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Activation of zinc particles with 3-(N-morpholino)propanesulfonic acid buffer and ultrasound for nitrite reduction

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ABSTRACT

Zinc (Zn^0) is a potent zero-valent metal (ZVM) capable of promoting both oxidation and reduction reactions in water. Similar to other ZVMs, Zn^0's reactivity is rapidly retarded in water. This study aims to improve the activation of zinc particles (Zn^0) by ultrasound in aqueous solutions buffered with 3-(N-morpholino)propanesulfonic acid (MOPS). Nitrite (NO_2^-) was chosen as a model compound to evaluate the effectiveness of ultrasonic zinc-MOPS treatment (US/Zn^0/MOPS). Under similar experimental conditions, the maximum percent nitrite removal by Zn^0 (8 g/L) in MOPS buffered solutions was around 45%, but it increased above 99% when ultrasound was introduced at 220.5 W. Results obtained from scanning electron microscopy-energy-dispersive X-ray spectroscopy and X-ray diffraction measurements have suggested that during US/Zn^0/MOPS treatment, nitrite was reduced to nitrogen gas (N_2) while Zn^0 was oxidized to Zn^{2+} and/or $Zn(OH)_2$. The results also indicated that the high nitrite reduction achieved by the combined method was due to a joint effect of both catalysts on zinc activation.

Keywords: 3-(N-morpholino)propanesulfonic acid; Reduction; Surface activation; Ultrasound; Zero-valent zinc

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1. Introduction

Groundwater nearby agricultural fields contain high concentrations of nitrite and nitrate due to the excessive use of nitrogen fertilizers and the remnants of animal and plant wastes. All these nitrogen-rich organic substances are biochemically degraded to ammonia, nitrite, and nitrate in a consecutive order through ammonification and nitrification reactions [1,2]. Such inorganic nitrogenous contaminants are then carried into groundwater by infiltrating rain and irrigation water. Among all nitrogen species, nitrite and Kjeldahl nitrogen are probably the most toxic ones and at high concentrations they cause sudden fish deaths in surface waters [3]. The maximum concentration level for nitrite in natural waters has been set to 1 mg/L in terms of nitrite–nitrogen (NO_2^-–N) [4].

The chemical denitrification of nitrite/nitrate to nitrogen gas has lately been a subject of extensive research [5]. In this context, iron (Fe^0), aluminum (Al^0), magnesium (Mg^0) or zinc (Zn^0) have been frequently tested for nitrite and nitrate reductions [6–9]. The suitability of a zero-valent metal (ZVM) in water and wastewater remediation may depend on a variety of factors including its target contaminant, physicochemical properties, or manufacturing cost. For example, iron (Fe^0) has received more attention in water treatment due to its low production cost and suitability for the Fenton reactions [10]. However, micro-scaled Fe^0 particles are not very effective for the reduction of contaminants due to its low electrochemical potential ($E° = 0.44$ V) [11–14].

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Zero-valent aluminum and magnesium are highly reactive zero-valent metals that can rapidly reduce NO_2^-/NO_3^- to N_2 or NH_4^+ especially under acidic conditions [8,15]. However, both metals are capable of reacting with water, and thus consumed in excessive amounts. Besides, aluminum and magnesium are light metals, and thus their recovery from water for reuse or disposal after treatment might be challenging. Zinc (Zn^0) is another alternative catalyst ($E° = 0.76$ V) having an electrochemical potential greater than iron ($E° = 0.44$ V), but lower than aluminum ($E° = 1.67$ V) and magnesium ($E° = 2.37$ V). Similar to other ZVMs, Zn^0 is also rapidly oxidized in water, and then coated with a thin passive oxide layer composed of $Zn(OH)_2$ [16,17]. A variety of chemical reagents such as strong acids, alkaline salts, and oxidants have been used to minimize the surface passivation of Zn^0 during water treatment [9,18]. Zn^0 is an effective reducing agent especially at low pHs, and thus consumed in excessive amounts. In addition, the resulting acid derivatives for pH control may cause secondary pollution in water [19].

An alternative to acidification, ultrasound seem to be promising for the activation of metallic particles due to its surface cleaning effects. The ultrasonic shear forces not only activate the metallic particle, but also increases its porosity, so does the adsorption capacity [20,21]. The ultrasonic activation of Zn^0 can be limited especially at alkaline and neutral pHs due to the high stability of zinc surface oxide layer [22–24].

