

# Photocatalytic removal of nitrate from water using activated carbon-loaded with bimetallic Pd-Ag nanoparticles under natural solar radiation

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## ABSTRACT

The increase of nitrate contamination of surface and groundwater has raised a concern, because of its impact on both environment and human health. In this study, photocatalysis for nitrate treatment in water was conducted using activated carbon prepared from date palm stone decorated with single and bimetallic nanoparticles using solar radiation. The prepared catalyst was characterized by XPS, SEM, EDX, TGA, and surface area analyzer instruments. The photocatalytic effect of the prepared catalyst was studied using nitrate solution and acid scavengers with different concentrations. Significant photocatalytic activity was observed for activated carbon when modified with Pd-Ag. The obtained results showed that the conversion of nitrate takes place mainly through nitrogen gas (N<sub>2</sub>) rather than nitrite (NO<sub>2</sub><sup>-</sup>) or ammonium (NH<sub>4</sub><sup>+</sup>). Formic acid as a hole scavenger with 0.05 M shows the maximum conversion for nitrate. The prepared photocatalyst shows stability for five cycles of nitrate ion reduction. Moreover, the results showed that the prepared catalyst could be applied for the removal of nitrate from groundwater and river water samples.

## 1. Introduction

Wastewater generated from different industrial activities and nuclear fuel cycle activities contains a high concentration of nitrate. Water produced from the backend of a nuclear cycle is produced as high-level and low-level liquid nuclear waste [1]. It is produced as an acidic or alkaline aqueous solution. The high-level nuclear waste contains from 2 to 7 M nitrate added as nitric acid [2]. The low-level nuclear waste contains about 1.6–2.2 M nitrate added as sodium nitrate beside 1.1 M sodium hydroxide [3]. Removal of nitrate is essential before the final disposal [4].

Also, nitrate can contaminate water resources including ground and surface waters as well as wastewater [5]. The increased concentrations of nitrates in water resources are caused primarily by anthropogenic sources such as the excessive use of fertilizers in agriculture, domestic and industrial wastewater, besides animal waste as well. High nitrate concentration may cause eutrophication of natural water resources such as rivers and lakes [6]. In drinking water, it can cause various damages to human health, in particular, cancer and methemoglobinemia (blue

baby syndrome) [7]. The recommended limit of nitrate in drinking water by WHO is 50 mg/L (as nitrate) or 11.3 mg/L (as nitrogen) [8].

Denitrification of water constitutes a great challenge due to the high solubility and stability of nitrate ion in water. Therefore, a great effort has been put to develop techniques for the removal of nitrate from water such as ion exchange, adsorption, reverse osmosis, electro dialysis, electrochemical, photocatalysis, membrane-based methods, and chemical and biological methods [9–15]. Catalysis is the best choice among these technologies because of no production of contaminated disposals, consumes less energy as it can be conducted at mild temperature and pressure, the ability to direct the reaction towards a specific product, and can be designed for use in any location (portable) [16]. In this technology, a heterogeneous catalyst is used to reduce nitrate ion into nitrogen gas (N<sub>2</sub>) with the help of a reducing agent, such as hydrogen (H<sub>2</sub>) gas. Several studies have been conducted to improve the catalytic reduction of nitrate. Catalytic hydrogenation of nitrate in water was conducted using monometallic catalysts such as Pt, Rh, Pd, Ru, Au, and Ag with the support of zirconia, alumina, ceria, titania, silica, and activated carbon [17,18]. Several studies have been reported on the use

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of bimetallic catalysts supported on activated carbon such as Pd–Cu, Pt–Cu, Rh–Cu, and Ir–Cu while Pd–Cu is supported on titania. These studies indicated that bimetallic catalysts are more efficient than monometallic ones [19–21]. Formic acid instead of hydrogen was used to reduce nitrate ion in water as well [22].

Photocatalytic denitrification of drinking water has shown high efficacy and great potential over other technologies [23]. Several photocatalysts have been used for nitrate reduction in water such as reduction of nitrate using formic acid under UV-radiation [24,25], and formic acid with Pd supported on alumina [18,25]. Titanium dioxide (TiO<sub>2</sub>) is one of the most studied in order to prevent the production of undesirable aqueous by-products (nitrite and ammonium) [23,26,27]. Commercial titanium oxide was used also for the same purpose under UV radiation including P25, P90, and hompicate [28]. Furthermore, silver oxide/commercial titanium oxide (P25) was used in the photocatalytic reduction of nitrate with formic acid as a hole scavenger using UV radiation [29].

A few attempts have been made to use the bimetal catalyst Pd/Ag for nitrate reduction in water. In these catalysts, Pd was used as the noble metal component. Palladium catalysts have shown high activity and selectivity for nitrite reduction [30]. Pd acts as an adsorption site for the generated hydrogen and a reduction site for the nitrate ion. It can also increase the lifetime of the generated charge (reduce the recombination rate of hole and electrons) [31,32]. Silver nanoparticles act as a promoter and a photosynthesizer due to their plasmonic properties [33]. Moreover, it has been reported that Ag could enhance the catalytic hydrogenation of Pd compared with other metals [30]. Bimetal catalyst Pd/Ag are used with different supporters including Al<sub>2</sub>O<sub>3</sub> [30,34], and SiO<sub>2</sub>-NH<sub>2</sub> [35].

Activated carbon as a support material has many advantages compared to silica and alumina: (i) it behaves as a semiconductor with an energy band gap, (ii) it is easy to modify its surface chemistry and surface area compared to other supporters [36]. To the best of our knowledge, reduction of nitrate in water using activated carbon decorated with bimetal Ag–Pd nanoparticles under natural solar radiation has not been reported.

