Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1115372

57 (2016) 20447–20456
September

Taylor & Francis
Taylor & Francis Group

Heterogeneous catalytic ozonation of 2, 4-dinitrophenol in aqueous solution by magnetic carbonaceous nanocomposite: catalytic activity and mechanism

Yousef Dadban Shahamat[a,*], Mahdi Sadeghi[b], Ali Shahryari[c], Niloofar Okhovat[d], Farshad Bahrami Asl[e], Mohammad Mehdi Baneshi[f]

[a]*Environmental Health Research Center, Golestan University of Medical Sciences, Gorgan, Iran, Tel. +98 911 1789457; Fax: +98 17 32436107; email: Dr.udadban@goums.ac.ir*
[b]*Department of Environmental Health Engineering, School of Public Health, Golestan University of Medical Sciences, Gorgan, Iran, email: kargar@goums.ac.ir*
[c]*Department of Environmental Health Engineering, School of Public Health, Golestan University of Medical Sciences, Tehran, Iran, email: al_shahryar@yahoo.com*
[d]*Faculty of Public Health, Department of Environmental Health Engineering, Shiraz University of Medical Sciences, Shiraz, Iran, email: nfr_okhovat@yahoo.com*
[e]*Department of Environmental Health Engineering, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran, email: farshadfba@gmail.com*
[f]*Social Determinant of Health Research Center, Yasuj University of Medical Science, Yasuj, Iran, email: mmbaneshi@yahoo.com*

Received 27 March 2015; Accepted 7 October 2015

ABSTRACT

Herein, the catalytic properties of a carbonaceous nanocomposite in the catalytic ozonation process (COP) of 2, 4-dinitrophenol (2, 4-DNP) were investigated and the results were compared with those obtained from single ozonation process (SOP). Magnetic carbonaceous nanocomposite, as a novel catalyst, was applied to optimize the condition for the removal of 2, 4-DNP in the COP, and the influential parameters such as pH, catalyst dosage, addition of radical scavengers, and durability were all evaluated. The results showed that the degradation efficiency of 2, 4-DNP and COD in the COP (98.2, 92%) was higher compared to the SOP (75, 61%) and the highest catalytic potential was achieved at an optimal pH of 6. The first-order modeling demonstrated that the reactions were dependent on the concentration of the catalyst, with the kinetic constants varying from 0.022 (1/min) in the SOP to 1.377 (1/min) in the COP at the catalyst dosage of 4 g/L and the optimum concentration of catalyst (2 g/L). The addition of radical scavenger noticeably diminished the removal efficiency of 2, 4-DNP in the SOP from 75% down to 54%, while the corresponding values for the COP dropped from 98.2 to 93%. Furthermore, a negligible reduction in the catalytic properties of the catalyst was observed (~5%) after five-time reuse. The results also revealed that the applied method is effectively suitable for the removal of 2, 4-DNP contaminant from industrial wastewaters.

Keywords: Catalytic ozonation; Magnetic carbonaceous nanocomposite; 2, 4-dinitrophenol; Wastewater

---

*Corresponding author.

1. Introduction

Nitrophenols (NPs) and their derivatives are among the most widely used compounds in chemical industries. They are frequently used as intermediates or raw materials in pharmaceutical, explosive, pigment, dyes, textiles, pesticide, and rubber factories [1,2]. Of the mentioned compounds, 2, 4-DNP has been classified as a major pollutant by USEPA and its concentration in natural bodies should be less than 10 ng/L [1]; meanwhile, according to the European standard regulations, the total concentration of phenolic compounds must be less than 500 ng/L in potable water and the concentration of each compound must be less than 100 ng/L [3]. 2, 4-DNP is a yellow crystalline solid with strong acidic properties ($pK_a = 4.03$). Due to high toxicity, nonbiodegradability, and carcinogenicity, it should be removed from industrial wastewaters [4]. Thus, it is necessary to modify conventional treatment methods for the effective removal of such bio-recalcitrant contaminants.

Up to now, a wide variety of chemical and physical treatment methods such as various types of chemical oxidation, UV/H_2O_2, Fenton, UV/Fenton, Fenton combined with cavitation process [4], low-temperature plasma, unmodified and modified activated carbons (ACs), wet electrocatalytic oxidation, electrocoagulation [5], evaporation, precipitation, incineration, and biological methods [2] have been used for the removal of DNP, but these mentioned methods suffer from a few drawbacks including low intensity and high cost [5].

Ozonation is one of the oxidation methods widely used for bio-recalcitrant wastewaters where ozone molecules break down recalcitrants and toxic organic compounds to smaller molecules. The ozonation reaction is accomplished through two pathways: direct ozone oxidation and indirect free hydroxyl radical oxidation. In direct ozonation, organic molecules can be destroyed in various ways, including: (a) the breakage of double bond and formation of aldehydes and ketones, (b) the addition of an oxygen atom to the benzene ring, and (c) the reaction with alcohols to form organic acids.

In indirect free hydroxyl radical oxidation, ozone is decomposed to free reactive radicals, which can significantly increase the removal efficiency of pollutants [6,7]. However, ozonation has some limitations such as: (1) high energy consumption for ozone generation which is costly; (2) in some cases, ozonation is selective for degrading resistant organics; (3) incomplete oxidation and low efficiency due to slow reaction kinetics and limited mass transfer [8]; and (4) incomplete mineralization of recalcitrant organics [9].

For instance, when ozonation is used alone, saturated intermediates may accumulate in the effluent solution, which are more toxic than the initial pollutants, especially at the early stage of ozonation [8]. Thus, a number of studies were focused on improving the ozonation efficiency and overcoming the weakness of the single ozonation process (SOP). Chang et al. and Wu et al. reported that the treatment process can be improved by combining ozonation with other agents such as UV, H_2O_2, and homogeneous catalysts. [7,10]. But, due to the high consumption of catalyst and complexity of these technologies, they are rarely employed as promising methods.