In this study, we aimed to enhance the activation of Zn^0 with ultrasound for nitrite removal at neutral pH conditions using 3-(N-morpholino)propanesulfonic acid (MOPS) buffer. MOPS is an organic acid with a pK_a of 7.2 suitable for buffering the pH of aqueous solutions to neutral values. The use of MOPS buffer in an oxidation–reduction process might be beneficial due to two important reasons. First, because MOPS is highly biodegradable, it is readily eliminated through biological treatment after being utilized in chemical oxidation processes. Second, MOPS neutralize the pH of the water around 7, and thus minimizes the consumption of metallic powder and eliminates the need for final pH adjustment.

2. Materials and methods

2.1. Materials

Zinc powder (–110 mesh, 7.13 g/cm³) of 99.9% purity was purchased from Alfa Aesar, UK. All other chemicals including sodium nitrite and MOPS buffer were analytical grade and used without further purification. A 1,000 mg/L of nitrite (NO_2^-–N) stock solution was prepared by dissolving 4.92 g sodium nitrite ($NaNO_2$) in 1-L de-ionized (DI) water, and subsequently used in oxidation–reduction experiments. Unless otherwise specified, the initial nitrite concentration in standard samples was always 10 mg/L as NO_2–N, which is roughly the average amount found in most relevant water and wastewater systems.

2.2. Experimental procedure

The batch experiments were conducted in a 250 mL of glass reactor containing 200 mL of nitrite solution. The nitrite solutions were saturated with argon gas to remove the oxygen from water. The reactor included a thin jacket through which cooling water was circulated to maintain temperature constant for the experiments made with ultrasonic treatment. 0.2–1.6 g of zinc powder (1–8 g/L) and 0.2 g of MOPS were weighed on an analytical balance and added into 200 mL nitrite solutions. The MOPS buffer was used to keep the pH neutral during the experiments. The nitrite samples containing zinc and MOPS powders were stirred simultaneously on a magnetic stirrer at 250 rpm (Zn^0/MOPS) and on separate experiments mixed only with ultrasonic treatment (US/Zn^0/MOPS). The ultrasonic mixing was performed using VibraCell 505 model (20 kHz) sonic instrument, equipped with a converter, power intensifying booster (2/1) and titanium probe screwed one another in a consecutive order. The titanium prob of 1.9 cm in diameter resonated at 20 kHz and 25%, 50%, or 75% of ultrasonic amplitudes. The average power delivered by booster-titanium probe to 200 mL of nitrite solutions at 25%, 50% and 75% of ultrasonic amplitudes were displayed on the main screen as 47.8 ± 1.5, 126 ± 1.2, and 220.5 ± 4.3 W, respectively. The titanium probe was immersed 3–4 cm below the surface of the liquid samples and resonated on a pulse mode (5 s on/5 s off). The sample aliquots were taken from the reactor at a regular time interval (10 min) using an automatic pipette, and subsequently filtered through 0.45 mm-pore sized Millipore membrane filters. The filtered liquid samples were analyzed for nitrite and its reduction product (NH_4^+ or NH_3) using appropriate analytical techniques. All experiments were conducted in duplicate. A schematic appearance of the experimental system is given in Fig. 1.

The effects of zinc powder dose (1–8 g/L), ultrasonic power (47.8–220.5 W), and initial nitrite concentration (2.5–20 mg/L) were examined for nitrite reduction by Zn^0 under magnetic and ultrasonic mixings. A separate set of batch experiments was also conducted to identify important reaction products and pathways during nitrite denitrification.