Single metal (Ag, Cu, and Pd), and bimetal (Pd–Cu and Pd–Ag) decorated activated carbon were tested separately for removal of nitrate under natural solar radiation. Bimetallic Pd–Ag activated (Pd–Ag Ac) showed the highest efficiency for nitrate removal, so it was used in this study. Activated carbon was prepared from a low-cost resource (date palm stone) using phosphoric acid followed by decoration with bimetallic Ag–Pd nanoparticles (NPs). The prepared composite was used for nitrate reduction under natural solar radiation as a costless, sustainable, and renewable resource of energy. Moreover, using this new approach, the effect of different scavengers' including formic acid, oxalic acid, acetic acid, and ammonium oxalate on the reduction of nitrate was investigated as well. The effect of water ingredients on nitrate reduction and the application of the catalyst on real water samples were studied as well.

## 2. Experimental

### 2.1. Chemicals

Silver nitrate, palladium chloride, phosphoric acid, sodium nitrate, oxalic acid, acetic acid, ammonium oxalate, and formic acid were obtained from Sigma-Aldrich (USA). All chemicals were of analytical grade and used without further purification. Deionized water was used in all experiments.

### 2.2. Catalyst preparation

Activated carbon used in this work was prepared from date palm stone collected from the United Arab Emirates campus. The collected date palm stone was washed then crashed and left to dry in the oven at

70 °C for 5 h. The dried palm stone was soaked in 50% phosphoric acid for 24 h. Subsequently, it was carbonized at 250 °C for 20 h then crushed and sieved [37].

The prepared activated carbon was impregnated with single metal (Ag, Cu, and Pd) and bimetal (Ag–Pd and Cu–Pd) using ion exchange and adsorption processes [38,39]. In this process, 5 g of the activated carbon was treated with a solution of each metal ion (500 mL, 500 ppm) separately. For bimetal impregnation, a mixture of 500 mL and 500 ppm of each metal ion was added to 5 g of activated carbon. The mixture was stirred at room temperature for 2 h. pH of the mixture was measured at the beginning and after 2 h of the stirring. A sharp decrease in the pH of the mixtures (from 6.5 to 3.4) was noticed. However, this decrease in pH was not noticed for the mixture of 5 g activated carbon and distilled water. Then, the impregnated activated carbon was separated by decantation and washed three times with distilled water. For reduction of adsorbed metal ions, 5 mL of hydrazine hydrate in 500 mL distilled water was added to 5 g of the impregnated activated carbon and stirred for 2 h. Finally, the obtained activated carbon was washed with distilled water and dried in a drying oven at 70 °C for 4 h. The obtained activated carbon was used for characterization and photocatalytic experiments. In addition, the impregnated amounts of silver and palladium ions on the surface of activated carbon were determined by the difference between the concentrations of the metal ions before and after mixing with activated carbon using a Varian 710 inductively coupled plasma optical emission spectrometer (ICP-OS). TGA analysis was used to confirm the amount of the impregnated metal on the surface of activated carbon.

### 2.3. Catalyst characterization

The morphology of the prepared activated carbon was characterized using Scanning Electron Microscope (Bruker) equipped with an energy dispersive X-ray analysis system (SEM-EDX). The elemental composition of the surface was characterized by X-ray Photoelectron Spectrophotometer (XPS) using an ESCALAB-250 system with Al-K<sub>α</sub> X-ray. A 90-Quantaqrom Autosorp instrument was used to measure the surface area of the prepared materials, while TA-60 Shimadzu thermal analyzer was used to perform the thermogravimetric analysis (TGA).

#### 2.3.1. Photocatalytic experiments

A mixture of 50 mL nitrate (80 ppm), formic acid (0.05 M), and 0.1 g of Ag–Pd NPs loaded activated carbon was prepared in sealed glass containers. The contribution of the adsorption in nitrate reduction was studied by measuring the quantity of nitrate adsorbed on the catalyst before starting the photocatalytic reduction therefore the mixture was kept in dark for 24 h. In the photocatalytic experiment, this mixture was exposed to sunlight for 8 h from 9 am to 5 pm at the United Arab Emirates university campus. The average sunlight intensity and temperature during the exposure time were 7.5 KWh/sq.m and 38.5 °C respectively. The mixture was kept at 25 °C during the photocatalytic experiments. Several sacrificial samples (1 mL) of this solution were withdrawn regularly at specific time intervals for analysis. For studying the effect of different scavengers, the photocatalytic reduction experiments were carried out in 0.02 M concentration of the scavengers (acetic acid, oxalic acid, ammonium oxalate, and formic acid). Nitrate (NO<sub>3</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), and formate (HCOO<sup>-</sup>) ions were analyzed in the collected solutions using an IC-90 Dionox system equipped with a column and suppressor with the use of carbonate as an eluent. Ammonium ion (NH<sub>4</sub><sup>+</sup>) was analyzed with colorimetric methods by HACK 509 spectrophotometer. All experiments were performed in triplicate and less than 4% (max error measured in this study) of difference was obtained. Therefore, the standard deviation is not plotted for the simplicity of the graphs.

#### 2.3.2. Reactive reducing species detection

The production of CO<sub>2</sub><sup>-•</sup>, reducing radicals formed during photocatalytic nitrate reduction, was detected by measuring the absorbance of

nitro blue tetrazolium (NTB) using UV-vis spectrophotometer at 260 nm [40]. The nitrate reduction experiment was repeated under the same conditions using NTB instead of the nitrate ion. The produced  $\text{CO}_2^-$  radical was analyzed by detecting the concentration of NTB with Varian carry Eclips-50 spectrophotometer. The experiment was carried out in the presence and absence of formic acid scavenger.

### 2.3.3. Effect of water ingredients

The effect of coexisting anions in water such as  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$  and humic acid on the photocatalytic reduction of nitrate using activated carbon decorated with Ag-Pd NPs was studied. The normal photocatalytic nitrate reduction experiments were carried out by mixing 50 mL of 80 ppm nitrate ion solution and 0.05 M formic acid. 0.1 g photocatalyst and 10 mL of 100 ppm  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$  and humic acid were added separately to the nitrate solution. The concentration of nitrate ions was measured after 20 h of the photocatalytic irradiation under natural sunlight radiation. Finally, the percentage of nitrate ion reduction was calculated according to the following equation:

$$\text{Nitrate reduction \%} = \frac{C_o - C_f}{C_o} \times 100$$

where  $C_o$  and  $C_f$  are the initial and final nitrate ion concentrations.

