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Application of magnetic activated carbon as a catalyst in catalytic ozonation process (COP) for removal and mineralization of humic acid from aqueous solution

Mohammad Ali Zazouli[a], Mitra Roohafzaee[a,*], Yousef Dadban Shahamat[b,*], MaryamYousefi[a]

[a]*Department of Environmental Health Engineering, Faculty of Health, Health Sciences Research Center, Mazandaran University of Medical Sciences, Sari, Iran, emails: roohafzaeem@gmail.com (M. Roohafzaee), mzazouli@mazums.ac.ir (M.A. Zazouli), maryam_u3fi7@yahoo.com (M. Yousefi)*
[b]*Environmental Health Research Center, Golestan University of Medical Sciences, Gorgan, Iran, email: ydadban@yahoo.com*

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ABSTRACT

Humic acid (HA) is a natural organic matter, which is naturally present in raw water sources due to the decomposition of dead animals and plants. Therefore, the catalytic properties of a carbonaceous nanocomposite in the catalytic ozonation process (COP) of HA were investigated, and the results were compared with those obtained from the single ozonation process (SOP). Magnetic carbonaceous nanocomposite, as a novel catalyst, was applied to optimize the conditions for the removal of HA in the COP, and the influential parameters such as pH, retention time, catalyst dosage, and addition of radical scavengers were all evaluated. This is an experimental study in which the removal of HA by a COP was investigated in a cylindrical glass reactor (a useful volume of 250 mL) with a semi-continuous flow. Catalyst raw material was the granular activated carbon (GAC) that has been stabilized on Fe_3O_4 nanoparticles by the calcination method. The results revealed that by increasing the retention time, pH, and catalyst dosage, HA and TOC removal efficiencies by both process (SOP and COP) was increased. The highest removal efficiencies of HA and TOC in the COP process were 95% and 87.67%, respectively while their removal efficiencies in the SOP process were 76.8% and 67.1% under the conditions including pH of 9, contact time of 60 min, and HA concentrations of 15 mg/L. The highest removal of the HA by the SOP and catalyst adsorption was obtained to be 76% and 5.8% after 60 min, respectively; however, it was observed to be 95.7% in the COP, in the same contact time. The presence of *tert*-butanol alcohol (TBA) did not significantly affect the removal of the HA in the COP. Practically, this study revealed that the magnetically activated carbon catalyst could be potentially employed in the COP for the treatment of the water having average concentrations of HA substances.

Keywords: Catalytic ozonation process; Humic acid; Magnetically activated carbon; Natural organic matter; Sole ozonation process; Precursors THMs

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1. Introduction

Organic compounds are harmful compounds, which have a natural or synthetic origin and can be easily found in surface water. Natural organic matter (NOMs) is a heterogeneous mixture of organic compounds that are derived from plants, animals, living and dead microorganisms, and their waste products and enter the water resources through decomposition [1]. Natural organic compounds are a group of organic substances that naturally occur in all surface and groundwater. Wherever organic matter is being

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* Corresponding author.

biodegraded, these compounds are produced and transported to water sources [1,2]. These compounds range from large colorless aliphatic to highly colorful aromatic compounds [3]. Some of these compounds are hydrophobic and others are hydrophilic. Humic acid (HA), fulvic acid (FA), humin, phenolic structures, and compounds with conjugated double bonds belong to hydrophobic natural organic compounds (HNOC), which account for approximately 55% of the amount of total organic carbon (TOC) in water [2,3]. Humic compounds are one of the most important natural organic substances [4,5]. HA is macromolecules that contain humic substances, which have dispersed in soil, natural waters, and sediments and have produced in the decomposition of plants and organic residues [6]. Commercial humic acid is extracted from coal [6]. It is very difficult to determine the exact properties of HA. The molecular weight of HA is 2,000 to 1,300,000 Dabson and has many functional groups, including phenolic, carboxylic acid, anolic, quinol, and ether groups, as well as carbohydrates and peptides. However, phenolic and carboxylic acid functional groups are abundantly discernible in the HA structure [5,7]. One of the major problems with NOMs such as HA in natural water sources (even at very low concentrations) is the formation of disinfection byproducts (DBPs) at the stage of disinfection with chlorine compounds [8,9]. More than 700 types of DBPs have been identified, among which trihalomethanes (THMs) and haloacetic acids (HAAs) have been introduced as two major groups with high concentrations in drinking water sources worldwide [8]. These compounds are toxic, carcinogenic, and mutagenic. THMs cause cancer of the bladder, kidney, colon, and bowel (10). THMs include trichloromethane (chloroform), bromodichloromethane, dibromochloromethane, tribromomethane (bromoform) [10,11]. The formation of cancer in laboratory animals by chloroform has been reported in many studies, and the association between these compounds and stillbirths has been reported by some researchers [11]. Public concern about the risk associated with THMs began after approving the carcinogenic potential of chloroform, and it was introduced as and classified a carcinogen for humans by the United State Environmental Protection Agency (USEPA) in 1975 [12,13]. Since most of the soluble organic matter in natural water is composed of humic substances and conventional water treatment processes can only remove a small percentage of these substances. Thus, the choice of methods that are highly effective in the removal of the precursors of THMs and HAAs should be considered [13–15].

Proportionally, some techniques such as electrocoagulation [2], advanced oxidation [14–17], membrane separation [8], adsorption [15,18], and sono-photocatalyst [19,20] have been assessed for removal of HA from aqueous solution.

Each of these removal methods has advantages and disadvantages that limit their use. In general, these methods have disadvantages such as cost, the complexity of application in developing countries, high sludge production, membrane clogging, and low adsorption capacity. Today, advanced oxidation processes (AOPs) have been considered for the degradation of toxic and resistant and non-degradable compounds [21,22]. The basis of AOPs is the formation of free and active radicals, which results in the effective and rapid oxidation of organic pollutants; these processes can also convert organic compounds to water and carbon dioxide completely [23–25]. Ozone, as a strong oxidizing agent, is one of the effective methods to oxidize organic pollutants in water; however, the ozonation process has problems such as low solubility of ozone in water, incomplete oxidation of organic compounds in water, and low stability in water [26]. For this reason, a catalyst is recently added to the ozone process, which is led to further decomposition of ozone and the generation of active radicals [27]. The catalytic ozonation process (COP) is used in both homogeneous and heterogeneous processes. The pollutant mineralization mechanisms are accomplished by two following methods: direct method using ozone molecules and indirect method through the production of hydroxyl radicals [28]. The heterogeneous ozonation process has been widely used due to the lack of production of secondary pollutants, catalyst recyclability, and low cost [28].