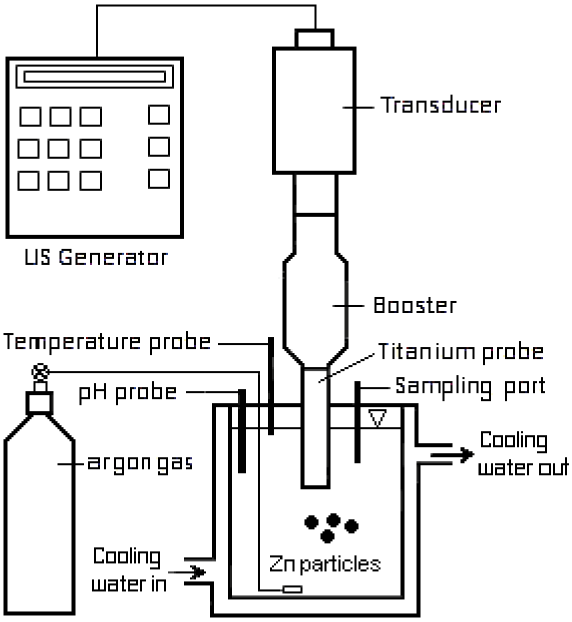

Fig. 1. Experimental apparatus for ultrasound-zinc system.

In this context, the samples treated with Zn^0/MOPS and US/Zn^0/MOPS were filtered through 0.45 mm-pore sized membrane filters. The filtered samples were examined for total dissolved zinc (TDZn) content, while the filter-trapped suspended matters were dried in an oven at 80°C overnight before being subjected to scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS) and X-ray diffraction (XRD) measurements.

2.3. Analytical and instrumental methods

Nitrite (NO_2^-) was detected by diazotizing with sulfanilamide and catalyzing with N-(1-naphthyl)-ethylenediamine dihydrochloride to generate a highly colored reddish-purple complex which was colorimetrically measured at 540 nm using a UV/visible spectrophotometer (DR5000, Hach). Ammonia/ammonium (NH_3/NH_4^+) was also determined spectrophotometrically at 635 nm by forming indophenol blue complex through its reaction with phenol and hypochlorite, catalyzed by sodium nitroprusside. The morphology and elementary analyses of zinc particles (Zn^0) before and after nitrite reductions were examined based on micrographs taken by a FE-SEM with an EDS spectrometer in a JSM-7100F model instrument (JEOL Ltd., Co., Tokyo, Japan). The Zn^0 particles were coated with Au-Pd for SEM analysis. The crystal structure and mineral components of zinc particles were analysed using XRD in 10°–80° 2q range with copper K-alpha radiation (40 kV and 20 mA) (Malvern PANalytical Empyrean).

3. Results and discussion

3.1. Characterization of zinc particles

The surface characteristics of original zinc powder were determined through SEM-EDS and XRD measurements. A SEM image of zinc powder clearly demonstrates that zinc particles exist in various forms, and their surface roughness can be clearly seen at greater magnifications (Fig. 2a and b). The EDS spectrum in Fig. 2c demonstrates that the surface of the zinc particle has been partially oxidized apparently due to its exposure to the surrounding atmosphere. The mineral distribution of the original zinc powder utilized in the tests is depicted by the XRD spectra in Fig. 2d. All of the peaks in the spectra are from zinc confirming the high purity of the zinc particles employed in the experiments.

3.2. Reduction of nitrite under different reaction conditions

The nitrite solutions were treated with zinc (Zn^0) alone or in combination with ultrasound (US/Zn^0) in the absence

