Original Article

Photocatalytic Removal of Nitrate from Aqueous Solutions Using Suspended and Immobilized Zinc Oxide

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Abstract

Aim: This research aimed to evaluate the efficiency of photocatalytic removal of nitrate from aqueous solutions using suspended and immobilized zinc oxide (ZnO). **Methods:** A comparison was made between the photocatalytic, suspended, and immobilized ZnO nanoparticles (ZnO NPs) for nitrate removal. In addition, the effect of ZnO NPs either suspended or immobilized was evaluated in the presence of ultraviolet irradiation. The transmission electron microscopy, scanning electron microscopy, and X-ray diffraction analyses were applied to survey the physiochemical properties of ZnO. Photocatalytic degradation of nitrate was investigated using a spectrophotometric approach. **Results:** The ideal function of removing nitrate (90%) was achieved with the concentration of 25 mg/l and in acidic pH. Immobilized catalysts can be used in continuous reactors due to the possibility of elimination of the phase segregation. The rising concentration of NPs to 0.8 g/L was associated with higher efficiency of the removal process. Maximum reduction performance of photocatalytic removal of nitrate (using immobilized and suspended ZnO) was 90% and 81%, respectively. Nevertheless, according to the findings, the immobilized method is highly more efficient for nitrate removal than the suspended method. The optimal time for the photocatalytic process was obtained at 150 min, and after 150 min, the reaction followed the first-order reaction kinetics. **Conclusions:** The photocatalytic technique is efficient for nitrate removal from water and wastewater.

Keywords: Aqueous, immobilized, nitrate, photocatalytic, suspended, zinc oxide

INTRODUCTION

Recently, the attention to pollution of water resources by nitrate has increased worldwide mainly because of the extended use of fertilizers in agronomic activities, dumping huge amounts of chattel manure, and ejecting weak effluent.[1,2] It is well-proved that nitrate causes damage to our health (e.g., methemoglobinemia also called blue baby syndrome and fatal disorders in infants [<6 months]). Moreover, it may cause carcinogenic nitrosamine formation.[3-5] The European Community, World Health Organization, and Environmental Protection Agency developed regulations regarding the maximum pollution level of nitrate at 50, 50, and 44 mg NO_3^-/L, respectively. In Iran, the recommended limit is 50 mg NO_3^-/L.[6-8] Remediation technologies include adsorption, membrane filtration, electrocoagulation, ion exchange, biological denitrification, electrochemical reduction, altered osmosis, electrodialysis, and catalytic remediation. Nevertheless, these methods suffer from not being cost-effective or need of effluents (i.e., post-treatment), and undesirable by-product formation.[9] Recently, the diversified photocatalytic reduction of nitrate on semiconductor substances has also been introduced as a novel technique to reduce contamination with nitrate. The photocatalysis procedure's first reaction is the ultraviolet (UV) radiation absorption by the catalyst with the creation of hollow-electron (h^+/e^-) pairs.[10] The photocatalytic process is capable of addressing the limitations of currently available traditional techniques, particularly biological nitrification.[1] Of different catalysts applied to photocatalytic procedures, titanium dioxide (TiO_2) and zinc oxide (ZnO) are

Access this article online

Quick Response Code:

Website:
https://journals.lww.com/IJEH

DOI:
10.4103/ijehe.ijehe_36_22

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How to cite this article: Panahi M, Fadaei A, Tirgir F, Sedehi M. Photocatalytic removal of nitrate from aqueous solutions using suspended and immobilized zinc oxide. Int J Env Health Eng 2025;14:24.

Received: 21-08-2022, **Revised:** 28-01-2023,
Accepted: 25-03-2023, **Published:** 30-06-2025

known as proper catalysts to degrade many environmental pollutants.[11]

Currently, heterogeneous photocatalytic reduction of nitrate over semiconductor materials has also been developed as a potential technique for controlling the level of nitrate in water.

One of the most disadvantages of these processes are release much value of nanoparticles in water and wastewater, future research should look into overcoming these problems.[12]

Furthermore, ZnO as a nanoparticle with a great area-to-volume ratio is capable of absorbing UV or visible light, inexpensive, nontoxic, unsolvable in water and hydrophilic, photostable against corrosion, has an appropriate flat band and a high band gap, and is more effective than TiO_2.[13] The total surface-catalyzed reduction reactions of nitrate to nitrite, ammonium, and nitrogen are presented separately by reactions (1), (2), and (3), correspondingly.[14]