Recently, heterogeneous catalytic ozonation process (COP), as a powerful treatment method, has been employed to increase the efficiency of the ozonation process. In this method, a synthesized catalyst is applied to increase the ozone decomposition and formation of highly reactive free radicals. Many catalysts including metals, metal oxides such as CO_3O_4/CeO_2, TiO_2, Pt/carbon nanotube (CNT), Ru/Al_2O_3, Mn/TiO_2, Au/AC, Mn/Co, Fe_3O_4/CoO, ZnO, Fe_2O_3, Fe_2O_3/CeO_2, CNT, Ru/CeO_2, Cu/ZrO, $CuFe_2O_4$, and AC have widely been used for enhancing the activation of the ozonation process [11–14]. Nevertheless, the main limitations of these catalysts are as follows: complexity, high cost of synthesis, and leaching of materials into the liquid system led by the creation of secondary pollutants in the treated wastewater. Hence, we centered on a new material with novel features such as high catalytic activity, reusability, and ease of production.

In this study, carbon nanocomposite, as a catalyst, was applied for the heterogeneous ozonation of 2, 4-DNP and the catalytic properties and durability of the catalyst were investigated. The application of this catalyst was previously performed by authors for phenol removal in the COP [15]. But, since DNP is more toxic and nonbiodegradable than phenol [16], the efficiency of this process has been studied for this contaminant removal.

In addition, the mechanism of reaction and the influence of some operating parameters such as initial pH of the solution, concentration of the catalyst, and reaction time on the DNP degradation, the chemical oxygen demand (COD), removal efficiencies, and the catalyst durability were all evaluated. For optimization, it is necessary to understand the role of the catalyst and the nature of reactions; therefore, physical and chemical properties of the nanocomposite, such as its specific surface area and composition, were determined [15]. In order to explain the nature of reactions, the experiments were performed using *tert-butanol* as radical scavenger. In addition, the kinetics of DNP degradation was determined and further discussed by SOP and COP experiments.

2. Experimental

2.1. Materials

2, 4-dinitrophenol (purity ≥ 98%; CAS No.: 51-28-5, as powder) was purchased from Aldrich Co. Then, the standard solutions were prepared with distilled and deionized water and protected from light and stored at 4˚C. Except for HPLC-grade methanol, all other chemicals used such as (KI), (Na_2SO_3), ($Na_2S_2O_5$), nitric acid, sulfuric acid, sodium hydroxide, (Ag_2SO_4), (KCr_2O_7), ($HgSO_4$), $Fe(NO_3)_3{\cdot}9H_2O$, and tert-butyl alcohol were of analytical grade.

Commercial powder AC was supplied by Merck Co. (CAS No.: 1.02183.1000) and used as a precursor for the synthesis of catalyst in this study, characterization of which was later compared with that of final magnetic catalyst shown in Table 1.

2.2. Characterization of catalyst

The nanocomposite catalyst in which nanoparticles of Fe_3O_4 was performed in powder AC was prepared via impregnation method. In this method, firstly, the AC was modified with nitric acid and dispersed in aqueous solution containing $Fe(NO3)_3{\cdot}9H_2O$ as a Fe_3O_4 precursor by an ultrasonic bath. Then, thermal treatment was conducted at 750˚C for 1 h in the presence of pure nitrogen [15]. The results regarding specific surface area, mineralogical characterization, distribution of elements, and morphology of catalyst are presented in Table 1. Moreover, the pH of point of zero charge (pH_{pzc}) of the catalyst was measured by acid–base titration as reported by Altenor et al. [17].

2.3. Semi-batch experiments and analyses

The gaseous ozone stream was generated from pure oxygen by corona discharge using an ozone generator (ARDA, Model COG-1A) with 5 g O_3/h capacity. Flow rate of the reactor was controlled with a gas rotameter (capacity, 3.5 L/min) at 0.5 L/min as the mass flow rate was adjusted at 33 mg/(L min); and the gas coming out of the reactor (exit gas) was destroyed by bubbling it through the traps previously filled with a concentrated potassium iodide solution [18].

The samples containing DNP were prepared from the stock solution. Residual concentrations of DNP and COD were measured by a Cecil CE 4100 HPLC (Hypersil C18 column (250-mm × 4.6-mm i.d., with 5-μm particle size); UV detector at 260 nm) and $K_2Cr_2O_7$ digestion, respectively [18].

The mobile phase consisted of a mixture of methanol/water (50:50, v/v) with a flow rate of 1.0 mL/min.

The catalytic ozonation experiments were performed in a semi-batch flow cylindrical stainless steel reactor with a total volume of 2 L (5 × 100 cm) fitted with other elements including a diffuser to distribute the ozone stream into the solution, an ozone generator, a cylinder of pure oxygen (up to 99.9%), an ozone destruction trap system, and a gas rotameter. In each catalytic ozonation experiment, the following procedure was performed:

(1) One liter of DNP solution with a known initial concentration was introduced into a 2-L glass beaker.
(2) The initial pH of the solution was adjusted by the addition of HCl/NaOH (1 M).
(3) A fixed amount of the synthesized catalyst was added to the solution.

Table 1
Specification of magnetic carbonaceous nanocomposite and its precursor

Parameters	PAC		Nanocomposite
Specific surface area (m^2/g)	907		814
Pore volume (cm^3/g)	0.42		0.26
pH_{pzc}	8.92		7.71
Average particle size	0.15–0.25 (mm)		24–31 (nm)
Assay (%) as carbon	99.99		89.2
Color	Black		Black
Mass fraction	C	Fe	O
Elements of catalyst			
Norm (weight %)	75.14	18.39	6.47
Atom (%)	89.20	5.04	5.76

Table 2
Experimental runs (steps and conditions)

		Experimental conditions			
Phase	Experiments	C_{DNP} (mg/L)	$C_{Catalyst}$ (g/L)	pH	Time (min)
1	Effect of initial pH	500	2^a	4–10	15
2	Effect of catalyst dosage	500	0.2–4^a	6^b	0–60
3	Effect of radical scavenger	500	2^a	6	0–60
4	Synergistic effect of catalyst	500	$2^{c,d}$	6	0–60
5	The COD removal at optimum condition	500	2	6	0–60
6	Catalyst durability	500	2	6	60

[a] The same experiments were carried out for SOP (without catalyst).