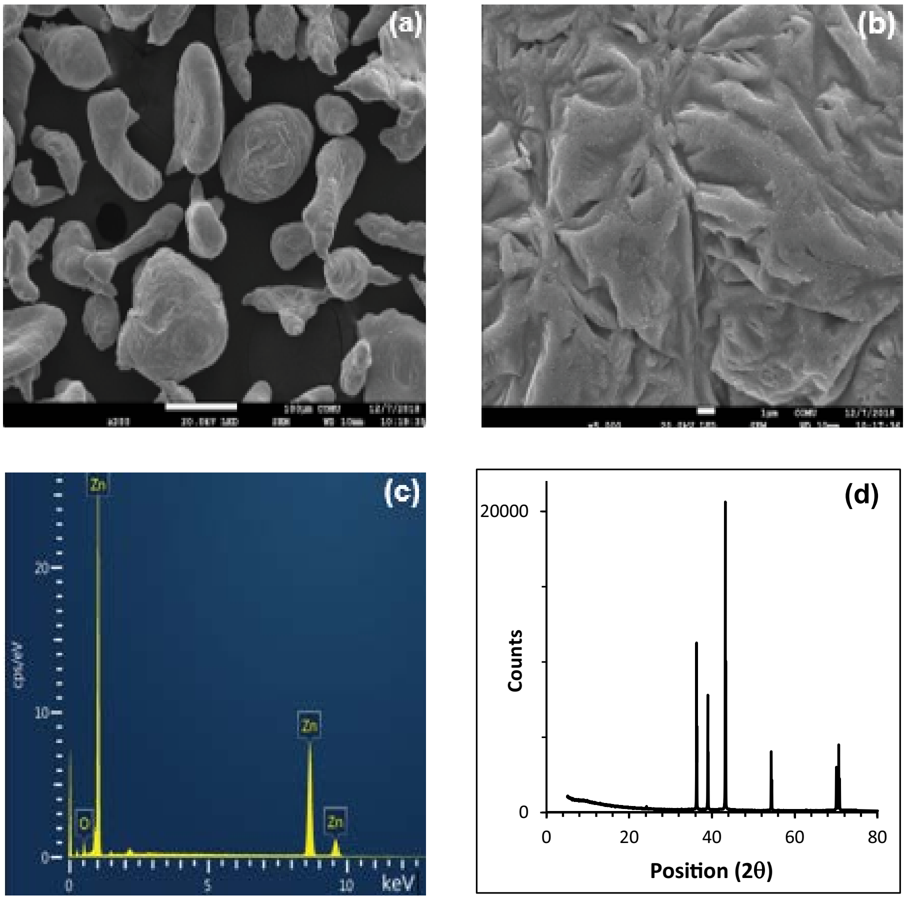

Fig. 2. Characterization of zero-valent zinc particles: (a,b) scanning electron microscopy images, (c) energy-dispersive X-ray spectrum, and (d) X-ray diffraction spectra.

and presence of MOPS buffer. The ultrasonic treatment was performed on a pulse mode (5 s on/5 s off) for 60 min. Fig. 3 depicts the concentration profiles over time from these experiments.

With Zn^0 or US/Zn^0 the nitrite reduction was less than 20% after 60 min. In the absence of MOPS buffer, ultrasound did not induce any significant effect on Zn^0's nitrite reduction. The low reduction capacity of Zn^0 at neutral pH conditions has also been reported in other studies [9,25]. Some metallic particles, particularly alkaline earth metals like magnesium, can be successfully activated by ultrasound, while the majority of others, such as iron, zinc, or aluminum, are difficult to corrode, since they have stable oxide surfaces ($Fe(OH)_2$, $Zn(OH)_2$, or $Al(OH)_3$) [19,26]. At this point, the MOPS buffer was used as an auxiliary surface activating agent to boost the zinc activity for greater nitrite removals. Using MOPS buffer, nitrite reduction of Zn^0 increased from 17% to 46% over the course of 60-min treatment. A similar positive effect of MOPS buffer has also been reported for the reduction of hexa-valent chromium (Cr(VI)) by metallic magnesium particles (Mg^0) [27]. The addition of ultrasound to Zn^0/MOPS treatment increased the nitrite reduction efficiency beyond 99.5% within 60 min. Ultrasound by itself was not effective for nitrite reduction (Fig. S1) due to the formation of strong oxidants such as hydroxyl radicals ($^{\bullet}OH$) and hydrogen peroxide (H_2O_2), both of which are similar oxidizing agents as nitrite. These results provide conclusive evidence that the combination of US and MOPS buffer has a synergistic effect on the nitrite removal of zinc.