$$NO_3^- + 2H^+ + 2e^-_{cb}\ NO_2^- + H_2O \qquad (1)$$

$$NO_3^- + 10H^+ + 8e^-_{cb}\ NH_4^+ + 3\ H_2O \qquad (2)$$

$$2NO_3^- + 12H^+ + 10e^-_{cb}\ N_2 + 6\ H_2O \qquad (3)$$

One study reported the concentration of nitrate to be nearly 50 mg/L and the hole scavengers (i.e., formic acid, potassium iodide, and humic acid) were put in (1.0 mmol/L), yielding a pH of 6.8. A 110 W high-pressure Hg lamp was used as a 365 nm UV light origin.[15] Many researchers have shown the removal of nitrate via a photocatalytic process. Rezaee *et al*. reported an efficiency of 13.10%.[16] Another research has investigated the nitrate photocatalytic reduction in an aqueous solution using the Fe-TiO_2/UV procedure. So far, no study has examined nitrate removal through simultaneous application of photocatalytic, suspended, and immobilized methods, we conducted it as a novel study. Generally, the nitrate reduction process requires the addition of an organic compound that functions as a hole scavenger to fill electron holes in the valence band. Moreover, it was noted that the most efficient hole scavenger for nitrate reduction over ZnO is formic acid.[14] On the other hand, formic acid is typically the preferred hole scavenger, although the potential importance of the other organics (i.e., methanol, and oxalic acid) should not be neglected. Various photocatalysts have been applied to nitrate conversion in water like reduction of nitrate using formic acid under UV-radiation.[17,18]

The main objective of this research was to assess the photocatalytic nitrate removal efficiency using suspended and immobilized NPs. The impact of pH (3, 5, 7, 9, and 11), primary nitrate concentration (25, 50, 100, 150, and 200 mg/L), contact time (30, 60, 90, 120, 150 min), and ZnO loading (0.1, 0.2, 0.4, 0.8, 1 g/L) was investigated.

Materials and Methods

Nitrate stocks were prepared from potassium nitrate (KNO_3, purity 99%) obtained from Merck, Germany. The solution pH was modified by 0.1 M NaOH, as well as 0.1 M HCL. The other reagents were of analytical grade.

Zinc oxide nanoparticles immobilization over glass microglobals

ZnO nanoparticles (ZnO NPs) were obtained from the US Research Nanomaterials. Using a thermal-attachment technique, the ZnO NPs immobilized over glass microglobals were prepared. The suspension was prepared using 10 g/L ZnO and distilled water. The pH was controlled to around 3.0, using diluted HCL. Initially, we put the glass plate in a solution of HF (5%) for half a day. In the following, we covered microglobals using a NaOH (0.1 N) solution for a day. After sonication (Elma, model E3OHS, 35 kHz and 170 W), we poured the obtained suspension on the glass microglobals for half an hour and then heated it at 150°C for 2.5 h. Afterward, the glass microglobals were placed within the 450°C-furnace for 2 h. The amount of ZnO NPs that were successfully coated onto each glass microglobal surface was determined from the difference in weight of the glass microglobals before and after the coating process. The NPs were also well immobilized on the microglobals. The size of glass microglobals was 450–550 mm.[19]

Suspension of zinc oxide nanoparticles

UV reactor includes an ultraviolet lamp (power: 150W; wavelength: 254 nm) with medium pressure, and formic acid (0.04 mol/L) as a hole scavenger. A 1-l vessel was used as a pilot plant [Figure 1]. The reactor content was mixed with a magnetic stirrer (150 rpm). Before each experiment, the solution was magnetically mixed in a dark place for half an hour to create an adsorption-desorption equilibrium. The main reason for selecting this technique was the heat generated by the lamp (cooling was performed using a vessel). Using the cooler water, we maintained a temperature of 25°C. An aluminum cover was used to protect the vessel against UV radiation. Afterward, at specific reaction periods, 10 mL of the sample was picked up. A centrifuge was then used to remove the catalyst (5000 rpm for 20 min). After that, the solution passed through a 0.22 μm Millipore filter to remove particles. A circulating water jacket (with an inside diameter of 5 cm and height of 30 cm) was used to maintain the reactor temperature around 25°C. Before all experiments, the solution containing

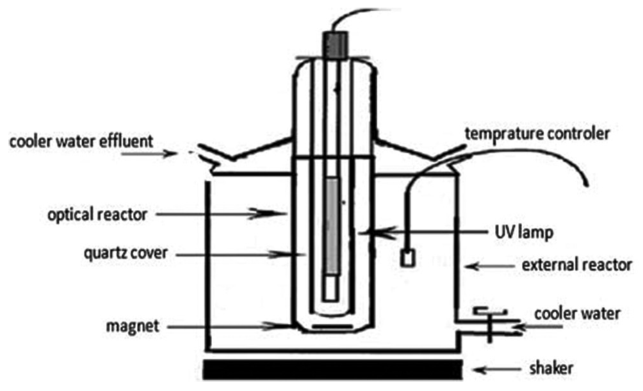

Figure 1: Dynamic relations of the batch mode experimental reactor

nitrate was circulated across the reactor to achieve adsorption equilibrium, whereas the reactor was in the dark. In the present study, the nitrate loss was minor before all experiments as it was adsorbed on the catalyst surface. Parameters important for nitrate reduction process, such as pH (3, 5, 7, 9, 11), NPs content (0.1, 0.2, 0.4, 0.8, 1 g/L), initial concentration of nitrate (25, 50, 100, 150, 200 mg/L), and exposure time (30, 60, 90, 120, 150 min) were studied.

