Performance of heterogeneous catalytic ozonation process using Al$_2$O$_3$ nanoparticles in dexamethasone removal from aqueous solutions

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ABSTRACT

Dexamethasone (DEX) is a type of corticosteroid medication that is commonly used for the treatment of human and animal diseases. The presence of its residual in wastewater can cause human mutagenicity and carcinogenicity. Therefore, this study aimed to evaluate the efficiency of the catalytic ozonation process (COP) in the presence of aluminum oxide (Al$_2$O$_3$) nanoparticles in DEX removal. This experimental study was conducted in a laboratory and batch scale. In this study, a batch reactor with a diameter of 5 cm and a height of 45 m was used. The ozone concentration was determined using an iodometric method. The effects of some parameters such as solution pH, contact time, ozone concentration, and catalyst concentration on the process efficiency were investigated. Al$_2$O$_3$ nanoparticles were characterized by the scanning electron microscopy X-ray diffraction and Fourier-transform infrared spectroscopy analyses. The DEX concentration was measured using an ultraviolet light spectrophotometer at a wavelength of 241 nm. According to the results, the optimal value of solution pH and catalyst dose in the COP was obtained to be 10 and 0.5 g/L, respectively. Under the optimal conditions, the process efficiency was 100% in the presence of 10 mg/L of the initial pollutant concentration after 12 min, and magnesium oxide nanoparticles caused an increase in the removal efficiency (67%) compared to the single ozonation process without catalyst). Due to the lack of sludge production and accessibility, this process can be used as a useful approach for the removal of a wide range of pharmaceutical compounds.

Keywords: Catalytic ozonation; Aluminum oxide nanoparticles; Dexamethasone; Wastewater

1. Introduction

A number of emerging pollutants as drug contaminants may enter the environment after consumption or even without consumption [1]. The most important effect in relation to the presence of drug contaminants is the growth of drug-resistant bacteria [2]. Corticosteroids are a large class of steroid hormones that are widely used for the treatment of human and animal diseases [3]. Corticosteroids are very strong, which are used to relieve inflammation in the human body [4]. Until now, several methods have been used to remove pharmaceutical substances from wastewater such as membrane bioreactors [5], carbon nanotubes [6], and anaerobic reactors [7]. In this regard, the sonochemical process [8], electrical coagulation [4], and adsorption processes with zeolites have received much attention for the removal of antibiotics, specifically dexamethasone (DEX) from wastewaters [9]. The biological treatment processes require much time [10], and the electrocoagulation processes require high energy and produce a large amount of sludge [11]. Moreover, adsorption processes require waste disposal operation, which is very expensive [12]. Advanced oxidation processes

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(AOPs) are a set of oxidation processes, which have several advantages such as easy to use, low cost [13–15], high removal efficiency and mineralization, and lack of sludge production [16]. Due to these advantages, the AOPs have received much attention for the removal of a wide range of pollutants. Ozone has been considered as the main oxidant in most of the AOPs for the treatment of contaminated water and wastewater [17]. Ozone offers high removal efficiency for a wide range of pollutants, while it has low mineralization efficiency, which often leads to the production of toxic by-products [18]. Nowadays, the catalytic ozonation process (COP) has received increasing attention as a new system of AOPs [19]. In this system, adding a catalyst to the ozonation process increases the amount of oxidation rate, reduces the amount of time required, and reduces the cost of the treatment process [13]. The COP is classified into two types [20]. Homogeneous involves the use of a soluble catalyst in the aqueous solution, and heterogeneous occurs when the catalyst is in a different phase than the aqueous solution [21]. In both methods, organic molecules are mineralized by direct (with ozone molecules) or indirect oxidation (with radicals) [22]. The heterogeneous COP has been known as a suitable process due to its advantages, such as low cost, the potential for catalyst regeneration, and lack of secondary contamination [23]. Several materials are wieldy used as the main catalysts, including metal oxides (e.g., MnO_2, TiO_2, and Al_2O_3), reinforced metal oxides (e.g., Cu/TiO_2, TiO_2/Al_2O_3, and Fe_2O_3/Al_2O_3) and some porous materials (e.g., granular activated carbon and zeolite) [18,24]. Alkaline earth metals as nanosized particles have a very wide application due to their absorption destructive properties, high surface reactivity, high adsorption capacity, and simple production from abundant and available minerals [25,26]. It has been reported that Al_2O_3 along with the ozonation process can improve the degradation rate of 6,4,2-trichloroanisole from aqueous solutions [27]. Moreover, catalytic ozonation using Al_2O_3 nanoparticles have been used efficiently for the removal of dye [28]. However, the catalytic effect of the Al_2O_3 nanoparticles in the COP has not yet been investigated for the removal of corticosteroids. This study aimed to use the Al_2O_3 nanoparticles as a catalyst in a heterogeneous COP in a batch reactor to remove DEX from aqueous solutions. The successful results of this study can be used for the treatment of pharmaceutical wastewaters and the same environments. It can be also considered as an effective step to protect the environment.