Many materials, such as activated carbon (AC), Al_2O_3, and TiO_2, have been employed as a catalyst in the ozonation process [29–31]. In a variety of studies, the presence of a catalyst in the ozonation process is led to increasing the degradation rate of HA. For instance, Lee et al. [32] have conducted a study for catalytic ozonation of HA with Fe/MgO and have addressed that ozonation in presence of Fe/MgO is led to a drastic reduction in HA compared to ozonation alone. Thus, catalysts can effectively lead to improve the removal of HA in the ozonation process.

Therefore, this study estimated the magnetically AC catalyzed ozonation process for the removal of HA and TOC from an aqueous solution. Considering the previous studies and lack of application of magnetic activated carbon as a catalyst in the ozonation process, its application can increase the production of ozone gas to the liquid phase and can enhance the production of hydroxyl radicals and recycling catalyst, which can finally lead to reducing the costs; this can be considered as one of the innovations of this study.

2. Materials and methods

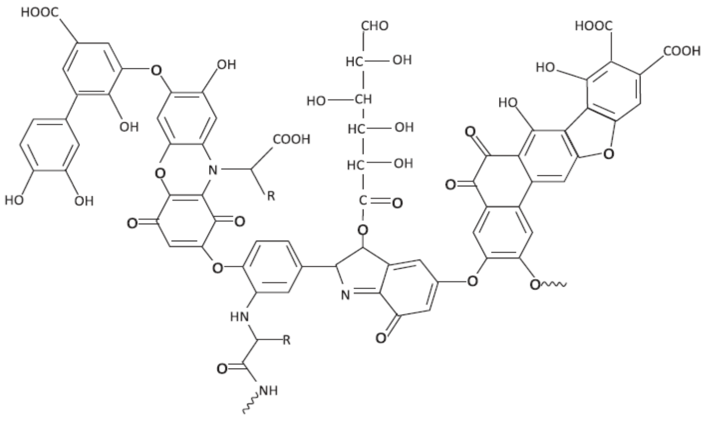
2.1. Materials

Humic acid (the purity of 99.5%, CAS NO: 1415-93-6) was purchased from Sigma Aldrich (St. Louis, MO, USA) (Table 1). Other required chemicals such as potassium iodide (KI), sodium hydroxide (NaOH), sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$), sodium sulfide ($Na_2S{\cdot}9H_2O$), ammonia (NH_3), ferric chloride ($FeCl_3$), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), sodium chloride (NaCl), and nitric acid (HNO_3) were purchased from Merck Co., (Darmstadt, Germany). To adjust the pH solution, 1 N HCl and NaOH were applied. In order to synthesize the catalyst, the granular activated carbon (GAC; purity of 99.99% and CAS NO: 1.02183) was used as raw material for the synthesis of the catalyst.

2.2. Synthesis of catalyst

This catalyst has a superparamagnetic property and its raw material is the GAC that has stabilized on Fe_3O_4 nanoparticles by calcination method. First, 50 g of GAC was crushed in a crucible and passed through a sieve with

Table 1
Chemical characteristics of humic acid (35)

Physical and chemical properties	Specifications
Appearance features	Black granular appearance
Odor	Slightly moldy
Solubility in water	Completely soluble
Melting point	>300°C
Color	Black granule
Storage at 70 F°	>1 y
pH	Not available
Chemical structure	

a mesh size of 30 (MESH = 30). Afterward, it was mixed in nitric acid solution with a magnet (36%) and stirred using a magnetic stirrer at 80°C for 3 h to obtain the hydrophilic property, and it was then washed with distilled water and dried at 105°C during the night. 25 g of modified carbon was placed in a 200 mL solution containing 100 g of $Fe(NO_3)_3·9H_2O$ and placed in an ultrasonic bath for 1 h. After filtering and drying, the sample was exposed to high purity nitrogen gas flow at 750°C for 1 h to form the Fe_3O_4 nanoparticles on the carbon substrate [33]. To determine the surface structural properties of the catalyst and morphology, the specific surface area and its elemental distribution were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis by X′Pert Pro diffractometer (Rigaku RINT2200, Japan), and energy dispersive X-ray spectroscopy (EDS). It should be noted that the characteristics of the catalyst have been reported in our previous study [34].

To determine the status of the distribution of electric charge on the surface of the synthesized catalyst, the value of pHpzc was measured. This parameter of catalysts is an indicator to determine and interpret the mechanism of the COP. NaCl (0.01 M), hydrochloric acid (0.1 M), and NaOH (0.1 M) were used to determine pHpzc.

2.3. Catalytic ozonation process

This study was an experimental study in which the removal of HA by a COP was investigated in a cylindrical glass reactor (with a useful volume of 250 cc) with a semi-continuous flow. In this process, the ozone-containing airflow was discharged from the reactor after contact with the solution. After trapping the surplus ozone, gas has been discharged into the gas washing bottle containing potassium iodide (20%). The connections between the reactor components were made of ozone-resistant silicone hoses. Fig. 1 shows the schematic of the catalytic ozone pilot. The ozone was injected into the reactor with an ozone generator (model ARDA-COG 0, France). The inlet gas to the reactor was adjusted by a rotameter (nominal capacity of 5 L/min) with a flow of 1 L/min. Potassium iodide concentration was adjusted to 11.67 mg/L.

The experiments are designed as One Factor at the Time method, which the operational factors as initial pH (5–9), retention time (10–60 min), and catalyst concentration (0.5–3 g/L). The concentration of HA in all samples was constant (15 mg/L), and it was prepared and used by a stock solution (1 g of HA powder in 1,000 mL of distilled water). It should be noted that in all the experiments investigated in the present study, the blank sample (which contains all the studied parameters except the HA pollutant) was first tested, and the test was then performed on HA degradation.