Analytical methods

A pH meter (Metrohm, Model 827 ph lab) was used to measure the pH of the solution. A UV-Vis spectrophotometer (DR-6000) at 220 and 275 nm was used for measuring nitrate (NO_3-N), at 220 and 275 nm. The efficiency of nitrate nitrogen removal (%) was measured according to the following equation: E (%) = $(C_0 - C)/C_0$ where C_0 and C are the nitrate levels at time zero and *t*, correspondingly. Scanning electron microscopy (SEM) (Philips XL 30, the Netherlands) was applied to investigate the surface morphology of the ZnO NPs coating over the glass microglobals. X-ray diffraction (XRD) (Siemens D5000, Germany) was utilized to study the ZnO NP crystalline phase and solid structure (at 200 keV). The ZnO NPs used in the study were a yellowish-white color with a specific surface area of about 50 m^2/g and 99.8% purity. The catalyst was activated at 200°C for 2 h.

Designation of catalytic activity and selectivity

The reduced amount of nitrate ions per time and catalyst weight (mmol/g. min) is defined by the catalytic activity for nitrate reduction. Assuming that only nitrite and ammonium are formed, the formed nitrogen amount to the reduced nitrate amount ratio is defined as the selectivity to nitrogen. N_2 selectivity is estimated based on Eq. (4):

$$\mathrm{SN2} = \frac{[\text{nitrate}]0 - [\text{nitrate}]t - [\text{nitrite}]t - [\text{ammonia}]t}{[\text{nitrate}]0 - [\text{nitrate}]t} \times 100 \tag{4}$$

Where S_{N2} shows N_2 selectivity, $[\text{nitrate}]_0$ denotes the initial nitrate level, and [nitrate]*t*, [nitrite]*t* and [ammonia]*t* are, respectively, the residual levels of nitrate, nitrite, and ammonia after reaction for 150 min.[3]

Statistical analysis

SPSS version 16 (IBM,United States) was used for statistical analysis. For the analysis of data, descriptive tests (mean, percentage, and frequency) were applied. Furthermore, the Chi-square test was used to evaluate the association between variables (R^2 values). The level of significance was set at 0.05.

RESULTS

X-ray diffraction, transmission electron microscopy, and scanning electron microscopy analysis

To further show the morphology of ZnO, transmission electron microscopy (TEM) images of the catalysts were taken and representative photographs are shown in Figure 2a. TEM images illustrate that the size of ZnO particles is bigger than 100 nm. The findings are consistent with the findings of XRD. The attained micrographs illustrate that the ZnO NPs have a good porosity and uniform size [Figure 2b]. The peaks of the XRD patterns of the ZnO NPs are quite sharp, demonstrating the crystalline nature of the nanoparticles [Figure 2c]. Illustrates SEM images of ZnO NPs coated on glass microglobal surfaces [Figure 2d].

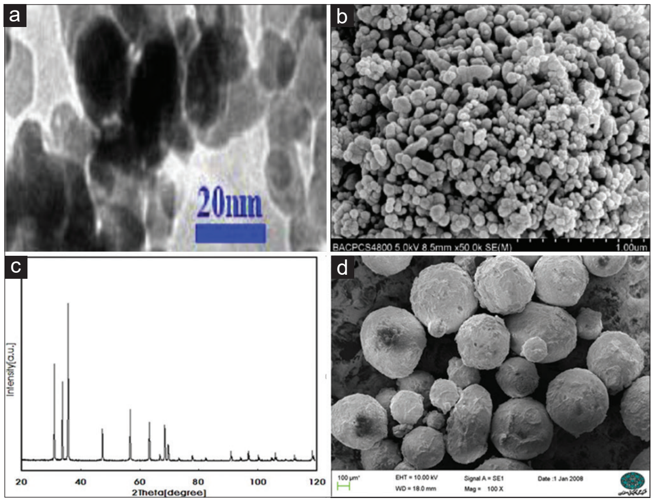

Figure 2: (a) Transmission electron microscopy image of Zinc oxide (ZnO) and (b) scanning electron microscopy images of the ZnO nanoparticles (ZnO NPs) at ×30,000 (c) X-ray diffraction patterns of the ZnO NPs and (d) ZnO NPs coating over glass microglobal surfaces at ×5000

Effect of pH on nitrate photocatalytic degradation

Results of pH variation (3, 5, 7, 9, and 11) concerning the efficiency of nitrate removal revealed a distinction of approximately 31% in the efficiency of removal for pH of 5 and 11 [Figure 3]. The maximum removal was found at pH 5 in ZnO suspended (90%), and immobilized ZnO (81%) [Figure 4]. Summarized effects of pH on the photocatalytic removal include: pH 5 (90%), pH 3 (81%), pH 7 (71%), pH 9 (64%), and pH 11 (56%); pH 5 (81%), pH 3 (71%), pH 7 (65%), pH 9 (59%), and pH 11 (53%) in suspended and immobilized methods, respectively.