2. Materials and methods

2.1. Chemicals and photoreactor

In this study, sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), and Al_2O_3 nanoparticle powder were purchased from Merck (Germany) Co. The accessible surface area and diameter of the catalyst pores were 155 m^2/g and 58 angstroms, respectively. The ampoules of DEX sodium phosphate (4,000 mg/L) were provided from the pharmacy. The size and particle surface morphology of the obtained powder was investigated using scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques, respectively. The contact reactor used in this research was cylindrical, made

of glass, and resistant to chemicals with a diameter of 5 cm and a height of 45 cm. A diffuser was installed at the end of the ozone zone pipe entering the reactor to provide a complete mixing. In order to reduce the effects of interventive factors, high-purity oxygen capsules were used as sources of oxygen for ozone production. To produce ozone gas, oxygen with high-purity was connected to an ozone generator (ARDA model COG-1A, made in France) with a capacity of 5 g/h, which was purchased from the Petrotech Company (Iran). The exhaust gas was passed through a potassium iodine (KI) solution to prevent leakage in the surrounding environment and health risk. The capacity of the ozone generator was calculated according to the standard method (E2350) [29].

2.2. Experimental procedures

The input parameter including DEX initial concentration (10–30 mg/L), initial pH of the solution (3–9), catalyst dose (0.25–2 g/L), reaction time, and ozone dose (1–5 mLO_2) were examined in the COP. Also, *tert*-butanol as a radical scavenger was studied to identify the dominant mechanism of oxidation in the COP. Finally, catalyst reusability was evaluated to reveal the reusability ability of the Al_2O_3 nanoparticle catalyst absorption capacity, catalyst presence, and as a radical scavenger (5 mM) on degradation of DEX in COP with Al_2O_3 nanoparticles were evaluated. To measure the DEX concentration in the reaction solution at the end of COP experiments, the ultraviolet-visible spectrophotometer (DR-5000 Hatch) at a wavelength of 241 nm was used, and the degradation efficiency was calculated according to Eq. (1).

$$E\left(\%\right) = \frac{\left(DEX_0 - DEX_t\right)}{DEX_0} \times 100 \qquad (1)$$

where E shows the degradation efficiency, and DEX_0 and DEX_t are concentrations of DEX before and after the reaction in the solution, respectively. Total organic carbon (TOC) analysis by means of Viro TOC element Co. instrument was applied to measure the mineralization potential of DEX over the treatment process. Also, the COD (chemical oxygen demand) of the solution was measured according to the standard method. Leaching value of Al^{+3} ions into the DEX wastewater during catalytic ozonation was measured by inductively coupled plasma optical emission spectrometry. A schematic of the experimental setup has been shown in Fig. 1.

3. Results and discussion

3.1. Catalyst characterization

SEM analysis was applied to characterize the morphology and structure properties of the Al_2O_3 compound, and related micrograph was displayed in Fig. 2. It is seen from the figure that the aggregates of aluminum nanoparticles have provided a porous spongy structure. According to scale bar and the dimension data of SEM image, size of the Al_2O_3 particles can be estimated to be lower than 100 nm. XRD analysis (Fig. 3) revealed the amorphous shape of Al_2O_3

1-Hood   2-Oxygen generator   3- Ozone generator   4-Magnetic Stirrer   5-Impinger
6-Gas outlet   7- KI Solution   8-Sampling valve