2.4. Analytical methods

At the end of experiments and for determination of the HA concentration, the samples collected at predetermined time intervals were filtered through a 0.45 µm membrane filter, and were analyzed using a UV-vis spectrophotometer (JENWAY, England) at the maximum wavelength (λmax = 254 nm). In addition, the TOC content of the humic acid was estimated using a TOC analyzer (Multi N/C 3100, Germany). It should be noted that 0.5 M sodium sulfite

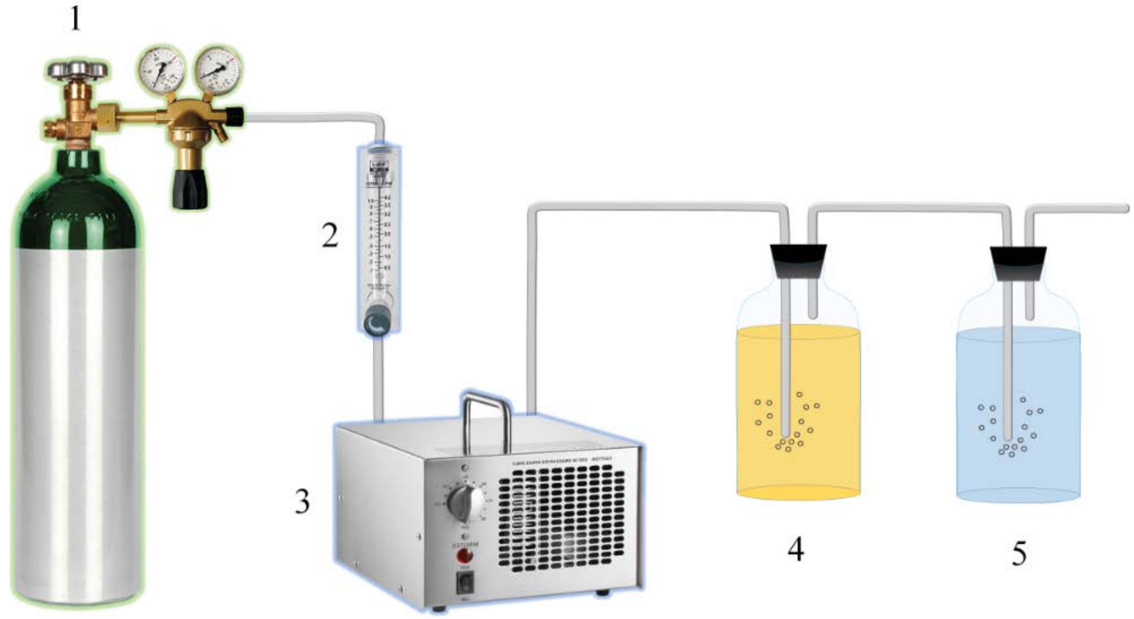


Fig. 1. Pilot of the catalytic ozonation system: (1) high purity oxygen capsule, (2) rotameter, (3) ozone generator, (4) reactor solution, and (5) potassium iodide.

(0.15 mL per 15 cc sample) was used to remove residual ozone before the detection of humic acid.

The efficiency of the magnetically activated carbon catalyzed ozonation process in the removal of HA was calculated using Eq. (1), and the removal efficiency of TOC in this process was determined using Eq. (2) [35]:

$$\text{HA Removal}\left(\%\right)=\frac{\left[\text{HA}\right]_0-\left[\text{HA}\right]_t}{\left[\text{HA}\right]_0}\times 100 \tag{1}$$

$$\text{TOC removal}\left(\%\right)=\frac{\left[\text{TOC}\right]_0-\left[\text{TOC}\right]_t}{\left[\text{TOC}\right]_0}\times 100 \tag{2}$$

where HA removal (%) indicates HA removal efficiency; $[\text{HA}]_0$ and $[\text{HA}]_t$ show the initial concentration of humic acid at the time 0 min and the concentration of humic acid at time t, respectively. $[\text{TOC}]_0$ and $[\text{TOC}]_t$ are related to the TOC before and after treatment, respectively. All experiments were performed at lab temperature (25°C).

To obtain limits of detection (LOD) and limits of quantification (LOQ), a blank was first prepared and measured with the device, and it was repeated at least 5 times, and then the standard blank deviation (S_b) was obtained. After that, LOD and LOQ were obtained using LOD = 3 S_b/m and LOQ = 10 S_b/m, respectively. According to the results, LOD and LOQ were 3.7×10^{-7} and 1.2×10^{-6}, respectively.

2.5. Effect of different parameters

2.5.1. Effect of initial pH

In order to investigate the effect of pH range (5–9) on the HA and TOC removal efficiencies by catalytic ozonation and single ozonation processes (SOPs), HA solutions (15 mg/L) containing catalyst dose of 1.25 g/L were prepared. The samples were taken at the time interval in the range of 0–60 min.

2.5.2. Effect of catalyst dose

In order to study the effect of catalyst dose on the HA and TOC removal efficiencies by catalytic ozonation and SOPs, some runs were conducted under the following conditions, for example, catalyst concentration of 0.5–1.0 g/L, pH of 7, HA of 15 mg/L, and the reaction time between 0 and 60 min.

2.5.3. Effect of scavenger radical

To determine the effect of radical scavenging on the catalytic ozonation and SOPs, *tert*-butanol was added to the samples at optimum pH and constant concentration of catalyst for the preparing the concentration of 1 mole per 250 cc, and the HA removal efficiency was measured in the catalytic ozonation system and the single ozonation system at different times.

2.5.4. Synergistic effect of the catalyst

In order to determine the synergistic effect of the catalyst on the HA removal mechanism, the catalyst was first contacted with water in absence of the ozonation process, and then sampling was done and the amount of contaminant adsorption by the catalyst was obtained using a spectrophotometer device at 254 nm. Afterward, the rate of contaminant removal under ozonation conditions was determined in the absence and the presence of catalyst by the device, and the synergistic effect of the catalyst was calculated using Eq. (3):

Synergistic effect = [COP efficiency – (single ozonation efficiency + adsorption efficiency)] (3)

2.6. Kinetic study

One of the fundamental and significant parameters in chemical studies is the determination of the reaction speed. Hence, the kinetics studies were employed to determine the quality of the HA and TOC removal reaction and modeling and executing the process on an applied. The kinetic studies were carried out using the pseudo-first-order kinetic studies at the optimum condition achieved. The pseudo-first-order model for HA and TOC removal was calculated using Eq. (4) [36,37]:

$$\ln\left(\frac{\left[C\right]_0}{\left[C\right]_e}\right)=kt \tag{4}$$

where $[C]_0$ and $[C]_e$ represent the initial and final concentrations of HA and TOC, respectively, and k is the constant of removal value; the rate constants (k) was calculated by plotting $\ln([C]_0/[C]_t)$ vs. electrolysis time (t).

3. Results and discussion

3.1. Characterization of the synthesized catalyst

SEM studies afford valuable information about the surface morphology of the materials. The SEM micrographs of the magnetically activated carbon catalyst are shown in Fig. 2a [34].

The XRD spectra are represented in Figs. 2b and c have introduced the Fe_3O_4 particles as the ferrous compound found in the carbon-based catalyst, which has superparamagnetic properties. It means that it is absorbed by magnets, but does not have a stable magnetic property. The graph peaks at 2θ = 24° show that the chemical structure of the catalyst is not destroyed after calcination and contains pure superparamagnetic Fe_3O_4 particles and carbon. The size of these particles is about 25–30 nm based on the SEM image shown in Fig. 2a, which due to the high surface area of the nanoparticles, their chemical reactions are greatly enhanced. Fig. 2b shows the constituents of the catalysts with different patterns. Most peaks are related to magnetite, and this indicates the magnetization of the catalyst. Also, in Fig. 2, the type of ferrous compound present in the carbon-based catalyst has been shown. The XRD spectrum test on the catalyst shows the comparison of its compounds with different patterns; so that the magnetite is the most possible type of composition [34].