Impact of primary level of nitrate on its photocatalytic degradation

The impact of primary nitrate level on photocatalytic degradation at five concentrations (25, 50, 100, 150, and 200 mg/L), whereas formic acid concentration was kept constant (0.04 mol/L) under the test state is shown in Figures 5 and 6.

The catalyst dosage effect on photocatalytic degradation of nitrate

As shown in Figures 7 and 8, in both suspended and immobilized methods, the optimum catalyst amount for nitrate removal is 0.8 g/L.

Kinetic research

Several experiments were carried out to study the kinetics of nitrate photocatalytic degradation under appropriate

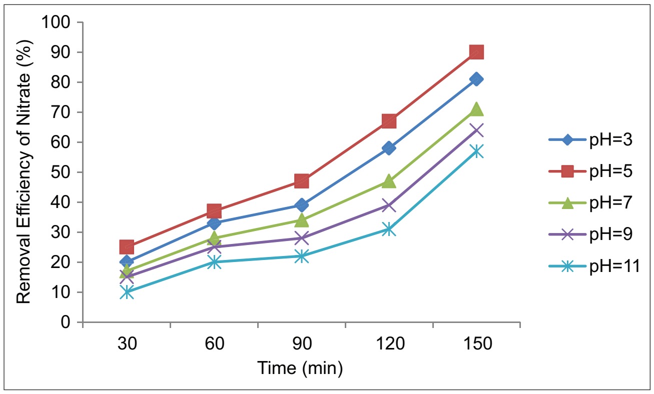

Figure 3: Effect of pH on photocatalytic nitrate; C_0 = 25 mg/L and zinc oxide immobilized = 0.8 g/L

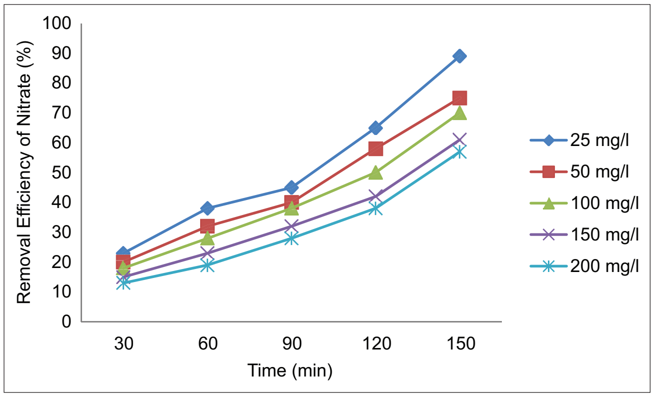

Figure 5: Initial level of NO_3 effect on its photocatalytic degradation; pH 5 and zinc oxide immobilized = 0.8 g/L

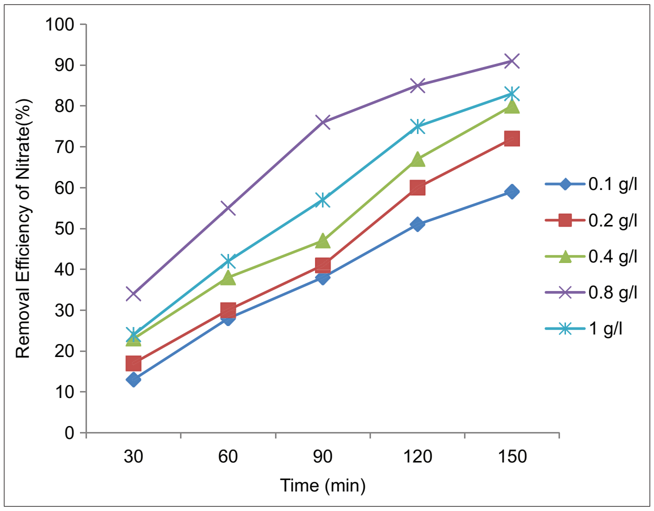

Figure 7: Effect of catalyst dosage on photocatalytic degradation of NO_3 (zinc oxide immobilized); C_0 = 25 mg/L, pH = 5

conditions ([ZnO] suspension = 0.8 g/L, initial nitrate concentration = 25 mg/L, solution pH = 5). The–ln([nitrate]/[nitrate]$_0$) versus duration of irradiation for nitrate photodegradation plots, k, the apparent rate constant in the presence of ZnO immobilized (0.0131 min^{-1}), and suspension ZnO (0.0115 min^{-1}) are shown in Figure 9. The nearly first-order kinetic of the photocatalytic reaction was shown by the good linearity of the –Ln (C/C$_0$) versus irradiation time plot with R^2 values of > 0.90 in both cases.