Photocatalytic nitrate reduction for real groundwater and river water samples was carried out to check the efficiency of the prepared photocatalyst for nitrate reduction. Two water samples were collected, one from groundwater near a cultivated land and the other from Nile River, Rached Branch, Near Elkanater Elkhyrea. The two samples were filtered and kept in the refrigerator at 4 °C for the analyses and photocatalytic experiments. Quantification of the major cations and anions beside total organic carbon TOC before and after photocatalytic nitrate reduction experiments was carried out. The anions chloride, sulfate, phosphate, nitrite, bromide, and iodide were measured using an ion chromatography IC (Dionex IC-90 supplied with an AS-14A column and conductivity detector. Major cations were analyzed using ICP-OS spectrophotometer. TOC was measured using Shimadzu TOC-VCHS. The samples were acidified with phosphoric acid before analyses. The photocatalytic nitrate reduction was carried out similar to the procedure in section 2.3.1.

### 2.3.4. Recycling of the prepared photocatalyst

The stability and durability of the prepared photocatalyst were studied by repeating the photocatalytic experiments for five cycles. The experiment was carried out by adding 0.1 g of photocatalyst to nitrate ion solution (50 mL, 80 ppm) in the presence of formic acid (0.05 M).

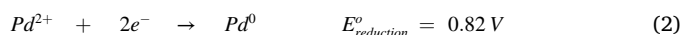
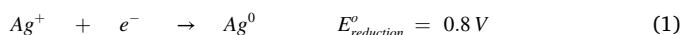
The reaction was conducted in a sealed glass container and exposed to direct sunlight radiation for 15 h. At the end of every cycle, the nitrate concentration was measured, and the mixture was separated by centrifuge. Afterward, the photocatalyst is washed with deionized water and used for the next cycle of photocatalytic nitrate reduction. The percentage of nitrate ion reduction was calculated at the end of each cycle.

## 3. Results and discussion

### 3.1. Photocatalyst characterization

Fig. 1(a) shows the SEM image of the activated carbon impregnated with Ag-Pd NPs. The figure indicates the morphological properties of the surface of the prepared catalyst and the distribution of Ag-Pd NPs on this surface. According to the SEM image, palladium and silver appear as globules and crystal aggregates on the surface of activated carbon with various sizes ranging between 30 and 60 nm. In addition, identification of the elemental composition by EDX is shown in Fig. 1(b), which confirms the composition of nanoparticles. X-ray photoelectron spectroscopy (XPS) is used to identify the valence state of silver and palladium as shown in Fig. 2(a). Although the spectrum contains multiple peaks as well as minor peaks, the main peaks relevant to Ag and Pd are convoluted. The deconvolution spectrum of the Ag XPS peaks that are relevant to Ag is shown in Fig. 2(b). In this figure, the binding energy 368 eV belongs to Ag 3d5/2 whereas 374 eV belongs to Ag 3d3/2. The appeared peaks and energies indicate that silver mainly exists as  $\text{Ag}^0$  [41]. The deconvolution of the palladium spectrum is depicted in Fig. 2(c). The figure shows two peaks, the first is at 340 for Pd 3d5/2 and the second is at 335 eV for Pd 3d3/2. The XPS intensity in the figure is used to estimate the percentage of Ag to Pd to  $\sim 2.5$ . The spectra confirm the complete reduction of palladium ion into the metallic palladium ( $\text{Pd}^0$ ) on the surface of the activated carbon [42].

Based on the XPS analyses, the loaded  $\text{Ag}^+$  and  $\text{Pd}^{2+}$  on the activated carbon surface are completely reduced into Ag and Pd NPs. As silver and palladium have almost the same oxidation/reduction potential [43], therefore, their ions can be reduced by the same reducing agent such as hydrazine hydrate ( $\text{N}_2\text{H}_4$ ) according to the following reactions (1 and 2):



TGA was used to study the thermogravimetric analysis of the prepared activated carbon loaded with Ag-Pd NPs as shown in Fig. 3. The figure reveals that the prepared activated carbon loaded with Ag-Pd NPs

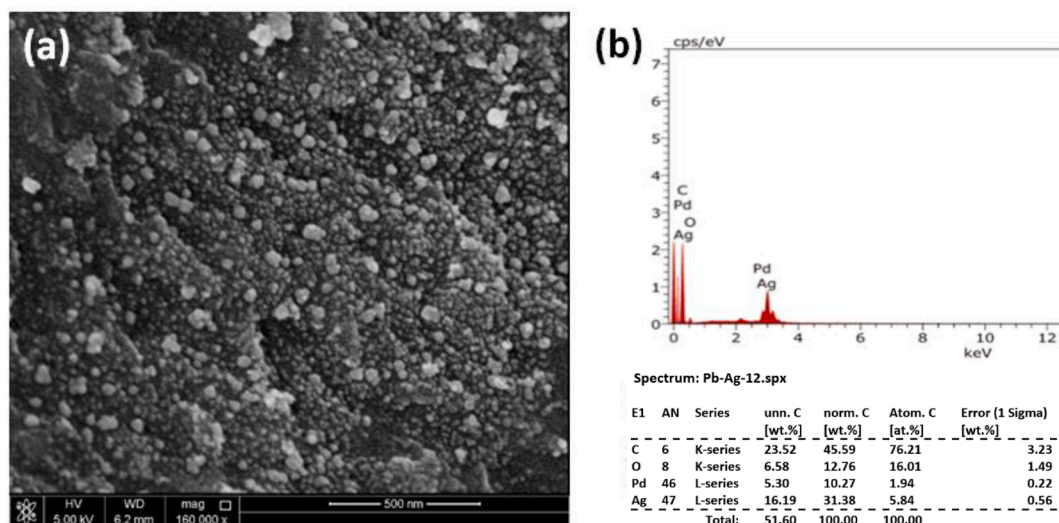


Fig. 1. (a) A representative SEM image of activated carbon loaded with Ag-Pd NPs. (b) EDX of activated carbon loaded with Ag-Pd NPs.