Surface properties and chemical constituents of a catalyst are among the most important properties involved in the conversion of ozone to active radicals [38]. The EDS spectrum test showed that the types of catalyst constituents were oxygen, carbon, and iron; the percentage of these elements were shown in Fig. 2d, and their weight and atomic percentages were represented in Table 2. According to the results of the EDS spectrum test in Fig. 2d and Table 2, the catalysts were composed of carbon, iron, and oxygen, which their atomic percentages were 89.20%, 5.04%, and 5.76%, respectively, and no other impurities can be observed. Furthermore, the weight percentages of carbon, iron, and oxygen were 75.14%, 18.39%, and 6.47%, respectively. In addition, the pHpzc of the synthesized catalyst was calculated to be 7.6 [34].

One of the most important features of catalysts is their specific surface area, which is directly related to the rate and speed of chemical reactions [39]. The specific surface area of activated carbon as the raw material of this catalyst was 907 m^2/g, and the specific surface area of the catalyst was 814 m^2/g (Table 2). According to the results, the synthesized catalyst had a 10% reduction in surface area, which could be due to the filling of carbon holes by Fe_3O_4 nanoparticles. The ozonation process causes physical and chemical catalyst changes. For example, the addition of oxygenated functional groups to the catalyst surface during the ozonation process modifies it and dramatically increases the specific surface area of the cavities [39,40]. However, in some studies, it was reported that the specific surface area of activated carbon decrease when it was ozonated [41]. Thus, as observed in the results, the effect of ozone on carbon-based catalysts depends on their properties and structure. The most important catalysts used in the COPs are metal oxides, and Fe_3O_4 particles are found as one of the most important metal oxides [42]. These particles act as active sites in the decomposition of ozone and participate in the formation of functional groups on the surface of activated carbon; when they immersed in water, they are coated with decomposed molecules of water, and they produce the metallic functional groups on the surface of activated carbon [43].

3.2. Effect of solution pH

In the chemical processes, especially AOPs, the pH of the environment plays a crucial role and affects the efficiency of the process in two ways, that is, the transfer of ozone from the gas phase to the liquid phase (direct effect) and the decomposition of ozone into hydroxyl radicals (indirect effect) [26,44]. The effect of pH changes on the efficiency of both SOP and COP in the removal of HA and TOC was evaluated by varying pH values in the range of 5–9 at catalyst concentration of 1.25 g/L and initial HA concentration of 15 mg/L. The results of determining the effect of pH changes were presented in Fig. 3. As can be seen in the figure, the process efficiency was increased by increasing pH from 5 to 9 in both processes until reaching its maximum value at a pH of 9. Thus, in general, it can be said that, at pH values higher than 7 and alkali, this process has more efficiency than acidic pH. According to the results of Fig. 3, in the SOP process, increasing the pH from 5 (53%) to 9 (77%) was led to a 24% increase in HA removal efficiency. However, the highest HA removal efficiency in COP was obtained at pH of 7 (95%), which indicates further degradation of HA by the catalyst. The results also showed that the degradation rate of HA increased about 2 fold by increasing pH from 5 (0.012 min^{-1}) to 9 (0.024 min^{-1}), while this increase was 1.7 fold by the addition of the catalyst. In the COP, the highest rate of HA degradation was obtained at pH of 7 and had a 2.3 fold increase compare to pH of 5. According to the results of Fig. 3, in the SOP process, an increase in pH values from 5 (60%) to 9 (67.4%) was led to a 6.9% increase in the removal efficiency of TOC,