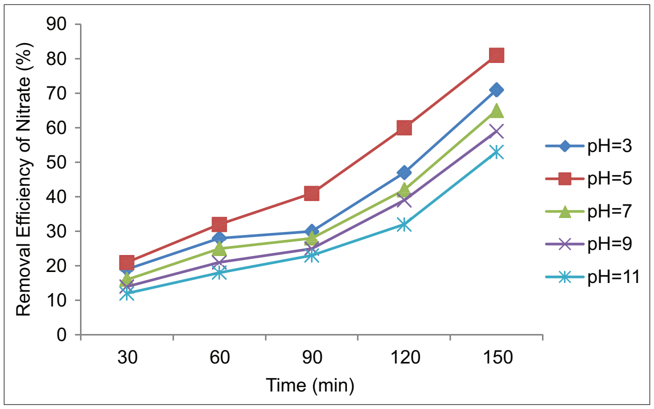

Figure 4: Effect of pH on photocatalytic nitrate; C_0 = 25 mg/L and zinc oxide suspended = 0.8 g/L

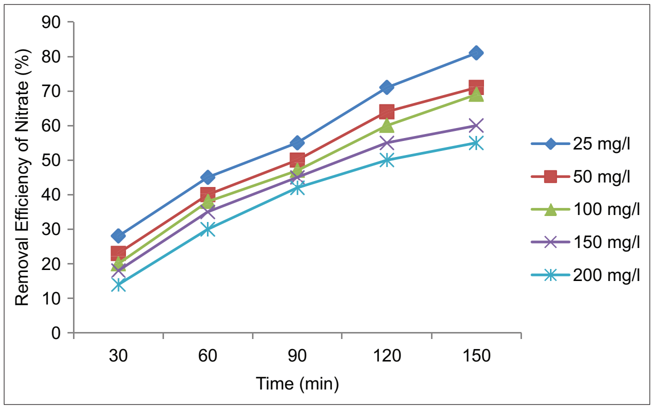

Figure 6: Initial level of NO_3 effect on its photocatalytic degradation; pH 5 and zinc oxide suspended = 0.8 g/L

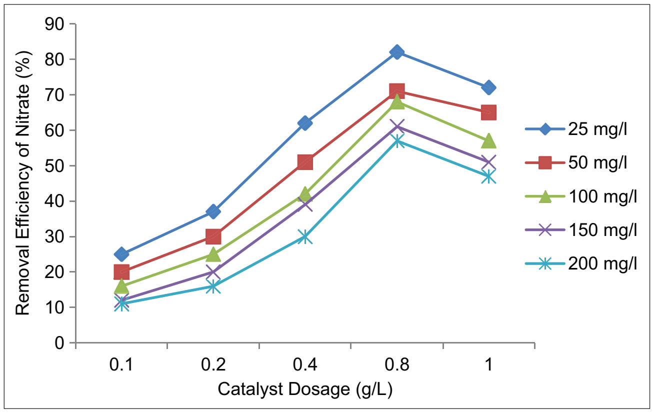

Figure 8: Effect of catalyst dosage on photocatalytic degradation of NO_3 (zinc oxide suspended); C_0 = 25 mg/L, pH = 5

DISCUSSION

In this study, a comparison of photocatalytic suspended and immobilized ZnO processes for the removal of nitrate from

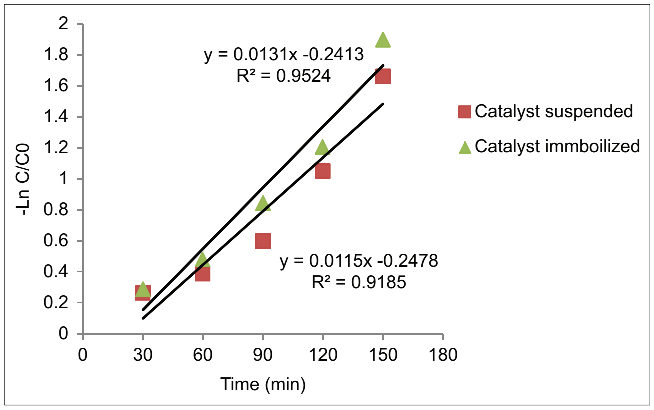

Figure 9: Degradation kinetics of nitrate by means of different studied processes zinc oxide ($c_0 = 25$ mg/L, and pH 5)

aqueous solutions was carried out. In the acidic and alkaline environments, the photocatalyst surface is protonated and deprotonated, respectively.[20] These findings indicate that this photocatalytic reduction reaction was significantly affected by pH in the reaction solution.