[b] Optimum pH in which the maximum DNP removal was obtained in the COP.

[c] The same experiment was performed for DNP adsorption on the catalyst.

[d] The same experiment was performed with DNP-saturated catalyst and powder AC, instead of a fresh catalyst.

(4) The solution was mixed and transferred into the steel reactor and the ozonation was initiated at a specific time (see Table 2).

At certain time intervals, 2 mL of the above solution was immediately withdrawn and mixed with 100 μL of sulfite solution (0.1 M) to remove the dissolved ozone [19]. The magnet and syringe filter (0.22 μm, PTFE) were used to remove the remaining catalyst. Finally, 60 μL of the above solution was injected into the HPLC for the final analysis of DNP. The experimental runs were performed based on “one factor at a given time” method, detailed in Table 2.

2.4. Kinetic studies

The kinetic studies in both COP and SOP were carried out using different experimental runs.

Since the oxidizing ability of the COP comes from either ozone molecules or hydroxyl radicals, the kinetic rate of DNP degradation can be formulated as given by Eq. (1):

$$-\frac{\mathrm{d}[\mathrm{DNP}]}{\mathrm{d}t} = k_0[\mathrm{DNP}][\mathrm{O_3}] + k_{\mathrm{OH}}[\mathrm{DNP}]\left[\mathrm{OH}^{\circ}\right] \qquad (1)$$

where [DNP] is the concentration of the DNP contaminant in the aqueous solution, $[O_3]$ and $[OH^{\circ}]$ are the concentrations of the ozone and hydroxyl molecules, and k_0 and k_{OH} are the respective kinetic constants. Since, in this study, the amount of ozone was in excess, Eq. (1) can be reformed to the pseudo-first-order equation (Eq. 2), where k is the pseudo-first-order or overall constant.

$$\frac{\mathrm{d}[\mathrm{DNP}]}{\mathrm{d}t} = -\left(k_0[\mathrm{O_3}] + k_{\mathrm{OH}}\left[\mathrm{OH}^{\circ}\right]\right)[\mathrm{DNP}] = -k[\mathrm{DNP}] \qquad (2)$$

2.5. Mechanism of DNP degradation

To evaluate the likelihood of the proposed mechanism, the degradation of DNP in the COP was investigated in the presence of 0.05 M of *tert-butanol* in aqueous solution, as a well-known radical scavenger, according to phases 3 and 4 of Table 2.

To calculate the synergistic effect of the catalyst on the ozonation of DNP, the following equation was used [20,21]:

$$\begin{aligned}\text{Synergistic effect} = {} & \text{degradation in COP} \\ & - (\text{degradation in SOP} \\ & + \text{removal by catalyst})\end{aligned} \qquad (3)$$

To further elucidate the role of the catalyst in the COP, an experiment was performed (phase 4 of Table 2) in which the catalyst was saturated with DNP and used instead of a fresh catalyst (i.e. unsaturated catalyst).

2.6. Catalyst durability

The durability of nanocatalyst was tested according to the following approach. After each run of the COP, the catalyst was recovered by a magnet and then an extraction solvent was applied to separate DNP and volatile by-product molecules adsorbed onto the surface of the catalyst. Following that, the extraction solvent was evaporated and dried in an oven at 80˚C for 120 min. Finally, the recovered catalyst was used in the next runs for five times under the same conditions described in phase 6 of Table 2.

3. Results and discussion

3.1. Effect of initial pH of the solution and pH_{pzc} of the catalyst

The pH of the solution can greatly affect the structural properties of the pollutant and the changes in the pH can alter the ions in solution, the ionic state of 2, 4-DNP, and the surface properties of the catalyst. The catalyst surface will be negative at $pH > pH_{pzc}$, positive at $pH < pH_{pzc}$, and neutral at $pH \approx pH_{pzc}$. The pH_{pzc} of the synthesized catalyst measured was 7.71 (Fig. 1), falling within the range of 6.08–7.7 as reported by various researchers for similar catalysts [21,22]. Results also demonstrated that the catalyst surface has slightly basic properties and these basic functional groups located on the surface of the catalyst are thought to be responsible for ozone decomposition, which results in the generation of reactive radical species [20].

Previous studies showed that the thermal modification of AC under N_2 stream could significantly gasify the oxygenated acids such as carboxylic acids formed in the acid treatment step. These oxygenated acids can reduce electron density on the carbon layers. Since ozone molecules are known to trigger the electrophilic reaction, the reduction of carbon electron density should decrease the ozone molecules' reactivity [23]. Thus, this thermal treatment could improve the catalytic properties of the catalyst.

As shown in Fig. 2, the degradation rate of DNP in the SOP is increased linearly from 42% at pH 4 to 65% at pH 10 within a 15-min reaction time and the corresponding first-order kinetic rate constants (Table 3) vary from 0.019 to 0.039 (1/min), respectively.

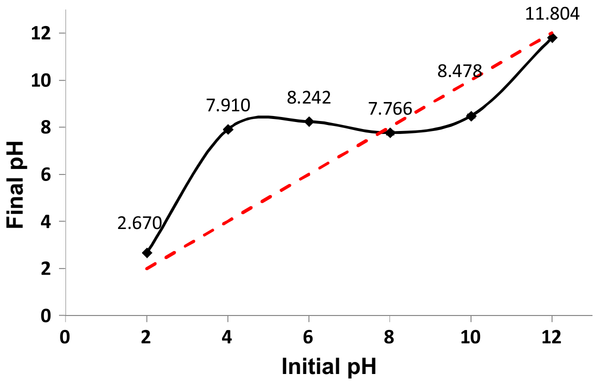

Fig. 1. pH drift for the determination of pH_{pzc} of the catalyst.