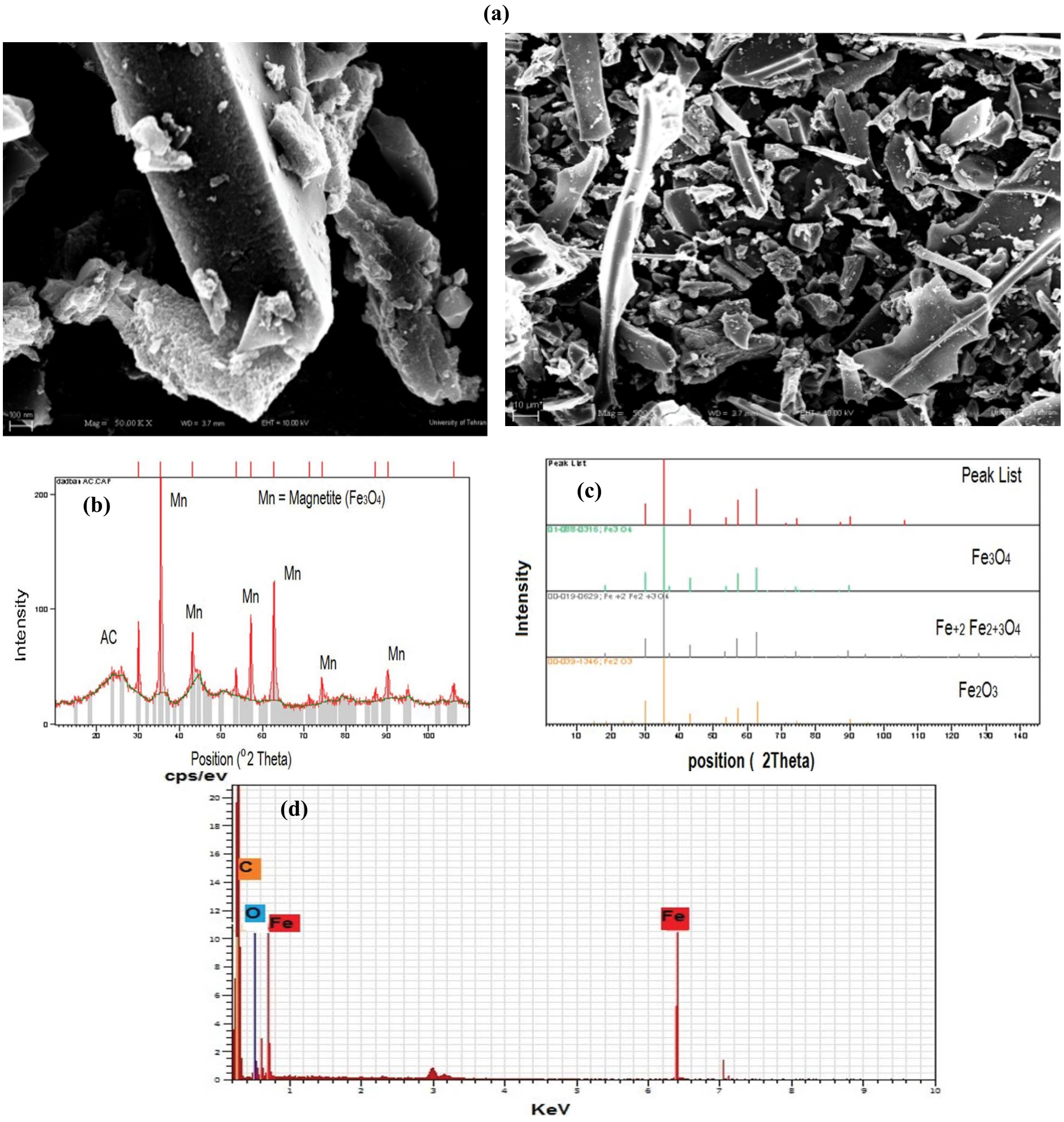


Fig. 2. (a) SEM images of the surface morphology at different magnifications, (b) XRD diffractograms of the catalyst, (c) identification of catalyst compounds based on spectrum pattern XRD, and (d) EDS diffractograms of the catalyst.

Table 2
Mass ratio of the catalyst constituents by EDS experiment and characteristics of Fe_3O_4/AC nanocomposite and granular activated carbon

Elements	Atomic number	Weight percentage (%)	Atomic percentage (%)
Carbon	6	75.14	89.2
Iron	26	18.39	5.04
Oxygen	8	6.47	5.76

Parameters	Granular activated carbon	Nanocomposite
Specific surface area (m^2/g)	907	814
pHzpc	8.9	7.6
Size of Fe_3O_4 nanoparticles	–	25–30
Purity percentage (in carbon)	99.99	89.2

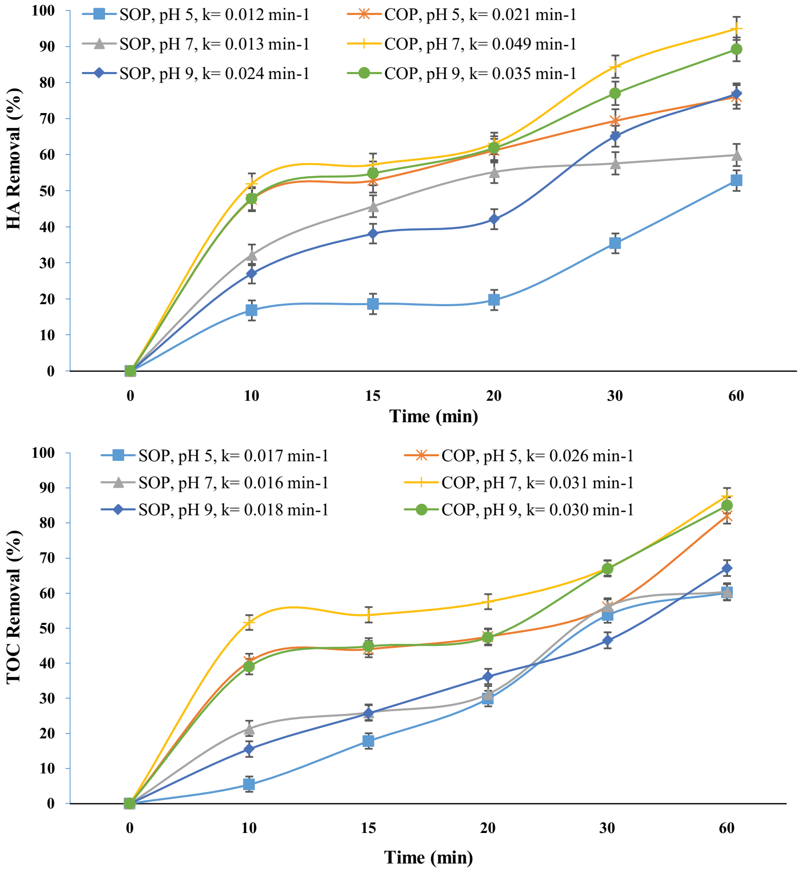


Fig. 3. Effect of initial pH on humic acid (HA) and TOC removal from aqueous solutions using single ozonation process (SOP) and catalytic ozonation process (COP) (initial HA concentration = 15 mg/L and catalyst dose = 1.25 g/L).

while the highest TOC removal efficiency in the COP process was obtained at pH of 7 (87.67%). Pollutant degradation is accomplished by the ozonation process in two ways including direct oxidation (using ozone molecules) and indirect oxidation (using hydroxyl radicals produced by ozone). The pollutant is indirectly oxidized in alkaline conditions and is directly degraded in acidic conditions. Indirect oxidation system has higher efficiency than direct oxidation due to the presence of hydroxyl radicals and their higher oxidation power compared to ozone [45,46]. In the COP process, changes in pH can cause changes in the amount of soluble ions, the ionizing state of the pollutant, and the properties of the catalyst surface. The pH of the solution also directly affects the shape of the pollutant molecules. Therefore, as the pH increases, the efficiency of the COP for the removal of HA and TOC increases, this is consistent with the study of Asgari and Salari [47]. Asgari and Salari [47] observed that the highest rate of HA removal by catalytic ozonation at alkaline pH (pH = 9.5) was 94%. They also revealed that direct oxidation is the chief mechanism involved in the degradation of HA at acidic pH, which occurs through attacking ozone molecules to a pollutant, while the oxidation pathway is generally accompanied with lower efficiency for refractory organic pollutants. With an increase in solution pH, indirect oxidation becomes the dominant pathway in the oxidation of HA; however, direct oxidation may partially participate in the oxidation process [47]. In the alkaline pH, active radical species, including $^{\bullet}$OH, $O_3^{\bullet-}$, and $O_2^{\bullet-}$, are produced through the reaction between ozone molecules and OH^- ions, and ozone molecules and the C–MgO, which have an advanced oxidation potential compared to the direct pathway of the oxidation process [47,48].

As previously shown, pH affects the structural properties of the pollutants and its effect on the catalytic degradation is described as electrostatic interaction between target contaminant and the catalyst surface properties measured by pHzpc [49]. Thus, the pH of the solution and the pHzpc of the catalyst are the important factors in the oxidation process, which influences the contaminant treatment mechanism [50]. The results show that the pH of the solution was effective on the decomposition of pollutants in the COP and is both dependents on the structure and composition of pollutants, as well as the characteristics of the catalyst surface.