In acidic circumstances that are usually utilized for NO_3^- reduction tests, hydroxylamine protonation reaction is done based on its acid-base Eq (7) with a pKa = 5.93. Hydroxylamine reduction yields ammonia (NH_3) through Eq (8), i.e., in equilibrium with NH_4^+, pKa = 9.25 (relation [9]).[21]

$$HNO + H^+ + e^- \rightarrow NH_2O^\bullet \qquad (5)$$

$$NH_2O^\bullet + H^+ + e^- \rightarrow NH_2OH \qquad (6)$$

$$H_2NOH + H^+ \leftrightharpoons H_3NOH^+ \; pKa = 5.93 \qquad (7)$$

$$H_3NOH^+ + e^- \rightarrow NH_3 + {}^\bullet OH \qquad (8)$$

$$NH_3 + H+ \leftrightharpoons NH_4^+ \; pKa = 9.25 \qquad (9)$$

Based on the photocatalytic reduction of nitrate nitrogen in water, the rate of nitrate nitrogen removal is raised over time [Figures 6 and 7]. Findings of this study illustrated that in the lack of UV light, no evidence was obtained over a 150 min period for consumption of nitrate or formic acid.

One study reported that the photocatalytic nitrate reduction reaction is time-dependent.[19] Such findings support the results reported by Shand and Anderson, indicating the incidence of nitrate reduction through nitrite and ammonia through TiO_2 NPs in the presence of oxalic acid.[22] According to another study, the ideal activity of nitrate removal was observed in acidic pH at the concentration of 100 mg/L through the Ag-doped TiO_2/UV process.[23] In a study by Malmir and co-workers indicated that the maximum value of nitrate elimination by ZnO/AgI graphene-based nanophotocatalyst in visible light was found as 77%, and 97% under the UV light in pH = 6 at the concentration of 100 mg/L.[24] A study reported that the best UV/sulfite process could efficiently decrease nitrate to nitrogen gas with about 100% denitrification performance in 90 min.[25] Another study found that the maximum nitrate removal of both Cu–nZVI and Cu–nZVI/TiO_2 processes occurred at a pH of approximately 5.0–6.0. Similar findings are found in the photocatalyzed degradation of organic contaminants.[26] In a study on photocatalytic nitrate removal using methanol, the maximum removal occurred in acidic pH.[27] In a study on ciprofloxacin decomposing using photocatalysis/ozonation, the highest removal efficiency was found to be at pH 7, and the removal efficiency was reduced to some limit as pH increased.[28] Another study reported that beneath an acidic situation, nitrogen gas was the final product. In neutral pH conditions, only the formation of nitrite was observed.[3]

The pollutant initial concentration significantly affects the removal efficiency in the photocatalytic process.[28] Nitrate removal was negatively associated with the initial level (suspended and immobilized methods). This can be attributed to an increase in the rate of nitrate light absorption due to its higher initial level.[23] Indeed, progression in reaction, particularly when the initial concentration is high, causes the formation of some intermediates, which begin to competitively adsorb on the catalyst surface.[3] In other words, degradation is negatively associated with pollutant concentration, while the catalyst is constant.[29] Application of +hvb scavengers such as oxalic acid, acetic acid, citric acid, sodium oxalate, ethanol, sucrose, humic acid, formic acid, or methanol enhances nitrate transformation through photocatalytic reduction. Formic acid is not a direct reductant in these experimental situations, but it rather behaves as a hole scavenger.[30] It is well-documented that to reduce nitrate ions, a sacrificial reagent is of paramount importance. Besides, various sacrificial reagents have different redox properties.[19] In a study, Krasae and Wantala reported the considerable effect of initial nitrate concentration on efficiency nitrate removal.[31] Another study indicated that nitrate removal was inversely associated with the initial level.[32]

Formic acid is the most efficient hole scavenger for the reduction of nitrate due to the simple structure of carboxylic acid and single-electron mechanism of direct transfer that only produces carbon dioxide anion radical ($CO_2^\bullet$—) reductant based on Eq. 13. However, there are additional benefits to the use of formic acid in photocatalytic reduction of nitrate. The nitrite production and formate consumption revealed that the reduction of nitrate to nitrogen gas was the main mechanism of nitrate removal.

According to the results of this study, the only product was nitrogen gas, so the reaction takes place according to Eq. (10). Consequently, one molecule of formic acid should reduce two holes (Eq. 15). First, formic acid adsorbs on the surface of ZnO and disprotionates into a formate anion and a proton (Eq. 12). $CO_2^{\bullet -}$ (Eq. 13) is formed as the formate reacts with one hvb$^+$ (Eq. 14). Hence, the overall reaction for formic acid can be described as Eq. (15).[14,22,33] Depending on the hole scavenger chosen, conversion differences can be attributed to the nature of the reactive species that are formed on the photocatalyst surface.[34] de Bem Luiz *et al*. found formic acid to be the most effective hole scavenger with regard to NO_3 to N_2 conversion selectivity.[35] In their study, Park *et al*. reported the ZnO nanomaterial degradation to be about 13% of nitrate. Moreover, the degradation rate was improved by five-fold with the addition of methanol as a hole scavenger.[36] Another study reported the formic acid rate to be twice as fast as oxalic acid.[37] In another study, Wehbe *et al*. stated that in the photocatalytic nitrate, UV irradiation considerably enhanced the reaction in the presence of both hydrogen and formic acid.[20,38] Another study reported that in the presence of formic acid, nitrate could be entirely removed by all catalysts.[34] A study by Soliman *et al*. indicated that formic acid as a hole scavenger with 0.05 M shows the highest conversion nitrate to nitrogen gas nitrite or ammonium.[17]