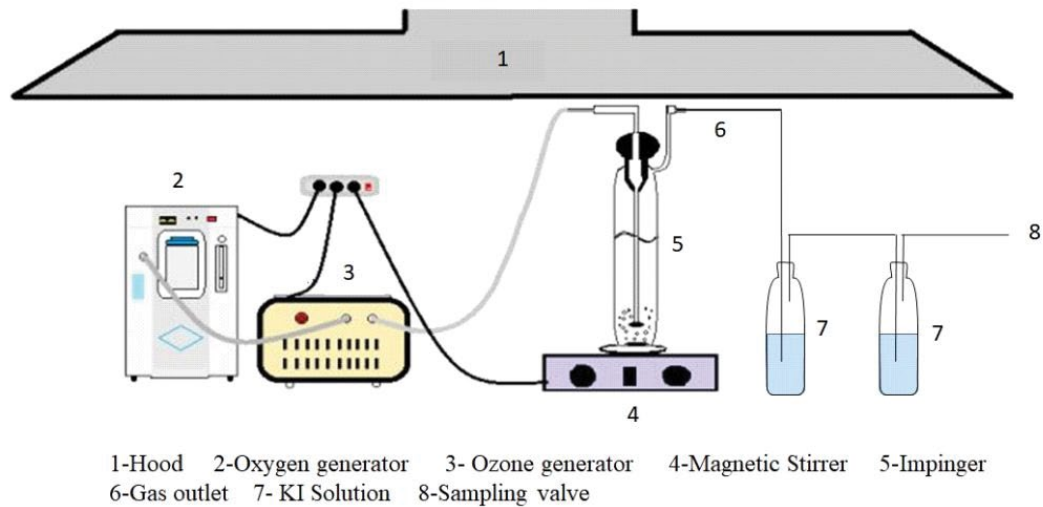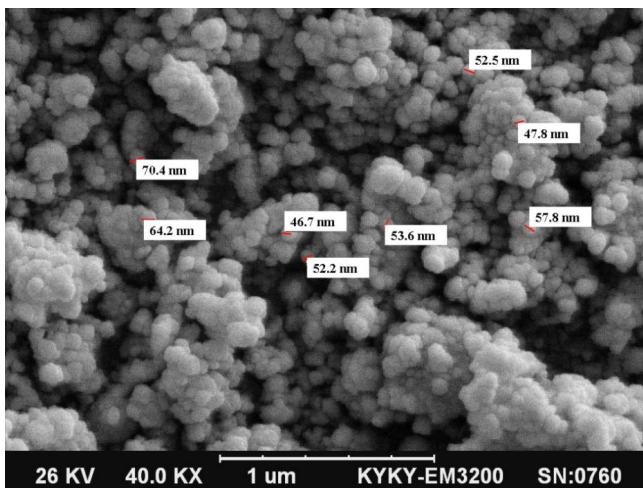Fig. 1. A schematic of the experimental setup.

Fig. 2. Scanning electron microscope (SEM) image of Al_2O_3 nanoparticle.

compound that has two peaks in the 2θ of 33.8 and 68.6. The functional groups of Al_2O_3 compound was explored using the FTIR spectrum (Fig. 4), where the major peaks appearing may be assigned to the following vibrational modes: (i) –OH stretching vibrations of the surface bonded (or) adsorbed water, (ii) OH stretching vibrations of structural water corresponding to M-OH stretching, (iii) –OH bending vibrations of structural water, corresponding to M–OH bending, and (iv) Al–O vibrations. The peaks at 3,468 and 1,636 cm^{-1} observed in Fig. 4 are attributed to –OH stretching bands and –OH bending vibration (these functional groups play a crucial role in the adsorption process).

3.2. Effect of pH and contact time on DEX removal

The pH of the solution is one of the most important parameters affecting metal oxides such as Al_2O_3 and ozone decomposition. As shown in Fig. 5a, the effect of pH on COP performance is obvious over a contact time of <20 min. The highest removal percentage by this process was obtained at pH 9. At this pH, 90% of DEX was decomposed after 5 min, and the removal efficiency increased to 99% after 10 min. By increasing contact time, the removal efficiency reached 100%. This result is confirmed by a kinetic study (Fig. 5b), where the kinetic rate constant for DEX removal at pHs of 3, 5, 7, and 9 were found to be 0.041, 0.0616, 0.0819, and 0. 141 min^{-1}, respectively.

Normally, the dominant superficial electrical charge at the surface of different types of catalysts may be positive
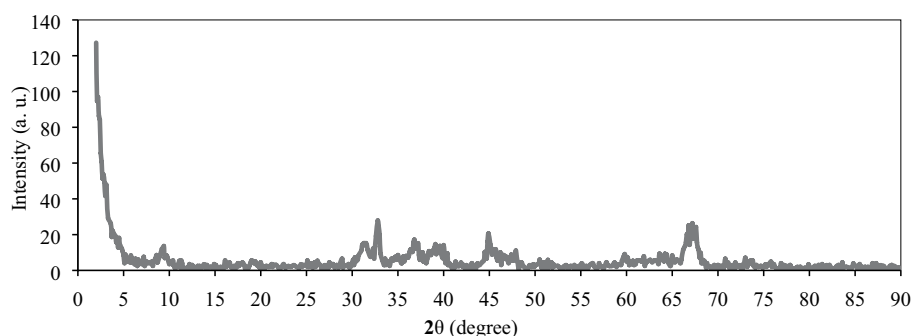