According to Table 2, the pHzpc of the catalyst was 7.7; this illuminates that the catalyst surface has basic properties, and these basic functional groups located on the surface of the catalyst are thought to be responsible for ozone decomposition, which is led to the generation of reactive radical species and better oxidation of pollutant [51]. Therefore, the most appropriate pH for COP is selected according to the specific needs of each experiment.

Furthermore, Gümüş and Akbal [3] investigated the removal of HA from aqueous solutions using ozonation processes, iron-coated zeolite catalyzed ozonation and GAC catalyzed ozonation. The results illuminated that the highest removal of HA was achieved at alkaline pH so that increasing the pH from 6.5 to 11 was led to enhance the HA removal efficiency from 65% to 80% [3]. The kinetics of degradation of HA and TOC at different pH values in the COP and SOP process were presented in Table 3. As observed, by increasing pH from pH = 5 (0.017 min^{-1}) to pH = 9 (0.018 min^{-1}), the degradation rate of TOC was increased by about 1.1 fold, whereas this rate was observed to be 1.18 fold after the addition of the catalyst. In the COP, the degradation rate of HA was increased about 1.2 fold at pH = 7.

3.3. Effect of catalyst concentration

To determine the effect of catalyst dosage changes on the efficiency of the COP for the removal of HA and TOC, different dosages of catalyst in the range of 0.5 to 3 g/L were investigated. The results showed that there is a direct relationship between increasing catalyst dosage and removal efficiency of HA and TOC; so that by increasing catalyst dosage from 0.5 to 3 g/L, the efficiency of COP process in the removal of HA and TOC was increased from 89.3% to 95.7% and 81.9% to 89.5%, respectively. In addition, according to the results, the efficiency of the SOP process in the removal of HA and TOC was 76.8% and 67%, respectively. The results indicate the positive effect of the catalyst dosage on the COP process efficiency on pollutant removal, compared to its effect on the SOP process (Fig. 4). According to the results presented in Fig. 4, increasing the presence of the catalyst to a certain extent, as a source of hydroxyl radical production (the strongest oxidizing radical in the environment), increases the production of this radical and thereby increases the degradation of the HA. The addition of the catalyst increases the surface area and the active site, which can increase ozone adsorption on the surface of the catalyst and thus increase the surface reactions and the production of hydroxyl radicals [52]. Catalysts act as initiators for the production of hydroxyl radicals, and the adsorption of ozone on their surface destroys the ozone molecules and produces active radicals [52].

The mechanism of the HA degradation reaction by the COP process takes place in two direct and indirect pathways. The steps of the HA degradation reaction mechanism are as follows: The direct pathway (according to Eq. (5)) is carried out through attacking the ozone to HA molecules for generating intermediates. However, catalyst, in an indirect pathway, decomposes the ozone molecules and forms free radicals and, subsequently degrades the HA, as shown in Eqs. (6)–(8) [53,54]. After that, as observed in Eqs. (9)–(12), formed $O_3^{\bullet-}$ radicals contribute to the formation of some free radicals and H_2O_2 molecules [53,55]. It is also capable of the decomposition rate of ozone for the formation of $^{\bullet}OH$ radicals:

$$O_3 + \text{Humic Acid}\left(\text{HA}\right) \rightarrow \text{degradation products} + O_3^{\bullet-}\left(\text{Direct}\right) \tag{5}$$

$$O_3 + OH^- \rightarrow HO_2^- + O_2^{\bullet-}\left(\text{Indirect}\right) \tag{6}$$

$$O_3 + OH^- \rightarrow HO_2^- + O_2\left(\text{Indirect}\right) \tag{7}$$

$$O_3 + HO_2^- \rightarrow HO_2^{\bullet} + O_3^{\bullet-}\left(\text{Indirect}\right) \tag{8}$$

$$O_3^{\bullet-} + H^+ \rightarrow HO_3^{\bullet} \tag{9}$$

$$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2 \tag{10}$$

$$HO_3^{\bullet} + HO_3^{\bullet} \rightarrow 2O_2 + H_2O_2 \tag{11}$$

$$HO_3^{\bullet} + HO^{\bullet} \rightarrow O_2 + H_2O_2 \tag{12}$$

In the COP, three major mechanisms occur due to the presence of the catalyst: at the first, the ozone is adsorbed

Table 3
Kinetics of degradation of humic acid and TOC at different pHs in the COP and SOP process (humic acid = 15 mg/L and catalyst = 1.25 g/L)

	Process	Parameters	pH = 5	pH = 7	pH = 9
Humic acid (HA)	COP	k (min^{-1})	0.021	0.049	0.035
		R^2	0.901	0.979	0.963
		Intercept ($\ln C_0$)	1.244	0.0319	0.46
	SOP	k (min^{-1})	0.012	0.013	0.024
		R^2	0.98	0.639	0.948
		Intercept ($\ln C_0$)	1.943	1.755	1.219
TOC	COP	k (min^{-1})	0.026	0.031	0.03
		R^2	0.971	0.959	0.984
		Intercept ($\ln C_0$)	1.4242	1.099	1.23
	SOP	k (min^{-1})	0.017	0.016	0.018
		R^2	0.871	0.886	0.99
		Intercept ($\ln C_0$)	2.197	2.041	1.946