3.3. Effect of zinc dosage and ultrasonic power

Fig. 4 shows the changes on nitrite concentration over time at different Zn^0 powder doses and ultrasonic powers. All experiments were conducted at neutral pH values using 1 g/L of MOPS buffer. The rate of nitrite removal increased by increasing Zn^0 dose, since more active sites on the zinc particles were available for the reactions. Using 4 g/L of zinc powder about 46.1% of nitrite was removed by Zn^0/MOPS within 60 min (Fig. 4a). The reduction was predominantly observed during the initial phase, but then slowed down and eventually halted as a result of the particle surface oxidation. The nitrite removal by US/Zn^0/MOPS at 47.8 W was extremely low, even lower than that of Zn^0/MOPS treatment (Fig. 4b). This appears to be the result of inadequate mixing provided by the low-powered ultrasound. Applying ultrasound at 126 W, approximately 38.3%, 50%, 75.4%, and 65.6% of nitrite were denitrified at 1, 2, 4, and 8 g/L of Zn^0 dosages, respectively (Fig. 4c). The optimum dose for nitrite removal at 126 W (Fig. 4c) was similar with those at 0 and 47.8 W (Fig. 4a and b). Increasing ultrasonic power to 220.5 W did not improve the reduction efficiency for the experiments made with 1 and 2 g/L of zinc powder. The effect of ultrasound on nitrite reduction was significant at higher zinc doses, particularly at 8 g/L. As shown in Fig. 4d, using 220.5 W of ultrasonic power nitrite was removed by 90.4% and 99.8% at 4 and 8 g/L of zinc powder, respectively. According to these results, the optimum zinc dose was found to be 8 g/L when the US power was 220.5 W. Increasing the dose or ultrasonic power has yet its own disadvantages including high chemical and energy consumptions. Furthermore, when ultrasound is administered at exceptionally high powers, its mechanical parts, such as transducer and titanium probe, gradually heat up, resulting in a failure of the ultrasonic device. Therefore, the maximum ultrasonic power, used in the experiments was limited to 220.5 W.

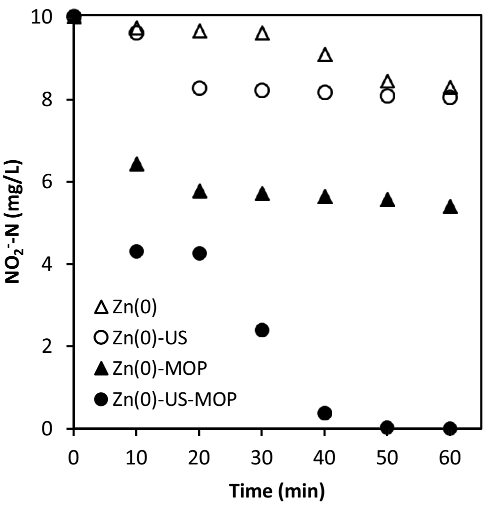

Fig. 3. Reduction of nitrite by Zn^0 and US/Zn^0 with/without MOPS buffer (Zn^0 = 8 g/L, US power = 220.5 W).

3.4. Effect of initial nitrite concentration

The reduction of nitrite by US/Zn^0/MOPS was examined at different initial concentrations (2.5, 5, 10 and 20 mg/L NO_2^-–N), and results are demonstrated in Fig. 5 as time vs. concentration profiles (C/C_o).

The removal of nitrite by US/Zn^0/MOPS increased as the initial concentration of nitrite decreased. The removal of nitrite was greater than 99.5% after 60 min at all initial concentrations except 20 mg/L-N. The nitrite concentration fell below the critical value of 1 mg/L in 10 min when the initial concentration was 2.5 or 5 mg/L, but it took about 30–40 min when the initial concentration was 10 mg/L. The reduction of nitrite was more rapid at low initial concentrations due to the availability of more surface area for nitrite molecules.

3.5. Identification of oxidation–reduction by-products

The oxidation–reduction products for nitrite removal by US/Zn^0/MOPS were identified at neutral pH conditions. The nitrite is possibly denitrified to nitrogen gas (N_2) and ammonium (NH_4^+), whereas Zn^0 can be initially oxidized to divalent zinc ion (Zn^{2+}) [28]:

$$NO_2^- + 8H^+ + 6e^- \leftrightarrow NH_4^+ + 2H_2O \qquad E^o_{red} = 0.89 \text{ volt} \tag{1}$$

$$2NO_2^- + 8H^+ + 6e^- \leftrightarrow N_{2(g)} + 4H_2O \qquad E^o_{red} = 1.50 \text{ volt} \tag{2}$$

$$Zn^0 \leftrightarrow Zn^{2+} + 2e^- \qquad E^o_{oxd} = 0.75 \text{ volt} \tag{3}$$

Because E°_{red} value for second reaction is much greater than that of first one, nitrite is expected to be mostly