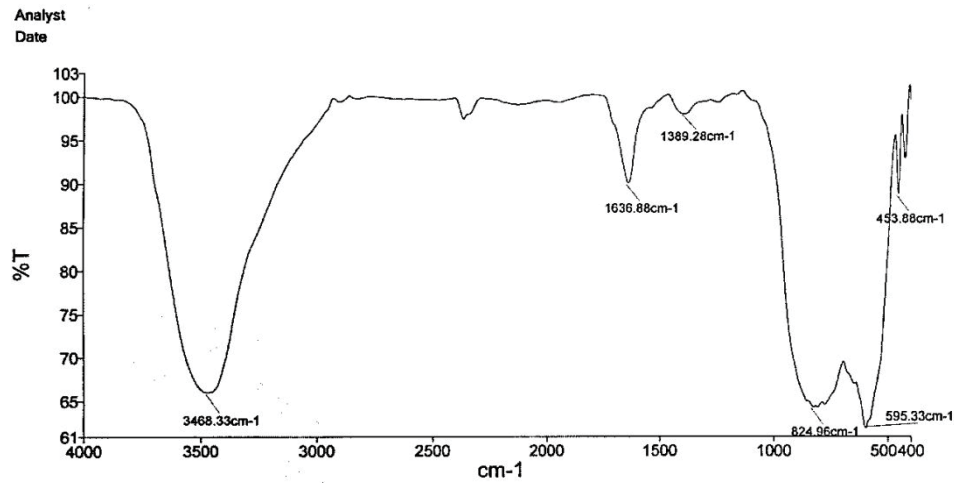
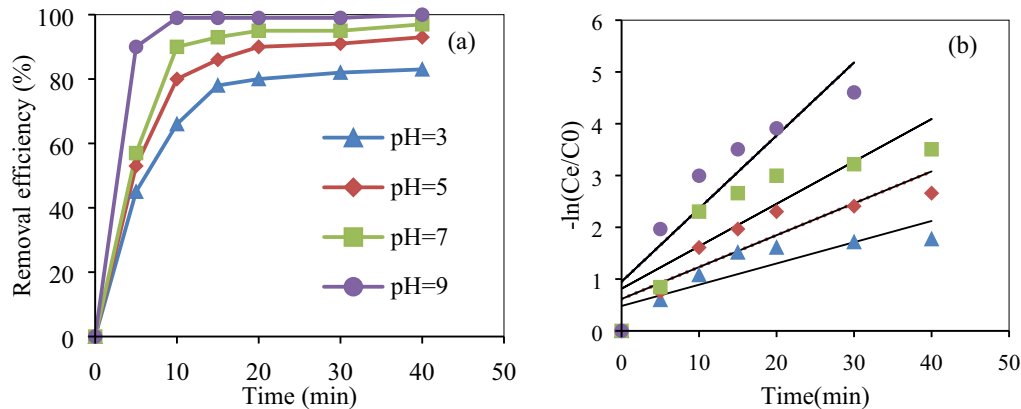Fig. 3. XRD analysis of Al_2O_3 nanoparticle.

Fig. 4. FTIR spectra of Al_2O_3 nanoparticle.

Fig. 5. Effect of initial pH on DEX removal efficiency (a) and kinetic rate constant (b) in the COP (DEX concentration 10 mg/L, catalyst 1 g/L, and ozone concentration 0.5 mg/L).

or negative. The surface properties of pHzpc, especially superfluid groups and catalyst components, play an important role in heterogeneous catalytic ozonation [30]. Due to the presence of unsaturated electrons, the surface of metal oxides can absorb water molecules, which leads to the formation of hydroxyl groups on the metal oxide surface. Then, the surface loads of metal oxides reach the proton balance, and, in turn, hydroxyl groups of the surface exhibit different patterns of electrical charge at different pH values [20,30]. At pH values higher than pHzpc, superficial functional groups are converted to the di-proton form [Eq. (2)] and at pH values lower than pHzpc, these superficial functional groups are protonated [Eq. (3).]

$$S-OH+OH^- \leftrightarrow S-O^- + H_2O \qquad (2)$$

$$S-OH+H^+ \leftrightarrow SOH_2^+ \qquad (3)$$

Deprotonation and protonation of superficial functional groups lead the catalysts to act as alkali and acid Lewis. This is one of the most important phenomena that acts as

a catalyst in the performance of Al_2O_3 nanoparticles [31,32]. Qi et al. investigated the effect of Al_2O_3 surfaces on catalytic ozonation of 2, 4, 6-trichloranizole [27]. They found that when the pH of the solution was closer to the pHzpc of the catalyst, alumina had more effect on ozone decomposition. In this study, the pHzpc of alumina was obtained to be 6.8. Due to economic problems caused by increasing pH, further experiments were carried out at pH 7. The reaction time as the time required to achieve the desired purpose in a purification process is considered as one of the important variables for designing and managing the oxidation process. As seen in Fig. 5, at the reaction time of higher than 10 min, removal efficiency, especially at pH 7 and 9, indicates no any remarkable change. In the ozonation process, pollutants can be degraded by two degradation pathways: the direct oxidation pathway (using ozone molecules) and the indirect oxidation pathway (using ozone-induced radicals). The indirect oxidation pathway has higher efficiency, which is due to the presence of hydroxyl radicals, and the high oxidation power of this radical compared to ozone molecules. Under alkaline conditions, the ozone decomposition increased, which leads to the production of more hydroxyl radicals [2]. Hence,

it is expected to be obtained the highest removal efficiency under alkaline conditions (due to the dominant indirect oxidation), slightly lower efficiency compared to the alkaline conditions, under acidic conditions (due to the dominant direct oxidation), and the minimum efficiency under neutral conditions (the middle of these two systems) [33,34].
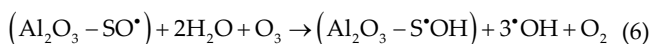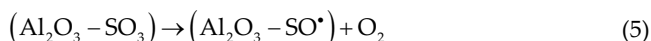
3.3. Effect of DEX initial concentration