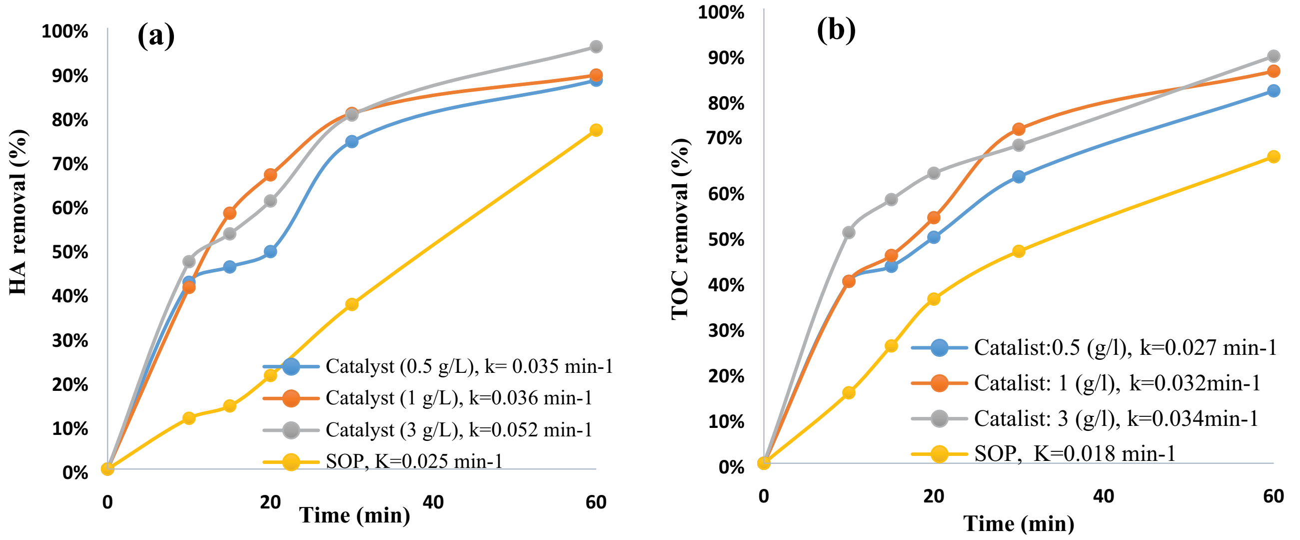


Fig. 4. Effect of catalyst dose on (a) humic acid (HA) and (b) TOC removal from aqueous solutions in catalytic ozonation process (COP) and SOP (HA concentration = 15 mg/L and pH = 7).

on the catalyst surface and rapidly decomposed in the presence of surface hydroxyl groups. Subsequently, after the decomposition of ozone, active atomic oxygen is produced and reacted with the hydroxyl groups present at the catalyst surface. Therefore, increasing the catalyst concentration in the solution increases the density of the surface hydroxyl groups, which is consequently led to increasing the decomposition of ozone molecules on the catalyst surface [56]. With the increase in ozone decomposition, the production of active hydroxyl radicals, and subsequently the oxidation of organic molecules will increase [56]. The lower effect of the catalyst at concentrations higher than the optimum value can be described as follows: the optimal catalyst concentration is strongly dependent on the type of catalyst, the reaction conditions, the target compound, and its surface area [56]. In a study conducted by Yang et al. [57], the rate of atrazine removal using a COP with TiO_2 nanoparticles was studied. The results showed that there is a direct relationship between pollutant removal efficiency and catalyst concentration [57]. Dadban et al. [33] conducted a study to assess the removal of 4,2-dinitrophenol from aqueous solutions by catalytic ozonation. The results showed that by increasing the catalyst dosage from zero to 4 g/L, the removal efficiency of Dinitrophenol from wastewater was increased [33]. Increasing the pollutant degradation is due to increasing the surface area of the catalyst and active sites of ozone adsorption, which in turn results in increasing the adsorption and decomposition of ozone and release of hydroxyl radicals into the liquid, which is consistent with the present study [33,57]. The kinetics of HA and TOC removal in presence of different catalyst concentrations and in absence of catalyst are also presented in Table 4. The results showed that there is a direct relationship between the degradation rate of HA and the increase in catalyst concentration; so that an increase in catalyst concentration from 0 (0.025 min^{-1}) to 3 g/L (0.052 min^{-1}) was led to increasing the degradation rate by the COP process. This can be due to the addition of ferrous compounds to the catalyst compound, which results in faster and effective removal of the pollutant in the COP process than in the SOP process.

Table 4
Kinetics of humic acid and TOC removal in present of different concentrations of catalyst and without catalyst (humic acid = 15 mg/L and pH = 7)

	Parameters	SOP	0.5 g/L	1 g/L	3 g/L
Humic acid (HA)	k (min^{-1})	0.025	0.035	0.036	0.052
	R^2	0.951	0.97	0.931	0.995
	Intercept ($\ln C_0$)	1.244	0.562	0.46	–0.444
TOC	k (min^{-1})	0.018	0.027	0.032	0.034
	R^2	0.99	0.978	0.967	0.963
	Intercept ($\ln C_0$)	2.708	1.526	1.386	1.065

3.4. Effect of radical scavengers on the COP and SOP process

The most important mechanism proposed in AOPs, including catalytic ozonation, is the production of active hydroxyl radicals with high oxidation potential [58]. To determine the effect of different radicals on the ozonation process, *tert*-butyl alcohol (TBA) was used as a hydroxyl radical scavenger [59,60], which has the lowest reaction rate with ozone (3×10^{-5} mol/s) and the highest reaction rate with hydroxyl radical (8×10^{8} mol/s). For this purpose, the efficiency of HA and TOC removal under single and catalytic ozonation were investigated in the presence of *tert*-butanol.

As shown in Fig. 5, the addition of TBA radical to the SOP process significantly reduced the HA removal efficiency, which had the least effect on the COP. According to the results presented in Fig. 5, with the addition of *tert*-butanol, the removal efficiencies of HA and TOC in the COP process was decreased from 95.7% to 88.6% and

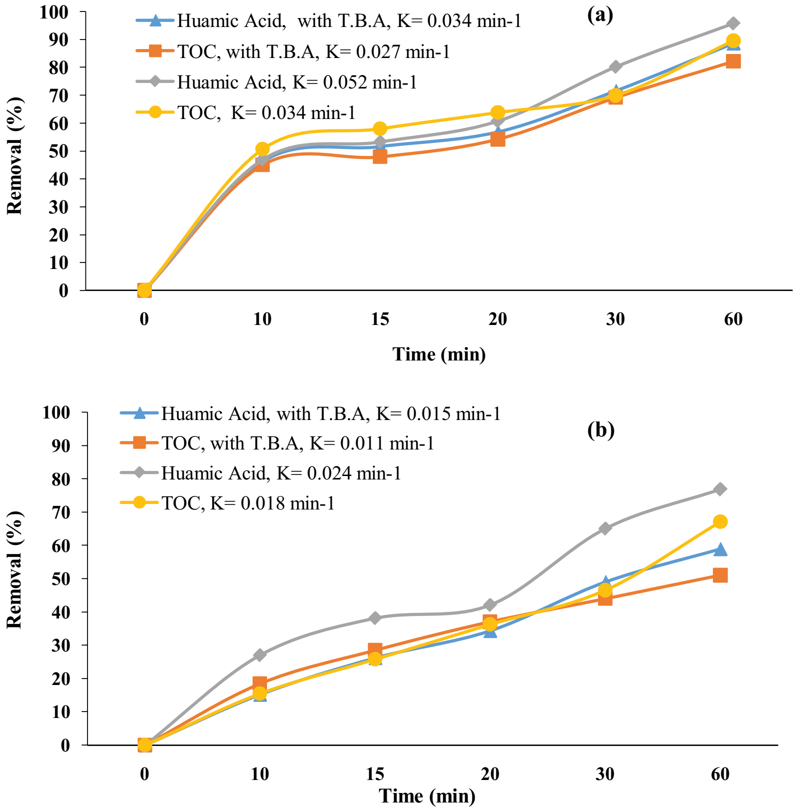


Fig. 5. Effect of scavenger radical on humic acid and TOC removal from aqueous solutions in (a) catalytic ozonation process (COP) and (b) single ozonation process (SOP) (initial HA concentration = 15 mg/L, pH = 7, and catalyst dose = 3 g/L).