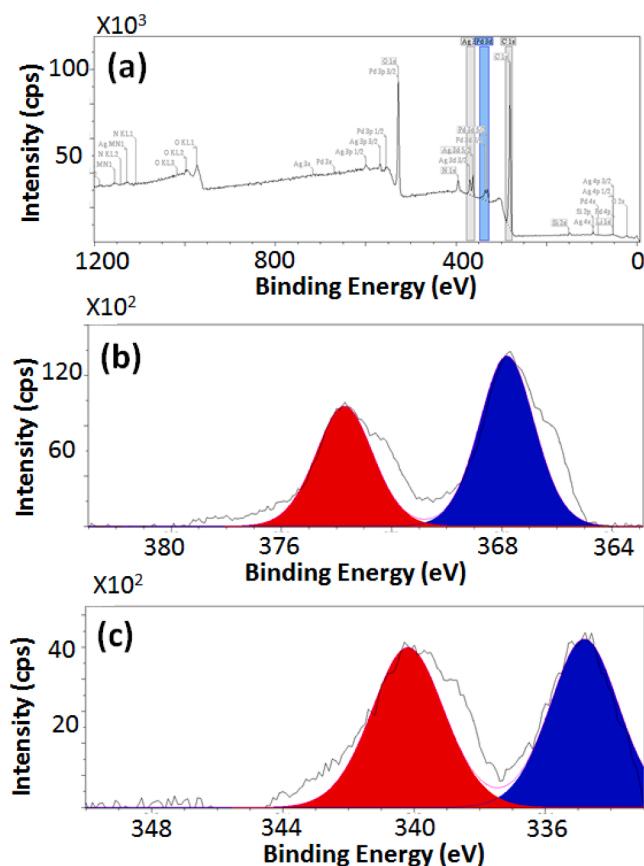


Fig. 2. (a) Elemental XPS scan survey of activated carbon impregnated with Ag-Pd NPs. (b) XPS spectra of Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub>. (c) XPS spectra of Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub>.

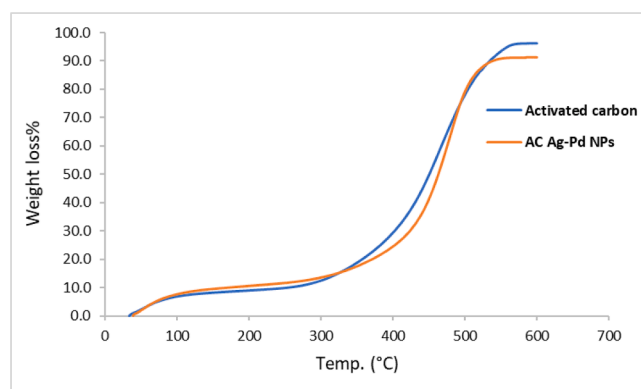


Fig. 3. TGA of the prepared Ag-Pd NPs on activated carbon.

is stable up to 300 °C. Two stages of weight loss appeared in the TGA curve. In the first stage, weight loss between 70 and 120 °C is attributed to the loss of adsorbed water on the surface of activated carbon. In the second stage, (from 300 to 550 °C) decomposition and oxidation of the activated carbon take place. It is worth mentioning here that the remaining ash percentage is high for activated carbon loaded with metals (8.7%) than without (3.8%). Accordingly, the percentage of silver and palladium on the activated carbon support is 4.9%. Based on these findings besides the results obtained from XPS analysis, and the chemical analysis using ICP of the metal ions during the preparation stage, the percentage load of silver is 3.26% and for palladium is 1.63%. The metallic phase obtained in the used samples keeps the same ratio as the fresh samples. In addition, the surface area of the prepared activated

carbon loaded with Ag-Pd NPs catalyst is 380 m<sup>2</sup>/g.

### 3.2. Nitrate photocatalytic reduction

The photochemical reduction of nitrate ion using activated carbon impregnated with different metal ions is shown in Fig. 4. The results showed that about 85% nitrate reduction was attained after 35 h of natural solar irradiation. So, this study was completed using this catalyst (Ag-Pd NPs on activated carbon).

Reduction of nitrate by formic acid was studied in the presence and absence of sunlight and the catalyst as well. Nitrate reduction was not observed if the nitrate is mixed only with formic acid, and without the use of the catalyst in both dark and under sunlight. Also, no nitrate reduction was observed for sample mixtures (catalyst and nitrate solution) treated under sunlight without formic acid. In addition, nitrate reduction by formic acid was not observed if the activated carbon is used without the loaded metallic nanoparticles or if it is loaded with a single metal (silver, palladium, and copper) or bimetallic (Cu-Pd). The obtained results indicated that nitrate ion cannot be reduced by formic acid without the existence of both solar radiation and Ag-Pd NPs. To confirm that reduction of nitrate was due to the reducing agent in the presence of the sunlight and the catalyst, nitrate and formic acid were mixed and stirred overnight in dark. The observed change in the concentration of nitrate was about 4% decrease. So, the decrease in the concentration of nitrate during sunlight irradiation is mainly due to photocatalytic reduction in solution rather than adsorption. Fig. 5 shows a simultaneous decrease in the concentration of nitrate and the formate indicating that the reduction of nitrated occurred by formic acid. The figure shows that traces of nitrite and ammonium are formed, indicating that nitrate could be photocatalytically reduced to nitrite, ammonium besides the nitrogen.