Figs. 6a and b show the effect of the DEX initial concentration on the COP efficiency and kinetic rate constant, respectively. Results (Fig. 6b) indicated that the removal efficiency and kinetic rate constant of the COP at 10 mg/L of DEX was higher than that of 20 and 30 mg/L for different contact times. The removal efficiency reached 100% at 10 mg/L of DEX, which showed an increase in the removal efficiency compared to the concentrations of 20 and 30 mg/L. This increase in the mentioned concentrations was 8% and 32%, respectively. The rise in the removal rate at the decreasing concentration of DEX can be assigned that the amount of nanoparticles, contact time, and pH are the same at the different initial concentrations of DEX; thus, the amount of radicals generated in each of the four concentrations is the same. DEX removal is therefore expected to increase in samples with lower concentrations. On the other hand, the decrease in the reaction rates by increasing the initial concentration of DEX can be attributed to further inactivity of catalyst surface at higher concentrations.

3.4. Effect of catalytic dose on DEX removal

Figs. 7a and b show the effect of the catalyst dose on the removal efficiency and kinetic parameters. Since the minimum required dose of a catalyst is considered as the initiator or promoter of ozone decomposition to active radicals, it is one of the main parameters in designing a new process [24]. To evaluate the effect of this parameter, the catalyst dose was raised from 0.25 to 1 g/L. The results indicated that, after 40 min, the efficiency of DEX removal increased from 66.43% to 100% with increasing catalyst content from 0.25 to 1 g/L. Similarity, the kinetic rate constant is raised from 0.0507 to 0.2384 min^{-1} with increasing catalyst dosage from 0.25 to 1 g. The process efficiency decreased with increasing the catalyst dose to more than 1 g/L. Based on the results, 1 g/L of

the catalyst was determined as the optimal concentration. An increase in ozone decomposition on the catalyst surface results in an increase in the surface radical concentration and liquid solution. The addition of a catalyst increases the surface area and active sites, which leads to an increase in ozone absorption at the catalyst surface and subsequently increases the absorption rate, surface reactions, and radical production during the COP [34]. The following reactions in the presence of Al_2O_3 and ozone can be a possible reason for increased efficiency in the presence of Al_2O_3 nanoparticles:

$$O_3 + (Al_2O_3) - S \rightarrow (Al_2O_3 - SO_3) \tag{4}$$

$$(Al_2O_3 - SO_3) \rightarrow (Al_2O_3 - SO^\bullet) + O_2 \tag{5}$$

$$(Al_2O_3 - SO^\bullet) + 2H_2O + O_3 \rightarrow (Al_2O_3 - S^\bullet OH) + 3^\bullet OH + O_2 \tag{6}$$

where, S represents the position of Lewis acid on the surface of Al_2O_3 [13]. In these reactions, the Al_2O_3 nanoparticles act as an initiator for radical production, and ozone absorption on the catalyst surface can cause the ozone decomposition and active radical production. In other words, at the position of Lewis acid, the nanoparticle reacts with ozone and consequently generates oxygen radicals. The produced oxygen radical generates hydroxide radicals in the presence of water, and then increases the process efficiency. As can be seen from the results, the exacerbation effect of activated alumina is remarkable in the COP for DEX removal.