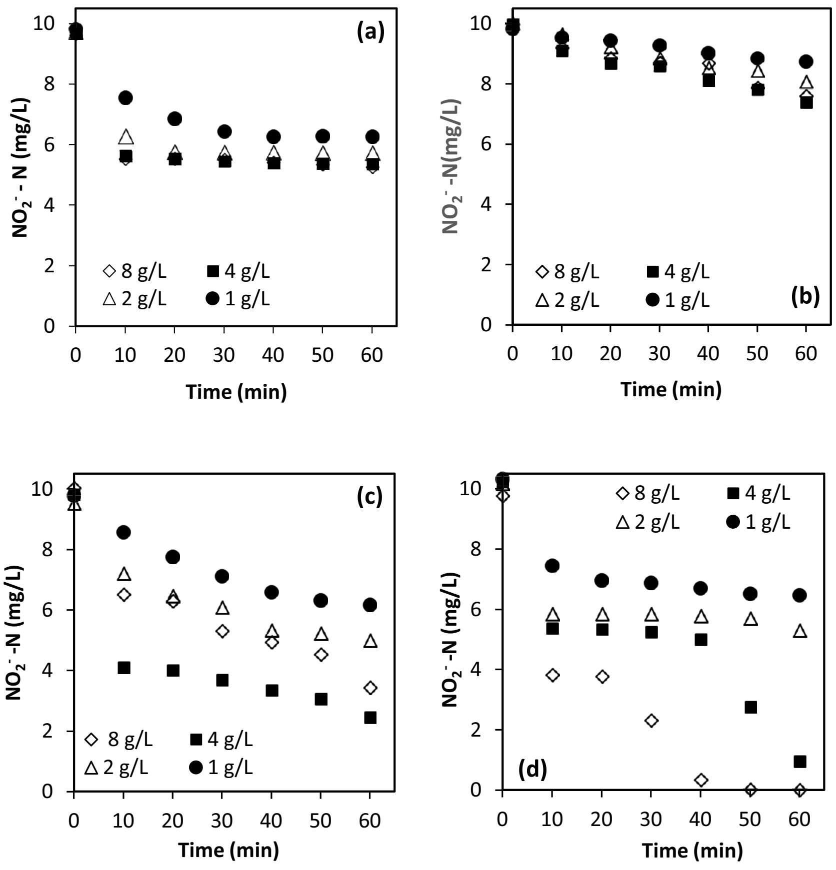

Fig. 4. Effects of ultrasonic power and zinc dose on nitrite reduction of Zn^0/MOPS/US treatment. US powers: (a) without ultrasound, (b) 47.8 W, (c) 126 W, and (d) 220.5 W.

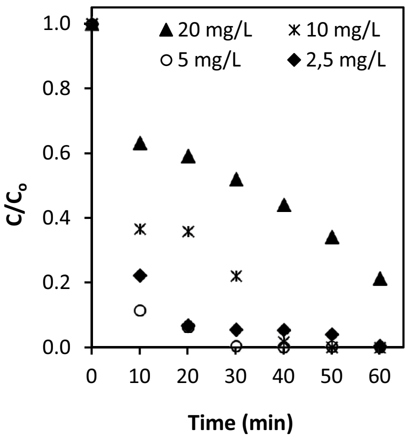

Fig. 5. Effect of initial concentration (NO_2^-–N) on nitrite removal by US/Zn^0/MOPS (US power º 220.5 W, Zn^0 dose = 8 g/L).

reduced to nitrogen gas (N_2). The formation of N_2 is desired in nitrite denitrification, since ammonia is toxic to aquatic species and causes eutrophication in surface waters. Combining reactions (2) and (3) yields:

$$2NO_2^- + 8H^+ + 3Zn^0 \leftrightarrow N_{2(g)} + 3Zn^{2+} + 4H_2O \quad (4)$$

The initial and remaining nitrite and ammonium concentrations were experimentally determined using standard methods, outlined in Section 2, while the mass concentration of nitrogen gas was estimated from nitrogen mass balance:

$$C^o_{NO_2^- -N} = C_{NO_2^- -N} + C_{NH_4^+ -N} + C_{N_2 -N} \quad (5)$$

where $C^o_{NO_2^- -N}$ initial nitrite concentration (mg/L); $C_{NO_2^- -N}$: remaining nitrite concentration (mg/L); $C_{NH_4^+ -N}$: the concentration of ammonium formed from nitrite reduction (mg/L); $C_{N_2 -N}$: the concentration of nitrogen gas formed from nitrite reduction (mg/L).