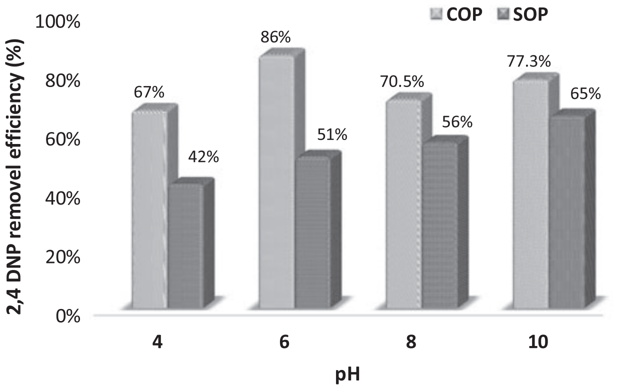

Fig. 2. Effect of initial pH on the removal efficiency of DNP in SOP and COP. $[DNP]_0$: 500 mg/L; catalyst concentration of 2 g/L; reaction time: 15 min.

This increase in DNP degradation can be explained by the fact that pH can have an impact on the ozone transfer rate from the gas stream to the liquid phase [20]. In other words, an increase in the concentration of OH anions results in converting ozone to the reactive oxidizing radical species having much higher oxidation potential than the ozone molecules in the solution [24].

In the COP, due to the functional properties of the catalyst surface, the maximum degradation and k obtained at pH 6 were 86% and 0.072 (1/min), respectively; while, at higher pH (pH 8 and 10), the corresponding values dropped to 70 and 77% and 0.041 and 0.06 (1/min), respectively [8,25].

As shown, at higher pH, the reverse trend was observed in the degradation of DNP, and the degradation rate of DNP was decreased under strong alkaline conditions (Fig. 2). This result could be interpreted by considering both pK_a of 2, 4-DNP ($pK_a = 4.11$) and the nature of the catalyst surface, with respect to the pH of the solution and the catalyst pH_{pzc}.

Table 3
Kinetic information of DNP removal as a function of pH in SOP and COP

pH	4	6	8	10
COP				
Order	1	1	1	1
Constant (min^{-1})	0.03	0.072	0.041	0.06
R^2	0.86	0.95	0.94	0.97
SOP				
Order	1	1	1	1
Constant (min^{-1})	0.019	0.022	0.032	0.039
R^2	0.96	0.89	0.97	0.95

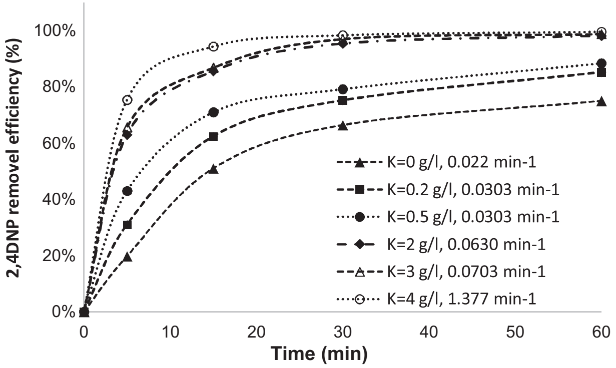

Fig. 3. Effect of catalyst concentration on DNP degradation efficiency in SOP and COP. $[DNP]_0$: 500 mg/L; initial pH 6.0.

Since the pH_{pzc} of the catalyst is 7.71, the negative charges are developed on the surface of the catalyst beyond this pH (≥8); and since the pK_a of 2, 4-DNP is 4.11, it is mostly ionized to the 2, 4-dinitrophenoxy anion form at $pH \geq pK_a$ [26].

On the other hand, the effect of pH on the adsorption of DNP can be explained by the electrostatic interaction between the surface of the catalyst and the target material. The affinity of the catalyst toward the anionic form of DNP is restricted under the strong alkaline condition, which leads to the fall in the degradation rate of DNP [20].

As expected, the results also underlined that the optimal pH fell in $pK_a^{2,4DNP} < pH < pH_{pzc}^{2,4DNP}$ range [24]. Over the above pH range, the positively charged catalyst and the negatively charged 2, 4-DNP molecules attract each other [21].

Hence, under neutral and weak acidic conditions (pH 6–7), the positive charges are predominant on the surface of the catalyst and the DNP molecules are mainly present in negative forms. Therefore, unlike charges are easily attracted toward each other through hydrogen bonding and this phenomenon gives rise to the adsorption and removal of DNP [25]. As previous studies pointed out, with an increase in the pH of the solution from 3 to 11, the degradation rate of nitrobenzene in the COP using the Mn catalyst was enhanced [27]. All in all, it can be deducted that the optimum pH of COP must be selected under each specific condition.

3.2. Effect of catalyst concentration

Based on the experimental conditions defined in phase 2 of Table 2, an increase in the catalyst concentration enhanced both the degradation efficiency and the reaction rate constant (k), particularly at the early stages of the reaction.

At a given reaction time of 5 min and at the catalyst concentration of 0.5 g/L, the degradation of DNP increased from 20 to 43% in the SOP and further up to 75% at the catalyst concentration of 4 g/L, which exhibits the role of catalyst concentration in the ozonation process. In the end, the total removal of DNP (~100%) was achieved when the reaction time was extended to 60 min (Fig. 3).