3.5. Effect of ozone concentration on DEX removal

Since the ozone generator used in this study was not possible to change the ozone flow rate, therefore, in order to change the ozone concentration, the flow rate of the oxygen generator was changed in the range of 1–5 mL/min. The iodometric titration method was used to determine the concentration of soluble ozone in the reactor [26]. In this method, the output of the ozone generator was determined using the gas passing from two containers containing KI for 10 min. The concentration of the dissolved ozone was calculated to be 0.5 mg/min when the flow rate of the oxygen generator was 5 mL/min. As shown in Fig. 8, the removal
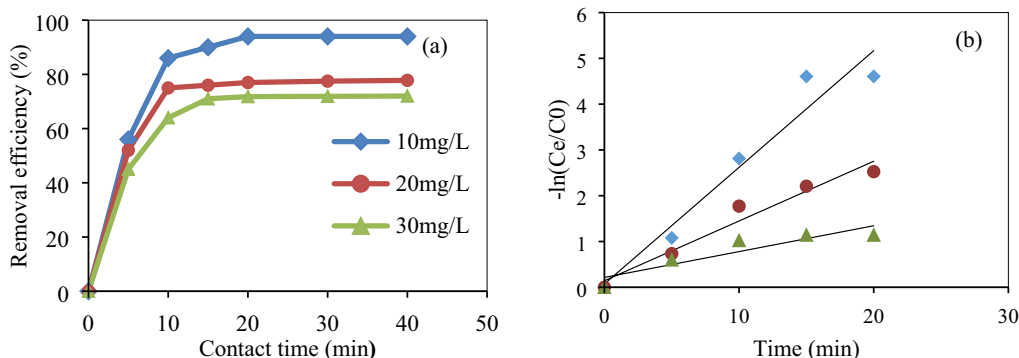
Fig. 6. Effect of DEX initial concentration on DEX removal efficiency (a) and kinetic rate constant (b) in the COP (pH = 10 and catalyst dose = 1 g/L).
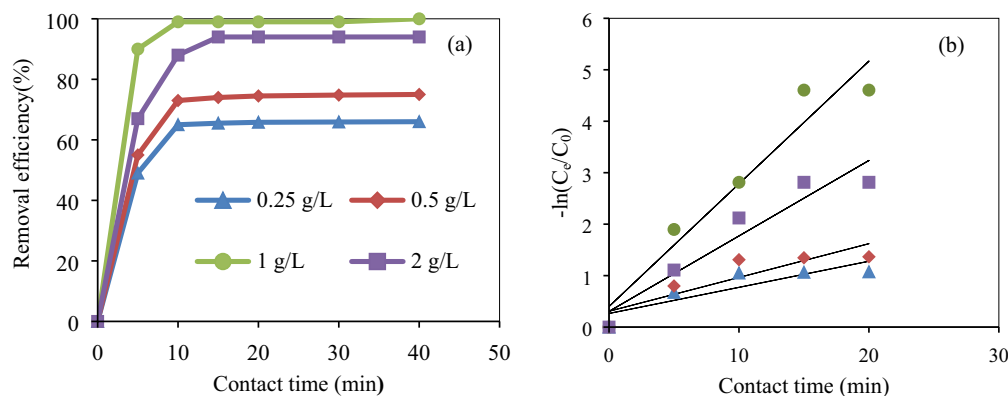
Fig. 7. Effect of catalytic dose on DEX on DEX removal efficiency (a) and kinetic rate constant (b) in the COP (DEX = 10 mg/L, ozonation time = 40 min, and pH = 7).
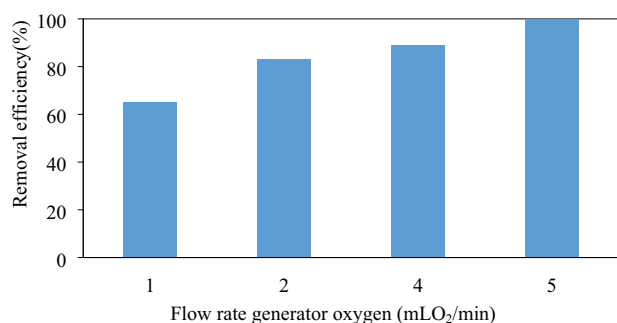

Fig. 8. Effect of ozone concentration on the COP (DEX concentration = 10 mg/L, pH = 7, catalyst dose = 1 g/L, and contact time = 40 min).

efficiency also increased with increasing the flow rate of the oxygen generator and consequently increases the concentration of soluble ozone in the reactor.

3.6. Effect of butanol butyric acid on DEX removal and compression of binary and single process

Radical scavengers, such as carbonate, sulfate, and *tert*-butanol, have the ability to control the processes of radical chain reactions. Fig. 9a and b exhibit the effect of *tert*-butanol as a natural scavenger of radical on removal efficiency and kinetic rate constant. The results of the effect of 5 mmol/L of *tert*-butanol on DEX removal by COP showed that *tert*-butanol alcohol reduced the removal efficiency of DEX by 29% after 40 min. The reason for the relatively high impact of butyl alcohol can be attributed to the high rate of this compound in reaction with hydroxyl radical compared to the ozone molecule. Eventually, the COP efficiency in the presence of the Al_2O_3 catalyst was compared with that in the absence of the catalyst. Moreover, the efficiency of the alone ozonation process was compared with Al_2O_3/O_3. As shown in Fig. 9a, alone Al_2O_3 had no significant removal efficiency (6%) after 40 min. The results of this study are consistent with other studies [35–37]. But, in the Al_2O_3/O_3 process, there was an obvious difference in the efficiency of DEX removal between alone ozonation and Al_2O_3/O_3 process, as the alone ozonation process had 65% of removal efficiency, while

Al_2O_3 increased its efficiency to 100%. The constant rate of oxidation for pseudo-first-order kinetics at concentrations of Al_2O_3, O_3, $O_3/5Mm$ TBA, COP, and COP/5Mm TBA was 0.2164, 0.1104, 0.0851, 0.0296, and 0.1325, respectively.