$$2NO_3^- + 5HCOO^- + 7H^+ \rightarrow N_2 + 5CO_2 + 6H_2O \qquad (10)$$

$$ZnO + hv \rightarrow e^- + h^+ \qquad (11)$$

$$HCOOH \rightarrow H^+ + COOH^- \qquad (12)$$

$$HCOO^- + hvb^{\,+} \rightarrow HCO_2{\bullet}- \rightleftharpoons H^+ + \mathrm{CO2}^{\bullet -} \qquad (13)$$

$$CO_2^{\bullet -} + hvb^+ \rightarrow CO_2 \qquad (14)$$

$$HCOOH + 2hvb^+ \rightarrow CO_2 + 2H^+ + 2e^- \qquad (15)$$

A catalyst dosage is a key parameter in the processes of heterogeneous photocatalysis.[39] In suspended methods, the catalyst level is among the most important design factors due to its effect on the light diffusion and subsequently, the photocatalytic activity. Similarly, in immobilized methods, the film thickness is an important factor owing to its direct effect on the amount of the light absorbed.[40]

Initially, the enhanced amount of catalyst was associated with an increased removal rate of nitrate, and then it decreased. However, the increased dosage of the catalyst reduced the efficiency of photo-degradation of nitrate. The rates of pollutants' photo-decomposition are dependent on the catalyst's active site and photoabsorption. Sufficient loading of the semiconductor enhances the rate of electron–hole pairs production for improving pollutant degradation. Nevertheless, the addition of semiconductor in a high dosage was associated with the reduced light piercing through the photocatalyst suspension.[34] One study revealed that the certain blocking effect of the suspended catalyst particles on UV irradiation is due to the high value of catalyst added, which is followed by the reduced usage of UV light.[41] Another study indicated that more increase in catalyst concentration reduces the photodegradation efficiency of nitrate. The catalyst's active site and photo-absorption affect the pollutants' photodegradation rates.[3]

These findings are consistent with the results obtained by de Bem Luiz *et al*. that showed nitrate ions are photocatalytically reduced in water over metal-modified TiO_2.[42] Another research showed a direct association between the pollutant degradation and the catalyst concentration that is among the properties of diverse photocatalysts.[43] Ge *et al*. found an increase and then a reduction in the rate of nitrate nitrogen removal by increasing the catalyst value. The highest rate of nitrate nitrogen removal was obtained at a catalyst dosage of 0.8 g/L.[44] Similar or even better results were obtained compared to those reported by other authors [Table 1].

These findings are consistent with the study by Shand and Anderson that reported nitrate reduction with TiO_2 NPs in the presence of oxalic acid reaction follows first-order kinetics.[22] Tugaoen stated that the reduction of nitrate with TiO_2 NPs in the presence of formic acid reaction follows pseudo-first-order kinetics.[21] Another study demonstrated that the NO_3^- degradation conformed well to the first-order kinetics with a rate constant (k) of 0.038 min^{-1}.[15] One study showed that the suspended system is highly more efficient compared to the immobilized system of the micropollutant clofibric acid removal.[40] Nitrate photocatalytic treatment in aqueous solutions increased a positive correlation between time and removal rate of nitrate nitrogen.[44] Anyway, the mechanism showed that the first two-stage reactions of nitrate to nitrite and nitrite to ammonia are reduction

Table 1: Comparison results of nitrate removal efficiency in an aqueous solution using advanced processes of oxidation

Process	NPs	Hole scavenger	Operation conditions	Removal efficiency (%)	Reference
VU/ZnO	ZnO=0.8 g/L	Formic acid 0.04 mol/L	Medium-pressure Hg lamp 150 W, pH=5, time=150 min, $(NO_3)_0$=25 mg/L	90	Present study
UV/TiO_2	TiO_2=0.25 g	Formic acid 1 mm	High-pressure Hg lamp 110 W, pH=6.8, time=120 min, $(NO_3)_0$=0.8 mm	52.5	[15]
UV/TiO_2	TiO_2=NR	Formic acid 40 mm	Medium-pressure Hg lamp 400 W, pH=2.6, $(NO_3)_0$=7.14 mm	64	[37]
UV/PANI@ $W_{18}O_{49}$ composite	Pure $W_{18}O_{49}$. PANI@ $W1_8O_{49}$=50 mg	Citric acid 2 mm	300 WXe lamp, $(NO_2^-)_0$=1.0 mm, pH=3.0, time=60 min	93.63	[45]
UV/Pd/$NaTaO_3$	Pd/$NaTaO_3$=0.8 g	Oxalic acid 60 mm	Hg lamp 500 W, $(NO_3)_0$=1.6, pH=3.0, time=60 min	100	[46]
UV/Fe-TiO_2	Fe-TiO_2=1 g/L	Nitrate and Formic acid of 1:8 (M/M)	15 W black light, $(NO_3)_0$=100 mg/L, pH=2.75, time=360 min	65.97	[47]