Results also showed that the reaction rate constant of DNP increased from 0.022 (1/min) in the SOP to 0.030 (1/min) in the COP (0.5 g/L of catalyst) and then up to 1.377 (1/min) with the catalyst concentration of 4 g/L, which indicates a 62-fold increase in the reaction rate constant in the COP compared to that of the SOP. The increase in both DNP degradation and the reaction rate constant with an enhancement in the catalyst concentration can be attributed to the enlargement of the catalyst surface area and the availability of more active sites to the DNP adsorption and ozone decomposition, which leads to the enhancement of the following reactions:

The contact surface area for the reaction of DNP and ozone molecules [28]; generation of reactive species of radicals [29–31]; and the improvement of DNP adsorption–catalytic oxidation process.

It is worth noting that the optimum concentration of the catalyst in the ozonation process strongly depends on the reaction conditions, the type of catalyst, the properties of target contaminant, and the desired level of efficiency [21]. Meanwhile, further increases in the catalyst concentration (up to 4 g/L) did not significantly affect the DNP removal efficiency. These findings are all in agreement with another related study [32].

Hence, in this study, the concentration of 2 g/L was chosen as the optimal catalyst concentration and applied to further experiments.

3.3. Mechanism of pollutant degradation

The radical scavengers present in wastewaters can significantly interfere with the removal of the target contaminant.

According to the results shown in phase 3 of Table 2 and Fig. 4, the addition of *t-butanol* noticeably diminished the efficiency of DNP degradation in the SOP from 75 to 54%, while the corresponding values in the COP dropped from 98 to 93%. In other words, the radical scavenger decreased the efficiency in the SOP and COP (21 and 5%, respectively), representing a 4.2-fold reduction in the degradation rate in the SOP compared to that in the COP.

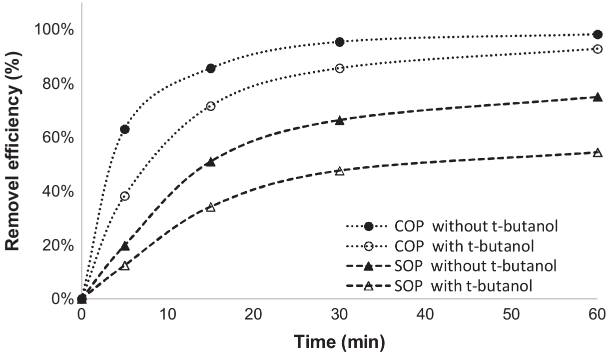

Fig. 4. Effect of t-butanol radical scavenger on DNP degradation in SOP and COP. $[DNP]_0$: 500 mg/L; catalyst concentration of 2 g/L; initial pH of 6.0.

Based on similar studies, the most likely mechanism proceeds in two steps: firstly, ozone molecules are adsorbed onto the functional groups of the catalyst surface followed by its decomposition with AC [8,11] and metal oxides including Fe_3O_4 nanoparticles to surface oxygenated radical species (SOR) [33]; secondly, the contaminants are rapidly degraded on the surface of AC [34–36].

Since hydroxyl radicals are more reactive than ozone molecules and *t-butanol* is a well-known hydroxyl radical scavenger [13,25], indirect oxidation seems to be the main degradation mechanism governing in COP as observed in similar related studies [37]; however, high removal efficiency can be due to the fact that the catalyst is capable of decomposing ozone and thereby enhancing SOR generation [35,36]. As seen in Fig. 4, the removal of DNP in the presence of *tert-butanol* in the COP was slightly less than that obtained in the absence of the scavenger under the same condition (~5%), indicating that the removal efficiency—especially at the end of reaction time—is not significantly affected by the presence of the radical scavenger in the solution. Meanwhile, as reported by others, the surface of the catalyst plays an important role in the degradation of phenolic compounds [20] and other radical species—especially hydroxyl—are the dominant species in the reactor [34].

As defined in phase 4 of Table 2 and the results of Fig. 5, the synergistic effect of the catalyst in the COP of DNP indicates that the proportion of DNP adsorption in the first stage of the reaction is about 20% and it falls to 0.6% as the reaction continues. This result also shows that the catalytic potential of the catalyst is not lowered by the adsorption [31]; meanwhile, it suggests that the catalytic degradation should be the dominant reaction—not the adsorption—in the COP, as reported by others [25,38].

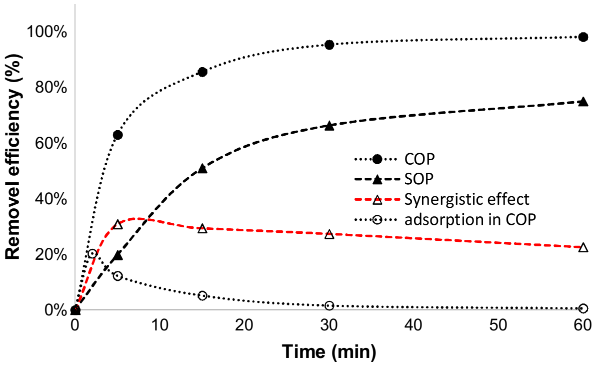

Fig. 5. Synergistic effect of catalyst on COP. $[DNP]_0$: 500 mg/L; catalyst concentration of 2 g/L; initial pH of 6.0.

As shown in Fig. 6 (phase 4 of Table 2), by applying a fresh catalyst, the DNP removal efficiency and the kinetic constant were determined to be 98% and 0.063 (1/min), respectively, while the results obtained with its saturated counterpart were 96.4% and 0.052 (1/min), respectively, which indicates that the degradation process is not under the influence of catalyst saturation.

Furthermore, in the use of powder AC as a catalyst, it is found that the removal efficiency had slightly diminished (10%), while this reduction for kinetic constant was considerable (twofold). This result showed the role of catalyst modification in the enhancement of operational efficiency in the COP.

