudo-first-order reactions are reactions in which the reaction rate is only a function of the concentration of a substance. The correlation between  $\ln C/C_0$  and the reaction time was linear. The kinetic expression can be presented as follows Eqs. [51].

$$\ln C/C_0 = -k t$$

**Table 3** Kinetics for the FA degradation process

	$K$ ( $\text{min}^{-1}$ )	$R^2$
Zero	0.0236	0.957
Pseudo first order	0.049	0.98
Pseudo second order	0.1564	0.92



**Fig. 5** Effect of initial soil concentration on removal efficiency of catalytic ozonation process (pH = 7, catalyst dosage = 1.25 g/L, inlet ozone concentration = 2.2 mg/L-min)

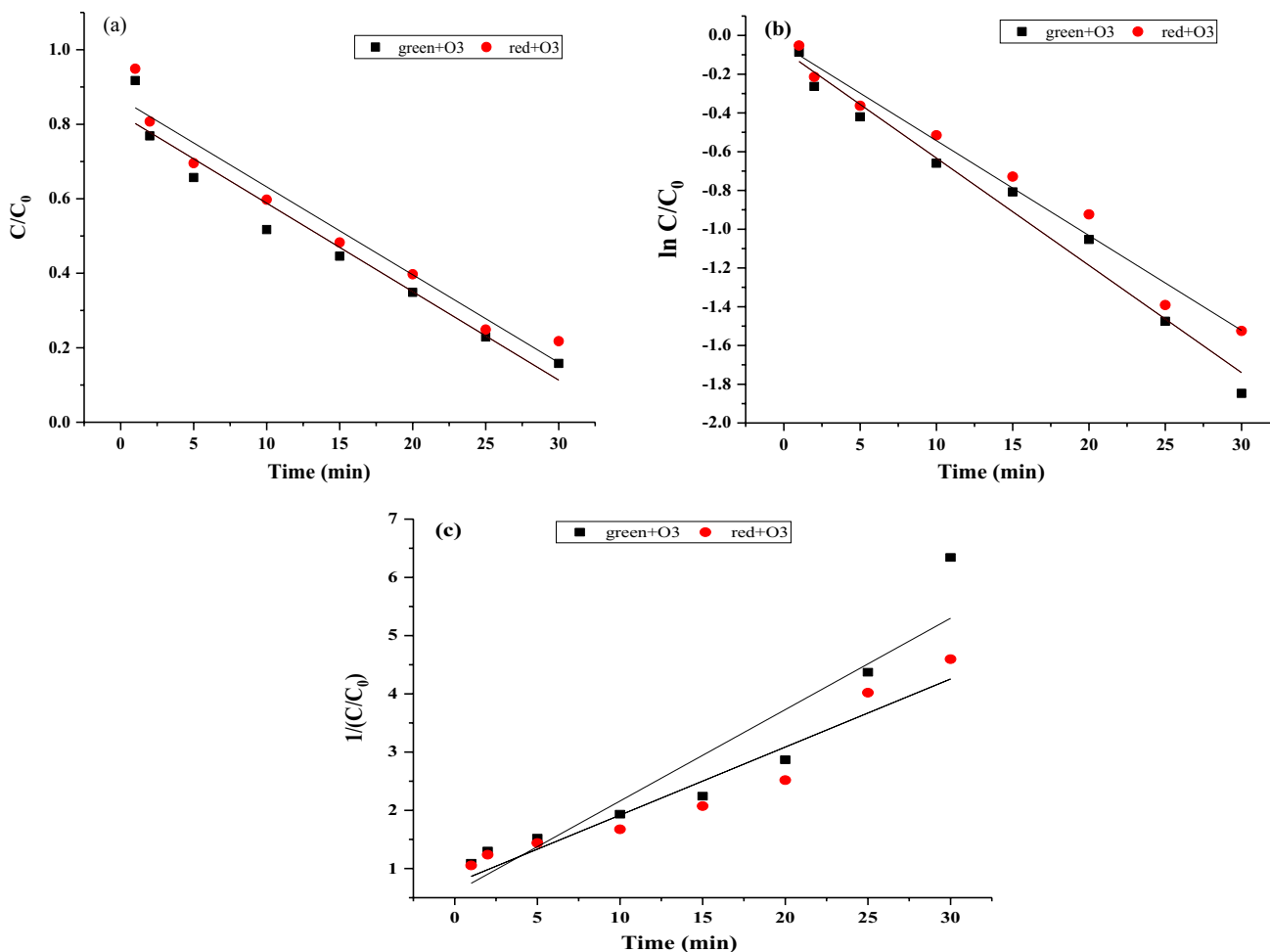


Fig. 6 Zero order (a), pseudo-first-order plot (b), and pseudo-second-order plot (c) for FA degradation by catalytic ozonation process

Where  $C$  is the FA concentration at instant  $t$ ,  $C_0$  is the initial FA concentration,  $k$  is the rate constant, and  $t$  is the time of reaction. The identification between the models' calculated values and the experimental data is expressed by  $R^2$ . A study by Feng et al. on the catalytic ozonation of humic acid in water with modified activated carbon showed that the kinetics removal of humic acid reaction was a pseudo-first order [52].

### 3.6 Effect of confounding factors in the catalytic ozonation process

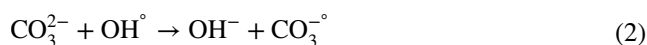
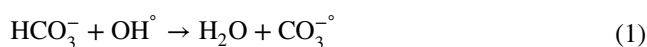
One of the major problems in advanced oxidation processes (AOPs) is confounding factors impacting the reactions. Some of these factors or radical scavengers are sulfate, carbonate, chloride, and nitrates. They are drastically present in natural waters and, in turn, reduce the efficiency of AOPs [53]. It was found that in the case of conventional ozonation process, in the presence of 300 mg/L of carbonate and sulfate, the removal efficiency of FA decreased to 51.2 and