3.7. TOC and COD reduction

Since DEX is initially converted to other degradation byproducts, which all may be organic compounds, it was therefore needed to measure TOC, which might further suggest the removal of toxicity. Also, the goal of the degradation of any pollutant is to obtain not only the pollutant degradation but also mineralization. In this perspective, DEX mineralization was analyzed by measuring the TOC concentration from samples taken at the beginning and end of the process. Fig. 10 displays the TOC and COD content of the sample at the selected condition. It is observed that the initial TOC of the sample has been measured to be 33.13 mg/L, while this reached to 13.2 mg/L after conducting the COP for a 40 min operating time. Therefore, the mineralization efficiency was calculated to be about 60%. Also, the COD reduction efficiency was obtained at about 69%. It is worth noting that the removal efficiency of DEX for the same contact time was yielded as 94%. As a result, to attain higher mineralization efficiency, the larger operating time is needed. For example, the TOC reduction efficiency was reached to 92% at the 120 min operating time (not shown in Fig. 10). In other words, the ecological toxicity of intermediate products could be avoided when the contact time was enough to mineralize the target pollutants into non-toxic CO_2 and H_2O by the COP. However, from an environmental point-of-view, intermediate products must be further identified or eco-toxicological tests were conducted with the time-scale.

3.8. Leaching value of Al^{3+} in reaction solution

In this research, the content of Al^{3+} leached from its surface to the solution was determined to investigate the stability of the Al_2O_3 nanoparticles. It should be pointed out that the loss of Al^{3+} from the catalyst was <0.2 mg/L, which was negligible. It confirms that the Al_2O_3 nanoparticles in the COP have good physicochemical durability. The results of different studies have demonstrated that the Al_2O_3 catalyst is
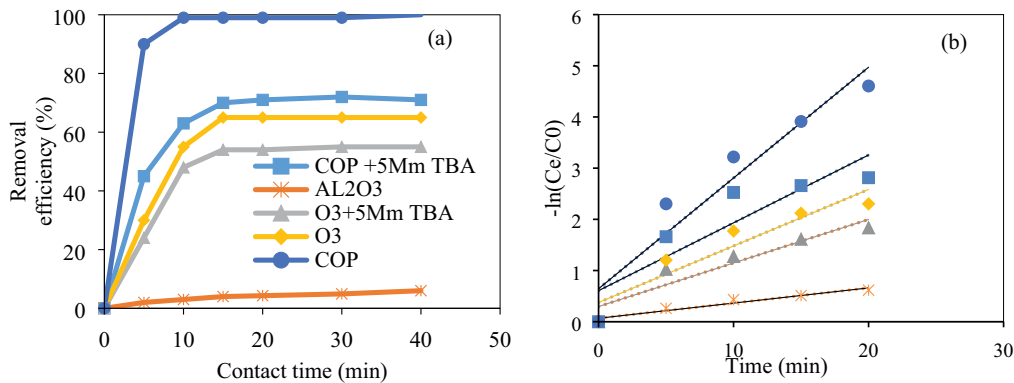
Fig. 9. Effect of *tert*-butanol on DEX removal efficiency (a) and kinetic rate constant (b) in the COP (DEX concentration = 10 mg/L, pH = 7, catalyst concentration = 1 g/L, and contact time = 40 min).
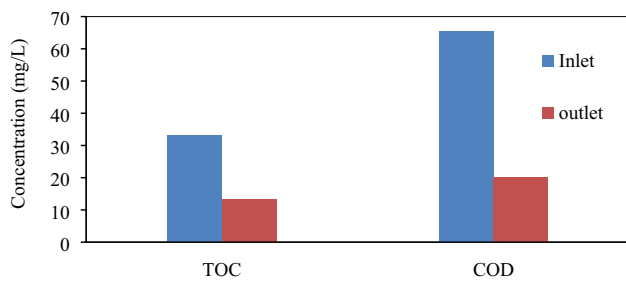

Fig. 10. Residual values of TOC and COD (initial DEX concentration = 10 mg/L, pH = 7, catalyst dose 1 g/L, and contact time = 40 min).
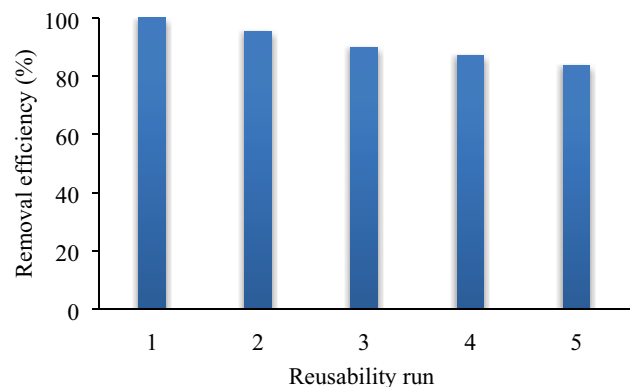

Fig. 11. Capability of the catalyst on DEX removal efficiency (initial concentration = 10 mg/L, pH = 7, catalyst concentration = 1 g/L, and contact time = 40 min).

physically stable in COP; and, due to its high density, it can easily be separated from the solution through a centrifuge instrument [38,39].