Photocatalytic nitrate reduction requires the presence of hole scavengers to trap the holes so photogenerated electrons will be available for nitrate reduction [23]. Small organic molecules could be used as hole scavengers. Organic acids, alcohols, and humic acid were tested in photocatalytic nitrate reduction. Sodium oxalate and oxalic acid were used for nitrate reduction for TiO<sub>2</sub> supported with bimetallic Cu-Ni [44]. Formic acid, oxalic acid, ethanol, methanol, and humic acid were used as scavengers for TiO<sub>2</sub> supported with Pd-Cu [45]. Formic acid has proven to be the most effective one for nitrate conversion to N<sub>2</sub> selectively and methanol for nitrate to ammonia conversion. Therefore, in this work, acetic acid, formic acid, oxalic acid, and ammonium oxalate have been investigated as hole scavengers for nitrate reduction as shown in Fig. 6. The obtained results show that the rate of nitrate reduction by formic acid is the highest among the investigated hole scavengers. These results are consistent with the reported ones [46]. In addition, changing the concentration of formic acid from 0.01 M to 0.1 M in the photocatalytic reduction of nitrate caused variable effects. Fig. 7 shows that

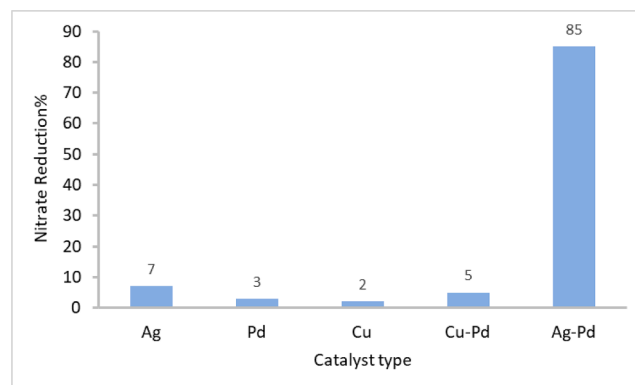


Fig. 4. % Nitrate reduction with activated carbon impregnated with different metals in 0.05 M formic acid after 30 h under solar radiation.



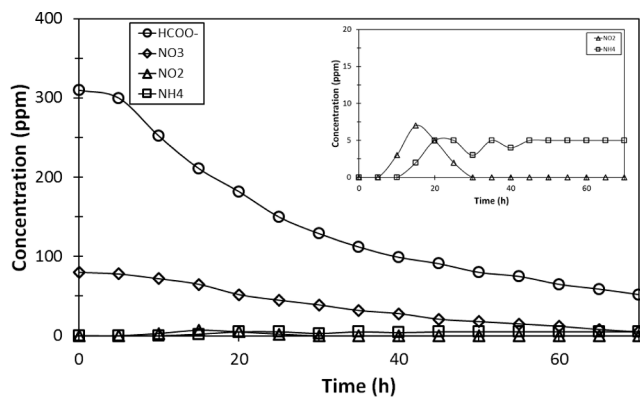


Fig. 5. Reduction of nitrate (80 ppm, 25 mL) under solar radiation in the presence of 200 mg catalyst. The inset is a magnification for the  $\text{NO}_2$  and  $\text{NH}_4^+$ .

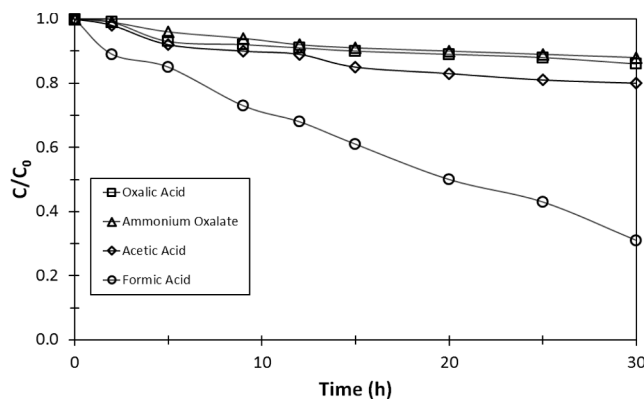


Fig. 6. Effect of hole scavengers (acetic acid, formic acid, oxalic acid, and ammonium oxalate) on photocatalytic reduction of nitrate ion.

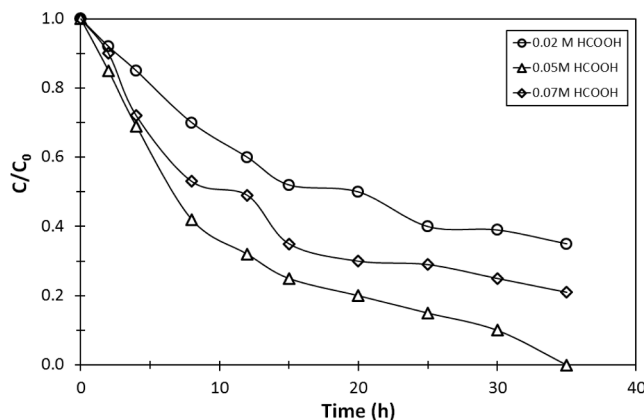


Fig. 7. Effect of the concentration of formic acid (0.02 M) on the photocatalytic reduction of nitrate.

0.05 M formic acid is the most effective concentration for the reduction of nitrate since it showed the highest reduction rate.

### 3.3. Mechanism of photocatalytic reduction

The effect of silver and palladium nanoparticles on the mechanism of nitrate reduction on the surface of the activated carbon was investigated. Investigation of the conductivity of the activated carbon showed that it has an energy band gap between 3.1 and 3.6 eV therefore it behaves as a semiconductor and can absorb light radiations in the regions:

ultraviolet, visible, and near-infrared (200–1200 nm) [47]. Several studies have been conducted on the photocatalytic behavior of the activated carbon irradiated with visible light and UV radiation such as photocatalytic degradation of phenol in water [48]. When carbon materials are exposed to solar radiation, the light will be absorbed causing electronic transitions between  $\pi$  and  $\pi^*$  orbitals and forming  $h^+$  in the valence band and  $e^-$  in the conduction band. If the incident photon has an energy larger than the band gap, it will be absorbed and create an electron-hole-like pair. The photogenerated electrons will be distributed between carbon layers forming a conduction band.