48%, respectively. In contrast, in the case the COP, by means of the green and red soils in the presence of the same content of carbonate and sulfate, the removal efficiency declined to just 5–3.8% and 5.8–4.1% respectively (Table 4). At pH values higher than  $pH_{zpc}$ , active Lewis sites react with ozone, because these reactions happening on the catalyst surface are less affected by radical scavengers, as mentioned previously [39]. The ozone decomposition declined in the presence of strong Lewis bases such as carbonate, sulfates, chloride, and nitrate that are generally present in natural waters. These ingredients compete with ozone to react with strong Lewis

Table 4 Effect of confounding factors in the catalytic ozonation process

	Carbonate (mg/L)	Sulfate (mg/L)
SOP	51.2	48
COP (green soil)	5	3.8
COP (red soil)	5.8	4.1

sites where ozone decomposition takes place [54]. However, because of the resonance structure of ozone and having high electron density on the one of its oxygen atoms, it has a strong tendency to react with Lewis acid sites on the surface of the catalysts compared with water compounds. This property of ozone causes decomposition of ozone that is less affected by radical scavengers [21]. Of course, one reason for the negligible impact of radical scavengers in the catalytic ozonation process may be owing to the production of non-hydroxyl radicals that these do not react with radical scavengers [55]. Khutina et al. in 2015 investigated the production of hydroxyl radicals from ozone and reported that the main inhibiting factors for hydroxyl radical production are carbonate and bicarbonate [56].