Some researchers also reported that some functional groups of the catalyst surface can be modified by ozone through enhancing the specific surface area and lowering the total volume of the catalyst [32]; however, others revealed that once the modified carbon is ozonated, the specific surface area is slightly

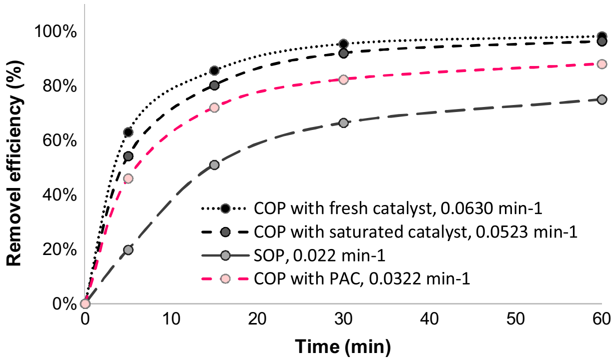

Fig. 6. Effect of saturated catalyst and PAC on DNP removal efficiency. $[DNP]_0$: 500 mg/L; catalyst concentration of 2 g/L; initial pH of 6.0.

diminished; as a result, the total volume of the pores remains unchanged [39]. Hence, it can be concluded that the impact of the ozonation process on the structure of carbonaceous catalyst is relative to the nature and origin of a catalyst.

3.4. Removal of COD in COP

In this section, the COP role in the removal of COD derived from aqueous solution, under the conditions defined in phase 5 of Table 2, was investigated.

Previous studies reported that the AOP causes a drastic reduction in the COD of recalcitrant organics [9] and our findings show that the COP is not exempt from this general principle as well. As shown in Fig. 7, DNP degradation efficiency in the COP was determined to be 86% after 15 min of the reaction, while about 58% of the COD of DNP was removed after the same reaction time. Then, COD removal efficiency increased up to 92% after 60 min, while the same results for the SOP were 33 and 61%, respectively. The results also show that the efficiency of COD removal was less than that of DNP degradation, particularly at the early minutes of the reaction. This phenomenon can be illustrated in such a way that the DNP molecules, especially at the initial steps of degradation, are converted to some intermediates and by-products prior to total oxidation [40]. However, the results of COD and DNP removal efficiency using this catalyst were better compared with the other catalysts [17,21].

As shown in Fig. 7, a dramatic fall in pH—especially in the first steps of the reaction—confirms that the acidic intermediates are generated during the oxidation of the phenolic compound. In addition, as the oxidation process is promoted by the COP, the gap between COD and the phenol removal curve is narrowed. This could be due to the fact that the intermediates are more efficiently mineralized in the COP than their corresponding parent compounds. Overall, when this catalyst was used in the COP, a high degree of degradation and mineralization of DNP was achieved compared to the other processes such as single ozonation [5,21], adsorption, TiO_2-photocatalytic, wet-air oxidation, and catalytic-based wet air oxidation [41].

3.5. Durability of catalyst

From the practical points of view, lifetime or durability is the most important characteristic of the catalyst which can be defined as the minimal deactivation and easy-to-recover by a magnet after a number of runs.

In order to determine catalyst durability, an experimental condition was defined (Table 2, phase 6). As shown in Fig. 8, super-paramagnetic and catalytic properties of the catalyst were retained after five-time reuse and the reduction in DNP removal efficiency was negligible (about 5%), which can be due to the washout of the catalyst from the system.

This can be illustrated either by *in situ* regeneration of the catalyst, or the predominance of catalytic properties and the adsorption/oxidation processes in the COP as mentioned by others [32]. Although some studies pointed out that the contaminant degradation is improved after reuse, due to the modification of chemical functional groups on the catalyst surface by ozonation and the rise in the number of pore volumes and the specific surface areas [42,43], others reported that ozonation decreases the catalytic properties of the AC due to the reduction in basic groups and an increase in the number of oxygenated functional groups on the surface such as hydroxyl and carboxylic acid groups and nitroaromatic compounds [44].

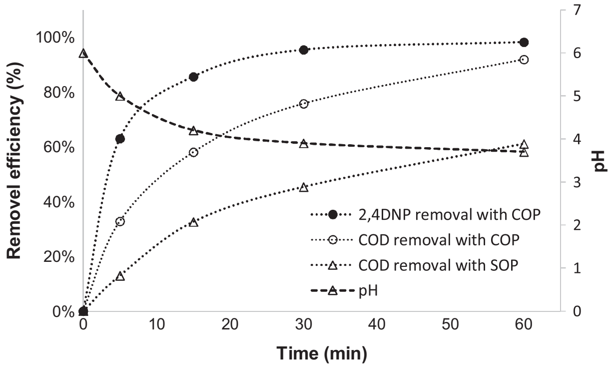

Fig. 7. Degradation and mineralization of DNP in COP under the optimal condition. $[DNP]_0$: 500 mg/L; catalyst concentration of 2 g/L; initial pH of 6.0.

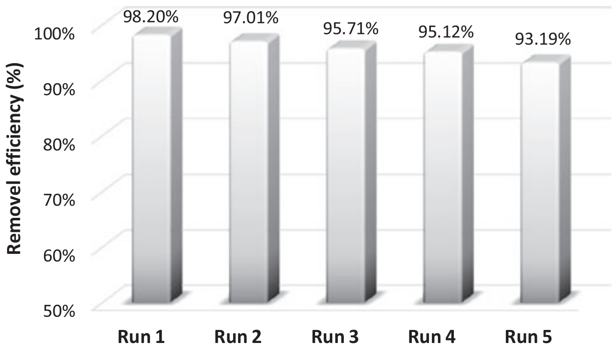

Fig. 8. Effect of catalyst recovery and reuse on DNP degradation in COP. $[DNP]_0$: 500 mg/L; catalyst concentration of 2 g/L; initial pH of 6.0.