Decorating activated carbon with a noble metal was found to enhance its catalytic effect. In addition, impregnating the activated carbon with bi-metallic nanoparticles such as Ag-Pd (as conducted in this study) improved the photocatalytic characteristics of the activated carbon for nitrate reduction. The proposed mechanism includes photo-excitation of the electrons from HOMO (valency band) to LUMO (conduction band) when irradiated with visible light therefore, electron-hole pairs will be generated [49–51]. Once Ag NPs are dispersed on the activated carbon surface, a heterojunction will be formed between silver nanoparticles and the surface of the activated carbon. The Ag nanoparticles on the surface of the activated carbon are considered as a photosynthesizer. It enhances visible light harvesting. The visible light with energy lower than the energy band gap of the activated carbon is absorbed by silver nanoparticles. The Ag with a dimension less than 10 nm ejects hot electrons to the conduction band of the activated carbon due to localized surface plasmonic resonance LSPR while Ag nanoparticle more than 10 nm ejects hot electrons due to the bulk plasmonic resonance [33]. The conduction band edge potential of carbon is + 0.207 NHE [52]. That is more negative than the reduction potential of  $2H^+ + 2e^- \rightarrow H_2$  which is 0 NHE. So, reduction of hydrogen ions generated from ionization of formic acid takes place. Interestingly, Pd nanoparticles have a high affinity toward hydrogen [53]. Most systems that use hydrogen for nitrate reduction, apply Pd as a catalyst [31]. Also, Pd nanoparticles on the surface of the activated carbon may act as a reservoir for the electrons from the conduction band of the activated carbon due to Schottky barrier formed at the metal semiconductor interface [32]. This reduces the electron hole recombination on the surface of the activated carbon resulting in enhancing its photocatalytic activity. So, nitrate reduction may take place through reduction by hydrogen adsorbed on the surface of Pd nanoparticles (Pd works as a reduction site).

Formic acid was used in this study to enhance nitrate photocatalytic reduction. When formate ion (as a nucleophile) attacks  $h^+$  in the valence bands of the activated carbon or silver nanoparticles impregnated on the surface of activated carbon, reducing radicals such as  $\text{CO}_2^-$  will be formed. The formate radical is a strong reducing agent with  $E^0(\text{CO}_2^-/\text{CO}_2) = -1.8 \text{ V}$  [48,54,55], so it can easily reduce nitrate ions. The formation of  $\text{CO}_2^-$  was confirmed by the decrease of the UV-vis spectra of NTB at 260 nm [49]. Fig. 8 shows the absorbance peak of NBZ at 260

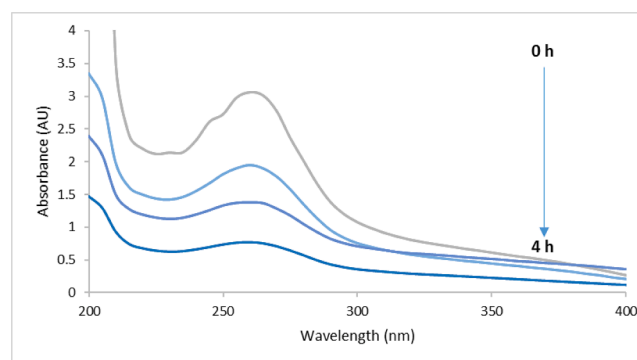
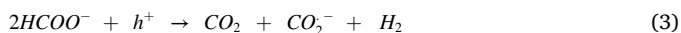


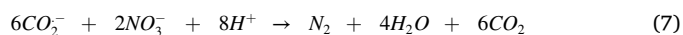
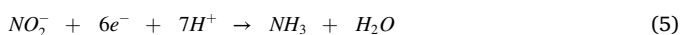
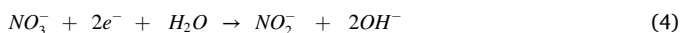
Fig. 8. The absorbance peak of NBZ at 260 nm at different intervals under solar radiation.

nm at different intervals under solar radiation. No change in the concentration of NBZ for samples was observed in dark. Moreover, no change in the concentration of NBT for samples was observed under sunlight without formic acid. So, the decrease of NBT was attributed to the selective reaction of NBT with the formed  $\text{CO}_2^-$  which reacts with NBT to form monoformazan precipitate as end product [40]. This confirms the production of  $\text{CO}_2^-$  reducing radical species which reduces  $\text{NO}_3^-$  as in scheme 1. Similar results were obtained for the formation of  $\text{CO}_2^-$  and reduction of nitrate ion by UV-Irradiation using P25  $\text{TiO}_2$  in the presence of formic acid [29] where the presence of the  $\text{CO}_2^-$  was confirmed by Electron Paramagnetic Resonance. Nitrate reduction in the present study mainly occurs by carbonyl radical and hydrogen generated from formic acid rather than hydrogen from water splitting. The nitrate reduction mechanisms could be summarized in Scheme 1 and equations (3 to 7).

In the reduction reaction of nitrate ion by formic acid, 1 mol nitrate needs 8 mol electrons to be reduced to nitrogen which is equivalent to 8 mol formic acid according to equation (3).