Fig. 6 depicts the time-dependent changes in NO_2^-, NH_4^+, and N_2 concentrations in nitrite solutions treated by Zn^0/MOPS and US/Zn^0/MOPS at various ultrasonic powers (0–220.5 W) and 8 g/L of zinc powder.

Fig. 6 clearly shows that nitrite was predominantly converted to N_2 gas. When ultrasound was used at 0, 47.8, 126, and 220.5 W, approximately 4.4, 3.5, 8.5, and 9.8 mg/L of N_2 were generated, respectively. Ammonium was formed in small amounts, less than 0.5 mg/L at all applied ultrasonic powers. According to these results, the nitrite reduction by US/Zn^0/MOPS appears to be an effective treatment, as nitrite is mostly converted to nitrogen gas rather than ammonia. These results are also supported by Limousy et al.

[25] indicating that the final products of nitrite reduction by Zn^0 were nitrogen gas (N_2) and ammonium (NH_4^+).

The oxidation by-products of nitrite reduction were also investigated using various techniques such as digital photography, SEM-EDS, XRD, and atomic absorption spectrophotometer (AAS). The zero-valent zinc (Zn^0) is initially oxidized to divalent zinc (Zn^{2+}), and nitrite is reduced to N_2 or NH_4^+. Zn^{2+} may precipitate as $Zn(OH)_2$ and participate in complex reactions with MOPS or hydroxide ions. To identify oxidation byproducts and determine the reaction mechanism, two identical nitrite solutions (10 mg/L-N) buffered with MOPS were prepared, and 1.6 g of zinc powder was added to 200 mL of each solution. Then, one of the solutions was mixed with a magnetic stirrer, while the other was treated with ultrasound for 60 min. The ultrasonic treatment was performed at 220.5 W on a pulse mode (5 s on/5 s off). Both solutions were photographed after the treatment s using a digital camera (Fig. S2). The solution subjected to the magnetic stirring (Zn^0/MOPS) was free of any suspended matter, but the one processed with ultrasonic treatment (US/Zn^0/MOPS) exhibited a distinct turbidity apparently due to the precipitation of Zn^{2+} ions. Both solutions were subsequently filtered through 0.45 μ pore-sized membrane filter, and solid phases remaining on the filters were separated and dried prior to XRD and SEM-EDS analysis. The XRD spectra of Zn^0/MOPS in Fig. 7 demonstrated no clear peak of $Zn(OH)_2$ as can be noticed from the graph all peaks belong to pure metallic zinc (Zn^0). The XRD spectra of original zinc particles (Zn^0) before nitrite reduction (Fig. 2c) was also found to be similar with that of Zn^0/MOPS after nitrite reduction (Fig. 7). It appears that the zinc hydroxide formation was not significant during the reduction of nitrate by Zn^0/MOPS. In contrast, the $Zn(OH)_2$ peaks at 2q = 20, 21, 27, 28 and 33 in the XRD spectrum of US/Zn^0/MOPS sample indicate that divalent zinc ions (Zn^{2+}) precipitated when ultrasound was used (Fig. 7).

These results were also supported with SEM-EDS measurements, shown in Fig. 8. In the SEM images of solid phases before and after nitrite reductions with Zn^0/MOPS (Figs. 2b and 8a), only a few small particles, supposedly $Zn(OH)_2$ were observed around Zn^0 particles. But the image of US/Zn^0/MOPS sample in Fig. 8b clearly shows cloudy layers of $Zn(OH)_2$.

The EDS spectroscopy of the SEM images also detected a high level of elemental oxygen on zinc surface (Fig. S3). The XRD and SEM-EDS measurements verified that zinc hydroxide ($Zn(OH)_2$) was an important oxidation products in US/Zn^0/MOPS treatment. In one of our previous studies, a similar catalytic effect of ultrasound was also observed on a different zero-valent metal (Mg^0) for Cr(VI) reduction,