89.85% to 82.08%, respectively while the removal efficiencies in the SOP were decreased from 76.8% to 58.9% and 67.1% to 51.0%, respectively. In other words, the reduction of HA removal efficiency by the hydroxyl radical initiator in SOP was about 2.5 fold compared to COP. Since hydroxyl radicals have higher oxidation potential compared to ozone [61] and *tert*-butanol also acts as a hydroxyl radical, the results show that indirect radical oxidation is the predominant mechanism in the process of HA degradation; but it does not pose problems associated with other AOPs processes, such as process inhibitors, such as carbonate, nitrate, and sulfate [61]. Asgari and Salari [47] studied the removal of HA from aqueous solutions using the COP, and their obtained results illustrated that the HA removal efficiency decreases by increasing the radical scavengers.

3.5. Synergetic effect of catalyst on removal of humic acid

The synergistic effect in the COP was evaluated after optimizing the effective parameters in the removal of the HA in the COP. For this purpose, the removal of the HA as a function of contact time was investigated in the SOP, COP, and adsorption process by catalyst. As represented in Fig. 6, the highest removal of the HA by the SOP and catalyst adsorption after 60 min was 76% and 5.8%, respectively, whereas it was increased by 95.7% in the COP, in the same contact time. One reason for the high synergistic effect of the catalyst is its modification via the ozonation process itself [62]. In other words, ozone improves the catalyst property by increasing the specific surface area of the catalyst and creating fine holes as well as by creating various functional groups, such as oxygenated groups, which decompose ozone into active radicals [63].

3.6. Mineralization of humic acid

To identify the efficiency of degradation and mineralization of humic acid by the catalytic ozonation and ozonation alone processes, the removal efficiencies of TOC was assessed using the obtained optimum conditions (HA concentration = 15 mg/L and pH = 7) in different catalyst dose (0.5–3 g/L) for COP process (Fig. 4b). The results showed that in the COP process, increasing the catalyst dose enhanced the TOC removal rates; so that increasing the catalyst dose from 0.5 to 3 g/L was led to increasing the TOC removal from 81.9% to 89.5% using the COP. Additionally, the TOC removal was increased from 16.0% to 67.0% for the SOP process by increasing the reaction time from 10 to 60 min (Fig. 4b).

3.7. Comparison of removal of humic acid using other methods

The comparison of the results obtained by the present study with the results of the other studies conducted for the removal of humic acid (HA) is represented in Table 5. Based on our observation, the removal of the HA has been evaluated

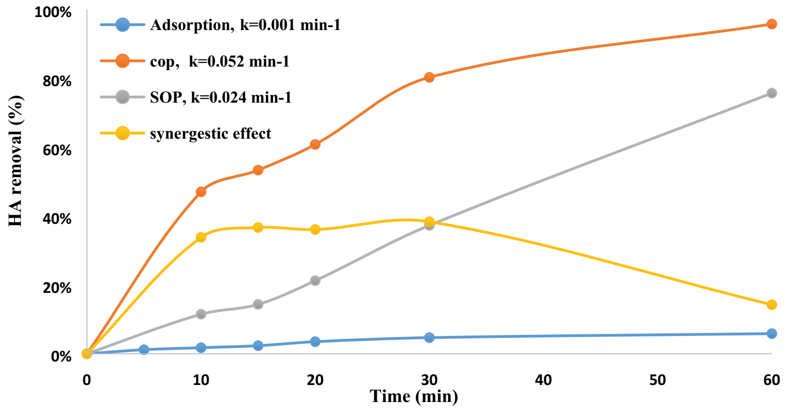


Fig. 6. Adsorption contribution, synergetic effect catalyst on humic acid degradation in COP process (humic acid = 15 mg/L, catalyst = 3 g/L, and pH = 7).

Table 5
Comparison of degradation of humic acid using other methods

Type of process	Parameters	HA removal (%)	Ref.
Adsorption process	Conc. HA (20 mg/L), conc. – PAC-MWCNTs (0.1–1.2 g/L), reaction time (60 min), and pH (3–12)	90	[4]
Electrocoagulation process	pH (4–8), current density (2–10 mA/cm^2), EC time (5–25 min), and conc. HA (10–50 mg/L)	98	[2]
Electro/Fenton process	Conc. HA (30 mg/L), conc. O_3 (5–20 mg/L), ICZ and GAC (0.25–2 g/L), reaction time (0–60 min), and pH (6.5–11)	70	[3]
Sono-photocatalyst process	Ultrasound power (40–100 w), catalyst dosage (0.25–2), initial HA concentration (30–50 mg/L), and time (20–120 min)	88	[20]
Adsorption process	Conc. HA (5–40 mg/L), conc. – montmorillonite dose (100 mg), reaction time (0–60 min), and pH (3–11)	85	[19]
Catalyzed ozonation process	Conc. HA (15 mg/L), catalyzer dose (0.25–1.5 g/250 cc), reaction time (0–30 min), and pH (4–12)	95	[53]
Photocatalytic process	Conc. HA (2–30 mg/L), intensity of radiation (2,030–3,950 μw/cm^2), reaction time (0–180 min), and pH (3–11)	94	[54]
Magnetically activated carbon catalyzed ozonation process	Conc. MNZ (15 mg/L), catalyzer dose (0. 5–3.0 g/L), reaction time (0–60 min), and pH (5–9)	96	Present study

by various methods such as adsorption process, electrocoagulation process, sono-photocatalyst process, photocatalytic process, and catalyzed ozonation process [2–4,18,19,63,64]. The comparison between our studied system and other studies used for removal of HA was performed with taking into account the various factors, that is, initial pH, reaction time, initial HA concentration, HA removal efficiency, and it can be concluded that our system can be a reasonably successful method to provide greater HA removal efficiency, compared to the mentioned studies.

4. Conclusion

This study assessed the capacity of a COP with magnetically activated carbon for humic acid (HA) and TOC removal from aqueous solutions. Magnetically activated carbon revealed an immense potent for advancing the removal efficiency of HA and TOC by ozonation. The results of this study showed that by increasing the catalyst dose and pH, the removal efficiency and the degradation rate of humic acid and TOC were increased. As the concentration of radical scavengers increased, the humic acid removal efficiency decreased. The synergistic effect of the COP compared to the SOP and adsorption process was observed to be about 38.3% after 30 min. According to the results obtained, the COP using magnetic activated carbon can be a suitable method for the removal of organic compounds such as humic acid due to its low cost and high efficiency.

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