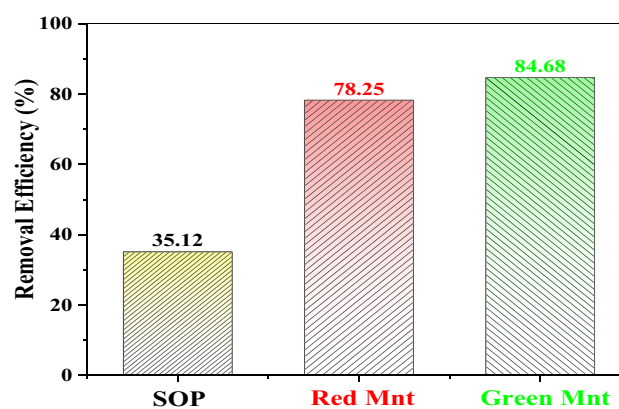
Carbonate prevents the chain reactions of ozone decomposition. At the alkaline pH, carbonate not only is a scavenger but also prevents the ozone breakdown to hydroxyl radicals. Thus, the presence of carbonate reduces ozone decomposition speed. Several investigators have shown that ozonation in the presence of radical scavengers is stopped or results in a great decrease in removal efficiency, while, under the same conditions, the catalytic process is less affected by these factors [18]. Although the experimental conditions in this study were different, the results showed that the findings obtained corresponded with those documented by other studies. Thus, according to the results, since the heterogenic catalytic ozonation process was less affected by the scavengers, this process can be used as an alternative to conventional methods.

### 3.7 COD changes in catalytic ozonation process simple

The results (Fig. 7) demonstrated that COD removal was slight compared with FA removal. The main reason for this phenomenon is that over FA ozonation the interfering compounds can be formed, which result in an increase in COD concentration [57]. For example, Sano et al. investigated the phenol removal and observed that COD removal was slower than phenol removal, and interfering compounds lead to an increase in COD throughput [58].

## 4 Conclusion

The results of this study indicated that using green and red soils dramatically increased the removal efficiency of FA; the findings revealed that, despite the presence of



**Fig. 7** COD removal in SOP and COP (pH = 7, FA concentration = 25 mg/L, time = 30 min, catalyst dosage = 1.25 g/L, inlet ozone concentration = 2.2 mg/L-min)

confounding factors and radical scavengers, which lead to a sharp decline in the efficiency of conventional ozonation processes, the presence of these agents in high concentrations had much smaller impact on the catalytic ozonation process when the soils were added. It was also observed that the COP process had a high performance in natural pH. Therefore, it can be concluded that green and red soils can be used as a catalyst for the catalytic ozonation of FA and other organic compounds, owing to advantages as follows: cost-effectiveness and high efficiency. Of course, the removal efficiency for other groups of organic compounds may result in different observations. Therefore, further evaluation is required to confirm the result of this manuscript for other pollutants. The results demonstrated that COD removal was slight compared with FA removal. The main reason for this phenomenon is that over FA ozonation the interfering compounds can be formed, which result in an increase in COD concentration. The Green Mnt was more effectual than the Red Mnt at pH: pH = 7, FA concentration = 25 mg/L, time = 30 min, catalyst dosage = 1.25 g/L, inlet ozone concentration = 2.2 mg/L-min; which gave COD removals of 84.68 and 78.25%, respectively. The area of specific surface of green and red soil is respectively calculated 13.02 and 2.88 m<sup>2</sup>/g. The kinetic data was found to follow the pseudo-first-order kinetic model. It should be pointed that it is necessary to study well the use of these catalysts in large-scale applications.

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**Authors' contributions** Mehdi Fazlzadeh and Yousef Poureshgh participated in the conceptualization and design of the research and supervised the work. Hossein Abdoallahzadeh, Shirin Afshin, and Yousef Rashtbari are responsible for experimental analysis and interpretation of data. Juliana Heloisa Pinê Américo-Pinheiro and Ali Azari



contributed to literature search and quality assessment. All authors have read and approved the final paper as submitted.

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**Data Availability** All the data and material pertinent to this manuscript are included and have been reviewed by all authors.

## Declarations

**Ethics approval and consent to participate** The authors of this article have covered all the ethical points, including non-plagiarism, duplicate publishing, data distortion, and data creation in this article. This project has been registered in Ardabil University of Medical Sciences.

**Consent to participate** Not applicable

**Consent for publication** Not applicable

**Conflicts of interest** The authors declare that they have no competing interests.

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