4. Conclusions

In this study, the catalytic properties of a carbonaceous nanocomposite in the catalytic ozonation of DNP were investigated. This paramagnetic nanocomposite catalyst exhibited a catalytic effect on the generation of reactive radicals. The catalyst was effectively separated from the aquatic solutions by applying a magnet and successfully recycled for several times. At the initial concentration of 500 mg/L of DNP and the optimal conditions including O_3 dosage of 33 mg/(L min) and pH 6, 98 and 92% of DNP and COD were removed in the COP, while the corresponding results obtained for the SOP were determined to be 75 and 53%, respectively. The first-order modeling demonstrated that the reactions are dependent on the concentration of the catalyst, with the kinetic constants varying from 0.022 1/min in the SOP to 1.377 1/min in the COP at the catalyst dosage of 4 g/L, whereby the optimum concentration of the catalyst was determined to be 2 g/L.

The findings also indicated that DNP is mainly decomposed through a series of oxidation reactions occurring on the surface of the catalyst, and the radical scavengers present in wastewater could not affect the catalytic reaction. Accordingly, it was concluded that this nanocomposite is an efficient and active catalyst in the degradation and mineralization of DNP in the COP.

Furthermore, the reduction in catalytic properties of the catalyst was negligible after five-time reuse. Finally, the findings revealed that this process is proven to be effectively suitable for the removal of 2, 4-DNP contaminants from industrial wastewaters.

Acknowledgment

The authors appreciate the Golestan University of Medical Sciences (project reference number: 910823168) for providing financial and instrumental support to conduct this work.

References

[1] Z. She, M. Gao, C. Jin, Y. Chen, J. Yu, Toxicity and biodegradation of 2,4-dinitrophenol and 3-nitrophenol in anaerobic systems, Process Biochem. 40 (2005) 3017–3024.

[2.] T. Hirooka, H. Nagase, K. Hirata, K. Miyamoto, Degradation of 2,4-dinitrophenol by a mixed culture of photoautotrophic microorganisms, Biochem. Eng. J. 29 (2006) 157–162.

[3] W. Zhong, D. Wang, X. Xu, Q. Luo, B. Wang, X. Shan, Z. Wang, Screening level ecological risk assessment for phenols in surface water of the Taihu Lake, Chemosphere 80 (2010) 998–1005.

[4] M.V. Bagal, B.J. Lele, P.R. Gogate, Removal of 2,4-dinitrophenol using hybrid methods based on ultrasound at an operating capacity of 7L, Ultrason. Sonochem. 20 (2013) 1217–1225.

[5] R. Dai, J. Chen, J. Lin, S. Xiao, S. Chen, Y. Deng, Reduction of nitro phenols using nitroreductase from *E. coli* in the presence of NADH, J. Hazard. Mater. 170 (2009) 141–143.

[6] A. Aguinaco, F.J. Beltrán, J.F. García-Araya, A. Oropesa, Photocatalytic ozonation to remove the pharmaceutical diclofenac from water: Influence of variables, Chem. Eng. J. 189–190 (2012) 275–282.

[7] C.-C. Chang, C.-Y. Chiu, C.-Y. Chang, C.-F. Chang, Y.-H. Chen, D.-R. Ji, J.-Y. Tseng, Y.-H. Yu, Pt-catalyzed ozonation of aqueous phenol solution using high-gravity rotating packed bed, J. Hazard. Mater. 168 (2009) 649–655.

[8] Y.-F. Rao, H.-J. Luo, C.-H. Wei, L.-F. Luo, Catalytic ozonation of phenol and oxalic acid with copper-loaded activated carbon, J. Cent. South Univ. Technol. 17 (2010) 300–306.

[9] P. Pocostales, P. Álvarez, F.J. Beltrán, Catalytic ozonation promoted by alumina-based catalysts for the removal of some pharmaceutical compounds from water, Chem. Eng. J. 168 (2011) 1289–1295.

[10] Z. Wu, M. Franke, B. Ondruschka, Y. Zhang, Y. Ren, P. Braeutigam, W. Wang, Enhanced effect of suction-cavitation on the ozonation of phenol, J. Hazard. Mater. 190 (2011) 375–380.

[11] M. Sui, S. Xing, L. Sheng, S. Huang, H. Guo, Heterogeneous catalytic ozonation of ciprofloxacin in water with carbon nanotube supported manganese oxides as catalyst, J. Hazard. Mater. 227–228 (2012) 227–236.

[12] Z.-Q. Liu, J. Ma, Y.-H. Cui, Carbon nanotube supported platinum catalysts for the ozonation of oxalic acid in aqueous solutions, Carbon 46 (2008) 890–897.

[13] G. Wu, T.-S. Jeong, C.-H. Won, L. Cui, Comparison of catalytic ozonation of phenol by activated carbon and manganese-supported activated carbon prepared from brewing yeast, Korean J. Chem. Eng. 27 (2010) 168–173.

[14] H. Zhao, Y. Dong, G. Wang, P. Jiang, J. Zhang, L. Wu, K. Li, Novel magnetically separable nanomaterials for heterogeneous catalytic ozonation of phenol pollutant: $NiFe_2O_4$ and their performances, Chem. Eng. J. 219 (2013) 295–302.

[15] Y. Shahamat, M. Farzadkia, S. Nasseri, A.H. Mahvi, M. Gholami, A. Esrafili, Magnetic heterogeneous catalytic ozonation: A new removal method for phenol in industrial wastewater. J. Environ. Health Sci. Eng. 12 (2014) 50–62.

[16] O.A. O'Connor, L.Y. Young, Toxicity and anaerobic biodegradability of substituted phenols under methanogenic conditions, Environ. Toxicol. Chem. 8 (1989) 853–862.

[17] S. Altenor, B. Carene, E. Emmanuel, J. Lambert, J.-J. Ehrhardt, S. Gaspard, Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation, J. Hazard. Mater. 165 (2009) 1029–1039.

[18] APHA (American Public Health Association), Standard Methods for the Examination of Water and Wastewater, twenty-first ed., American Public Health Association, Washington, DC, 2005.

[19] T.F. de Oliveira, O. Chedeville, H. Fauduet, B. Cagnon, Use of ozone/activated carbon coupling to remove diethyl phthalate from water: Influence of activated carbon textural and chemical properties, Desalination 276 (2011) 359–365.