3.9. Reusability of Al_2O_3 nanoparticles

The economical and applicability of catalysts are evaluated in actual approaches through reusability. For the assessment of the reusability of the Al_2O_3 catalyst in COP, the capability of the catalyst was studied via five consecutive experiments under the same operating conditions. And, 0.2 M H_2SO_4 solution was utilized to recover the spent Al_2O_3 in a 40 min stage after each experiment. The reaction solution was centrifuged at 10,000 rpm to separate the catalyst, which then was used for the next reusability test. DEX removal percentages at the first to the fifth cycles ranged from 100% to 83.5%. (Fig. 11). As can be observed, DEX removal efficiency using the Al_2O_3/O_3 declined 16.5% after four cycles; thus, it can be claimed that Al_2O_3 is recoverable it can be applied as a beneficial catalyst with high reusability. After each run, the competition between intermediates and parent compounds enhance, which may result in a decrease in catalytic activities of Al_2O_3. As a result, active sites on the catalyst surface are deactivated over washing and drying processes. Moreover, when the surface areas are reduced, the adsorption capacity of the catalyst declines because of the fact that the pores on the catalyst's surface are blocked by contaminants or products.

3.10. Reaction pathways

In the case of heterogeneous catalytic ozonation, solid catalysts are used and reactions occur in a liquid solution or on the of catalysts' surface. It should be noted that catalytic effects are often because of hydroxyl radicals formed over the reactions. As can be seen in Fig. 12, the catalytic effects happen if there is at least one of the three conditions: (i) adsorption of ozone on the catalyst's surface, (ii) adsorption of DEX on the surface of the catalyst's surface, (iii) adsorption of both ozone and DEX on the surface of the catalyst's surface. When neither ozone nor DEX is adsorbed on the catalyst's surface, the catalytic effect does not happen [40].

4. Conclusion

In this study, the capability of the single ozonation process and COP with active alumina was investigated in the removal of DEX from aqueous solution. Moreover, the effects of some parameters were evaluated on the performance of both processes to determine the optimum conditions. The results showed that the increase of catalyst dose, contact time, pH, and ozone concentration could increase the removal efficiency of DEX, COD, and TOC. Moreover, the
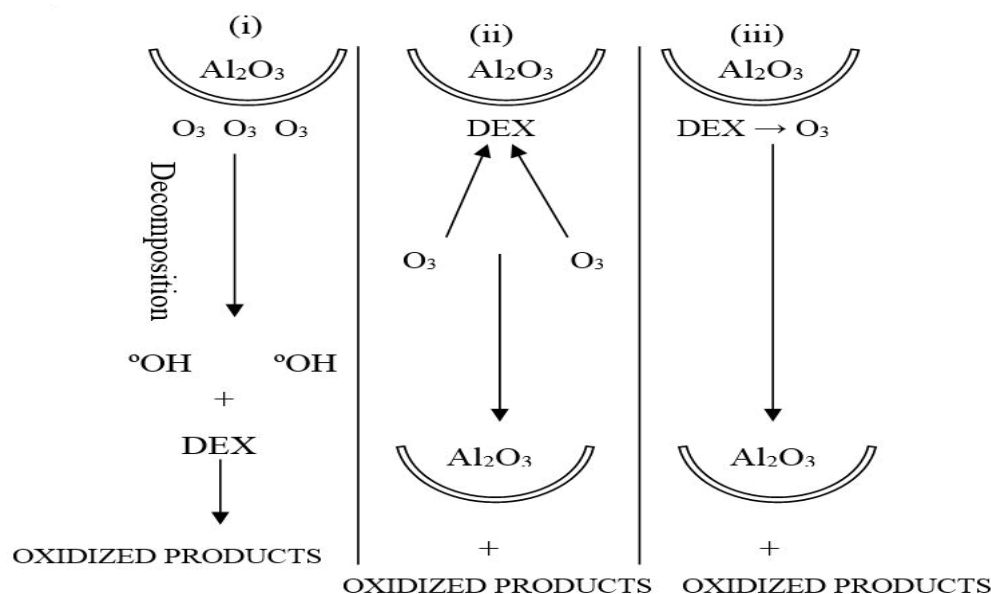
Fig. 12. Possible cases of DEX removal in heterogeneous COP using Al_2O_3.

results indicated that the COP showed a greater effect on DEX removal than the SOP. The catalyst of Al_2O_3 nanoparticles offers a very low adsorption potential and reduces the influence of harmful interfering agents and radical inhibitors. According to the results, the active catalyst alumina ozonation process as an appropriate and economical approach can be used for the treatment of pharmaceuticals from relative wastewaters and the same aqueous environments.

Acknowledgments

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