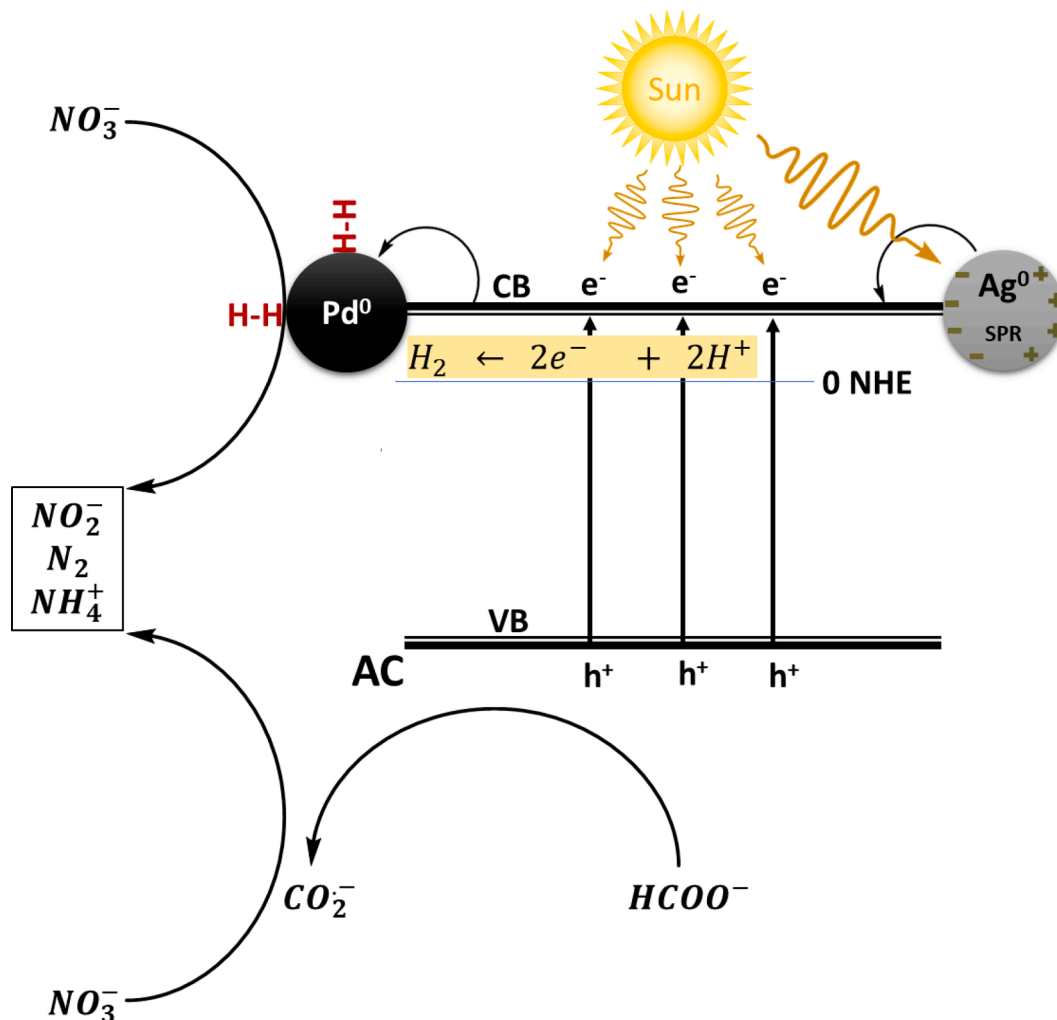
The reduction of nitrate can be expressed as follows:



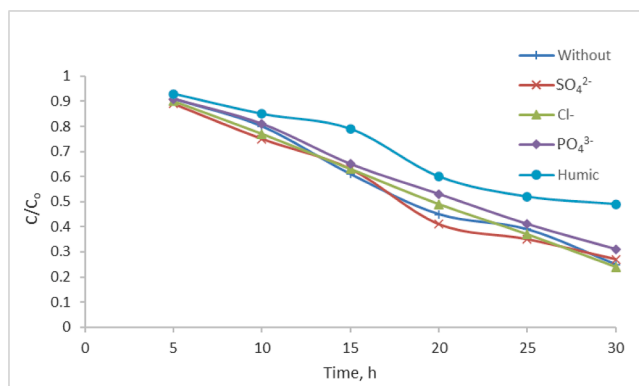
In this mechanism, carbon dioxide produced in equation (7) from the decomposition of formic acid can neutralize  $\text{OH}^-$  produced in equation (4) working as *in situ* buffering. This mechanism that occurred on the catalyst surface is important for the reaction to proceed further.

### 3.4. Effect of water ingredients

Together phosphate and nitrate are the top pollutants in surface and ground waters globally. So, the effect of coexisting anions such as  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$  and humic acid on the photocatalytic reduction of nitrate using activated carbon decorated with Ag-Pd NPs was investigated in the presence of 0.05 M  $\text{HCOOH}$  as scavenger as shown in Fig. 9. The effect of  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and  $\text{Cl}^-$  on the reduction and removal of nitrate is minimal compared with humic acid. Significant inhibition effects were noticed only with humic acid. This effect may be due to the adsorption of humic acid and occupation of the active site of the photocatalyst [56] and tarping of the reactive  $\text{CO}_2^-$  radicals by humic acid [57]. However, it is reported that  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  showed a moderate inhibitory effect on the reduction of nitrate using Pd-Sn/ $\text{Al}_2\text{O}_3$  whereas  $\text{SO}_4^{2-}$  has shown more effect than  $\text{Cl}^-$  [58]. In another study,  $\text{Cl}^-$  showed a more inhibitory effect than  $\text{SO}_4^{2-}$  on the reduction of nitrate using Cu-Pd/AC, and this effect may be attributed to the competition between  $\text{NO}_3^-$  and these ions on the metal active sites [59]. It is reported also that phosphate influenced the nitrate reduction slightly higher than chloride, sulfate, and



Scheme 1. The proposed photocatalytic mechanism of AC loaded with Ag and Pd in nitrate reduction.



**Fig. 9.** Effect of different ions and humic acid on the photocatalytic reduction of nitrate over activated carbon decorated with Pd-Ag NPs under natural solar radiation and 0.05 M HCOOH as a scavenger.

bicarbonate over Ag-TiO<sub>2</sub> in the presence of oxalic acid. The high effect of phosphate on the nitrate reduction may be explained by the number of H<sup>+</sup> released from phosphate being more than that released from other ions so it consumes more electrons [13].