[20] G. Moussavi, R. Khosravi, Preparation and characterization of a biochar from pistachio hull biomass and its catalytic potential for ozonation of water recalcitrant contaminants, Bioresour. Technol. 119 (2012) 66–71.

[21] G. Moussavi, A. Khavanin, R. Alizadeh, The investigation of catalytic ozonation and integrated catalytic ozonation/biological processes for the removal of phenol from saline wastewaters, J. Hazard. Mater. 171 (2009) 175–181.

[22] M. Danish, R. Hashim, M.M. Ibrahim, M. Rafatullah, T. Ahmad, O. Sulaiman, Characterization of acacia mangium wood based activated carbons prepared in the presence of basic activating agents, Bioresources 6 (2011) 3019–3033.

[23] H. Valdés, C.A. Zaror, Ozonation of benzothiazole saturated-activated carbons: Influence of carbon chemical surface properties, J. Hazard. Mater. 137 (2006) 1042–1048.

[24] H. Valdés, V.J. Farfán, J.A. Manoli, C.A. Zaror, Catalytic ozone aqueous decomposition promoted by natural zeolite and volcanic sand, J. Hazard. Mater. 165 (2009) 915–922.

[25] F.J. Beltrán, F.J. Rivas, R. Montero-de-Espinosa, Mineralization improvement of phenol aqueous solutions through heterogeneous catalytic ozonation, J. Chem. Technol. Biotechnol. 78 (2003) 1225–1233.

[26] H. Yin, Y. Zhou, R. Han, Y. Qiu, S. Ai, L. Zhu, Electrochemical oxidation behavior of 2,4-dinitrophenol at hydroxylapatite film-modified glassy carbon electrode and its determination in water samples, J. Solid State Electrochem. 16 (2012) 75–82.

[27] L. Zhao, J. Ma, Z.-Z. Sun, X.-D. Zhai, Catalytic ozonation for the degradation of nitrobenzene in aqueous solution by ceramic honeycomb-supported manganese, Appl. Catal. B: Environ. 83 (2008) 256–264.

[28] A. Bhatnagar, W. Hogland, M. Marques, M. Sillanpää, An overview of the modification methods of activated carbon for its water treatment applications, Chem. Eng. J. 219 (2013) 499–511.

[29] L. Lei, L. Gu, X. Zhang, Y. Su, Catalytic oxidation of highly concentrated real industrial wastewater by integrated ozone and activated carbon, Appl. Catal. A: Gen. 327 (2007) 287–294.

[30] P. Alvárez, J. García-Araya, F. Beltrán, I. Giráldez, J. Jaramillo, V. Gómez-Serrano, The influence of various factors on aqueous ozone decomposition by granular activated carbons and the development of a mechanistic approach, Carbon 44 (2006) 3102–3112.

[31] M. Sánchez-Polo, R. Leyva-Ramos, J. Rivera-Utrilla, Kinetics of 1,3,6-naphthalenetrisulphonic acid ozonation in presence of activated carbon, Carbon 43 (2005) 962–969.

[32] X. Qu, J. Zheng, Y. Zhang, Catalytic ozonation of phenolic wastewater with activated carbon fiber in a fluid bed reactor, J. Colloid Interface Sci. 309 (2007) 429–434.

[33] S. Tong, R. Shi, H. Zhang, C. Ma, Catalytic performance of Fe_3O_4-CoO/Al_2O_3 catalyst in ozonation of 2-(2,4-dichlorophenoxy)propionic acid, nitrobenzene and oxalic acid in water, J. Environ. Sci. 22 (2010) 1623–1628.

[34] A.G. Gonçalves, J.J. Órfão, M.F. Pereira, Ceria dispersed on carbon materials for the catalytic ozonation of sulfamethoxazole, J. Environ. Chem. Eng. 1 (2013) 260–269.

[35] P. Faria, J. Órfão, M. Pereira, Activated carbon catalytic ozonation of oxamic and oxalic acids, Appl. Catal. B: Environ. 79 (2008) 237–243.

[36] H. Valdés, C.A. Zaror, Heterogeneous and homogeneous catalytic ozonation of benzothiazole promoted by activated carbon: Kinetic approach, Chemosphere 65 (2006) 1131–1136.

[37] S. Mortazavi, G. Asgari, S. Hashemian, G. Moussavi, Degradation of humic acids through heterogeneous catalytic ozonation with bone charcoal, React. Kinet. Mech. Catal. 100 (2010) 471–485.

[38] S. Lin, C. Wang, Adsorption and catalytic oxidation of phenol in a new ozone reactor, Environ. Technol. 24 (2003) 1031–1039.

[39] M. Sánchez-Polo, U. von Gunten, J. Rivera-Utrilla, Efficiency of activated carbon to transform ozone into OH radicals: Influence of operational parameters, Water Res. 39 (2005) 3189–3198.

[40] A. Babuponnusami, K. Muthukumar, Advanced oxidation of phenol: A comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes, Chem. Eng. J. 183 (2012) 1–9.

[41] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, Technologies for the removal of phenol from fluid streams: A short review of recent developments, J. Hazard. Mater. 160 (2008) 265–288.

[42] H.-L. Chiang, P.C. Chiang, C.P. Huang, Ozonation of activated carbon and its effects on the adsorption of VOCs exemplified by methylethylketone and benzene, Chemosphere 47 (2002) 267–275.

[43] H. Valdés, M. Sánchez-Polo, J. Rivera-Utrilla, C. Zaror, Effect of ozone treatment on surface properties of activated carbon, Langmuir 18 (2002) 2111–2116.

[44] J. Rivera-Utrilla, M. Sánchez-Polo, V. Gómez-Serrano, P.M. Álvarez, M.C.M. Alvim-Ferraz, J.M. Dias, Activated carbon modifications to enhance its water treatment applications. An overview, J. Hazard. Mater. 187 (2011) 1–23.