NPs: Nanoparticles, UV: Ultraviolet, PANI@$W_{18}O_{49}$: Polyaniline-decorated three dimensional $W_{18}O_{49}$, ZnO: Zinc oxide, TiO_2: Titanium dioxide, NR: Not Rated reactions, but some oxidation reactions are involved in the conversion of the ammonia to nitrogen and hydrogen. Indeed, photocatalysis is appropriate for both reduction and redox reactions due to the simultaneous production of e^- and h^+ on ZnO under UV irradiation. The highest nitrate degradation efficiency (suspended and immobilized methods) occurred at pH = 5, initial nitrate 25 mg/L, and 0.8 g/L ZnO [Figure 10]. One of the problems with these processes is NPs recycling, which can be addressed by metal oxide nanomaterials doping and co-doping, NPs immobilization using suitable matrices, and nano-based filtration by clay/ZnO NPs combination.[11,28] Therefore, the effect of both ZnO oxidation and reduction on appropriate light irradiation, and electron-hole recombination on ZnO play a role in the weak removal of nitrate.[48]

TiO_2/ZnO and other photocatalysts are utilized as suspended slurries in most research studies.[40,49] However, there are many disadvantages to slurries, including decreased proficiency caused by the solutions' turbidity and light dispersion, agglomeration of catalyst, and the need for isolation after purification.[49] To overcome these problems, immobilized ZnO photocatalysts were studied as an alternative to slurry methods.[40] Moreover, immobilized catalysts can be used in continuous reactors due to the possibility of elimination of the phase segregation. There are many advantages to immobilized method, including no need for final separation of catalysts, more steady for reproducibility reaction, and synergistic effect process with aeration.[12]

CONCLUSIONS

Photocatalytic degradation of nitrate was carried out in ZnO (suspended and immobilized techniques) under UV irradiation. The impacts of time, pH, and dose efficiency (suspended and immobilized methods) occurred at pH = 5, initial nitrate 25 mg/L, and 0.8 g/L ZnO. The degradation of nitrate was negatively associated with initial concentration. Also, in this research, findings revealed that the immobilized technique is highly more efficient for nitrate removal compared to the suspended technique. In addition, findings showed a higher rate of nitrate photodegradation in the presence of immobilized ZnO as compared with the suspended ZnO. Nitrate reduction happens through nitrite and ammonia. To overcome slurry method problems, immobilized ZnO photocatalysts were studied as an alternative to slurry methods. However, based on the finding, both processes are efficient for removal for nitrate removal from water and wastewater. Nevertheless, in full scale, much more nanoparticles are release in the environment, and future research should look into overcoming these problems. It can be argued that the aforementioned technique is efficient for nitrate removal from water and wastewater.

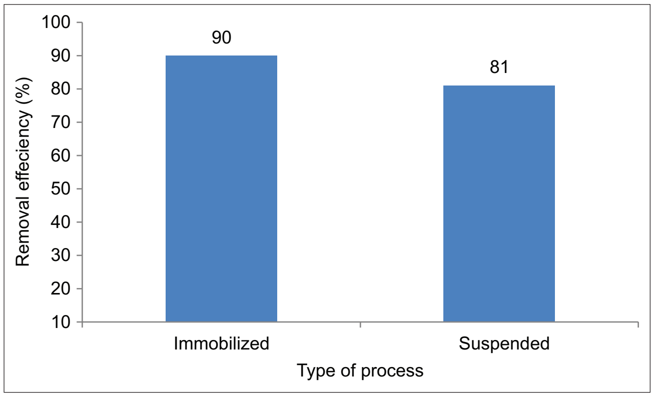

Figure 10: Nitrate removal (%) by means of different studied processes (C_0 = 25 mg/L, zinc oxide = 0.8 g/L, and pH 5, $P < 0.05$)

Financial support and sponsorship

The authors are grateful to Deputy of Research and Technology of Shahrekord University of Medical Sciences (SKUMS) for financial support and laboratory assistance of the Department of Environmental Health Engineering, School of Health, SKUMS, Shahrekord, Iran.

Ethics code

IR.SKUMS.REC.1389.186.

Conflicts of interest

There are no conflicts of interest.

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