### 3.5. Real water sample application

The study of the photocatalytic degradation of nitrate in real water samples is important for real applications and nitrate removal from water generated from various activities. In this work, two control samples were carried out simultaneously with photocatalytic nitrate reduction for river and groundwater samples. The first one was conducted without a catalyst under solar radiation while the second sample was conducted with a catalyst in dark. No significant reduction of nitrate for the two control samples was noticed. These results indicate that there is no adsorption for nitrate ions in dark and also no photolysis of nitrates or direct interaction between nitrate and formic takes place under solar radiation. In addition, river water and groundwater samples were treated as shown in Table 1. The obtained results show that the nitrate ion is completely removed after photocatalytic experiments from river water and 94% from groundwater. It is worth mentioning here that the TOC concentration decreased dramatically after photocatalytic degradation experiments in river water and was completely removed from the

**Table 1**

Analysis of real water samples (river and ground) after photocatalytic nitrate reduction experiments.

Anions and cations	Concentration (ppm)			
	River water		Groundwater	
	Before photocatalytic experiments	After photocatalytic experiments	Before photocatalytic experiments	After photocatalytic experiments
PO <sub>4</sub> <sup>3-</sup>	2	2.1	34	35
SO <sub>4</sub> <sup>2-</sup>	1.5	1.4	15	12
NO <sub>3</sub> <sup>-</sup>	3.5	*	42	2.4
NO <sub>2</sub> <sup>-</sup>	*	*	*	1.2
Cl <sup>-</sup>	60	62	90	92
Br <sup>-</sup>	*	*	*	*
I <sup>-</sup>	*	*	*	*
Na <sup>+</sup>	54	55	83	81
K <sup>+</sup>	4	3.8	15	15
Ca <sup>2+</sup>	3.5	3.4	18	17
Mg <sup>2+</sup>	12	12.5	25	26
NH <sub>4</sub> <sup>+</sup>	*	*	*	*
TOC	4.9	1.6	2.1	*

\* = Not detected.

Operating conditions: A mixture consists of 50 mL real sample, formic acid (0.05 M), and 0.1 g of Ag-Pd NPs.

groundwater sample. This indicates that mineralization of TOC takes place during photocatalytic nitrate reduction. No considerable change of other anions was detected. Table 1 shows that no, or very small amounts of NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in the real samples after photocatalytic nitrate reduction were detected, indicating high selectivity of our catalyst toward nitrogen gas. However, it is reported that Pd-Ag supported on alumina showed that 56% of nitrate was reduced into ammonium ions [30].

### 3.6. Recycling of the photocatalyst

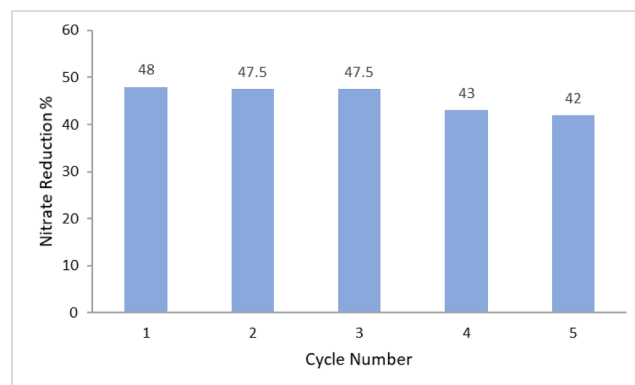
For evaluation of the stability and durability of the Activated carbon decorated with Pd-AgNPs as an efficient photocatalyst for the removal of nitrate ion from water, the photocatalytic reduction of nitrate ion under natural solar radiation was carried out in five cycles. The percentage of nitrate reduction was measured after 15 h using 0.05 M HCOOH as a scavenger. The results are shown in Fig. 10. The photocatalyst showed stability for the first three cycles and a slight decrease in the fourth and fifth cycles. This decrease could be attributed to an unavoidable decrease in the weight of the photocatalyst material during separation and washing between cycles. The results indicate that the photocatalyst could be used efficiently for five cycles of photocatalytic reduction of nitrate.

## 4. Conclusions

Purifying drinking water from nitrate is essential to protect both human health and the environment. Activated carbon prepared from date palm stone as a low-cost source and loaded with bi-metallic Ag-Pd nanoparticles provided a new approach for water denitrification. Nitrate photocatalytic reduction was conducted under solar radiation with the presence of several scavengers as reducing agents. The obtained results showed that nitrate reduction by formic acid was strongly enhanced when the activated carbon was impregnated with Ag-Pd nanoparticles. The maximum conversion and selectivity were found at 0.05 M formic acid. The conversion of nitrate takes place mainly through nitrogen gas (N<sub>2</sub>) rather than nitrite (NO<sub>2</sub><sup>-</sup>) or ammonium (NH<sub>4</sub><sup>+</sup>). No effect was observed on the photocatalytic reduction process due to the presence of sulfate, phosphate, and chloride as coexisting ions. However, humic acid has been found to decrease the efficiency of the processes. The prepared photocatalyst shows stability for five cycles of nitrate ion reduction. Also, a separate systematic study will be carried out on the effect of humic material on the photocatalytic denitrification using the prepared photocatalyst.

### CRedit authorship contribution statement

**Ahmed M. Soliman:** Writing – review & editing, Data curation, Conceptualization. **Dalal Alshamsi:** Methodology, Funding acquisition.



**Fig. 10.** The photocatalytic nitrate reduction using activated carbon decorated with Pd-Ag NPs for five cycles and 0.05 M HCOOH as a scavenger.

**Ahmed A. Murad:** Data curation, Conceptualization, Writing – original draft. **Ala Aldahan:** Supervision, Conceptualization. **Ismail M. Ali:** Writing – review & editing, Formal analysis. **Ahmad I. Ayesh:** Methodology, Conceptualization, Funding acquisition, Writing – original draft. **Ismail A. Elhaty:** Writing – review & editing, Formal analysis.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

No data was used for the research described in the article.

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