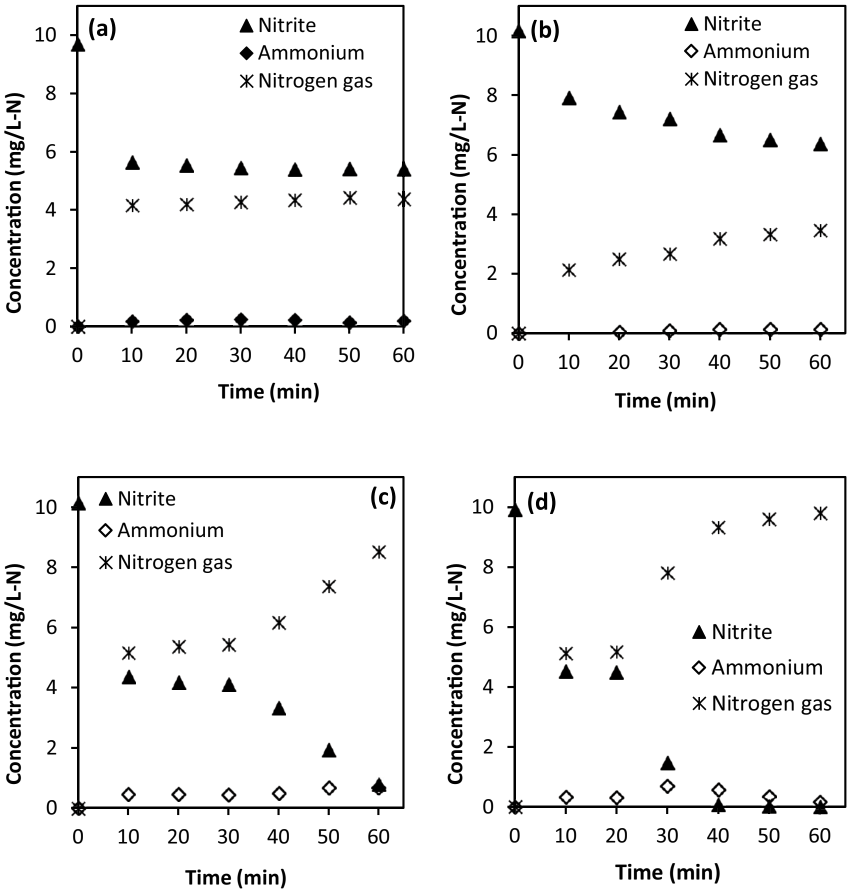

Fig. 6. Nitrogen mass balance for the sonocatalytic treatment (US/Zn^0/MOPS) of nitrite at neutral pH conditions: Zn^0 dose = 8 mg/L, US power: (a) without ultrasound, (b) 47.8 W, (c) 126 W and (d) 220.5 W.

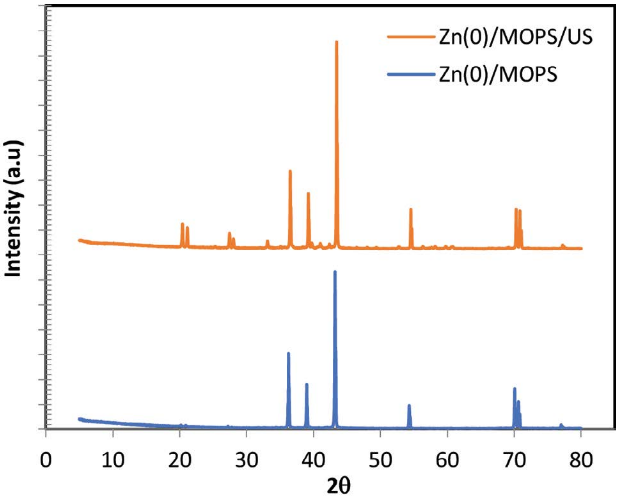

Fig. 7. X-ray diffraction spectrums for the solids of samples subjected to Zn^0/MOPS and US/Zn^0/MOPS treatments after nitrite reduction (Zn^0 dose = 8 g/L, US power = 220.5 W, C_o = 10 mg/L NO_2^-–N).

and a similar metal hydroxide ($Mg(OH)_2$) came out as the major oxidation product [19].

The total dissolved zinc (TDZn) concentrations in the filtrate samples along with pH values during each treatment were measured using atomic absorption spectrophotometry (AAS) (Fig. 9). The total dissolved zinc (TDZn) concentration in Zn^0/MOPS sample increased to 73.5 mg/L at the first 10 min, then gradually decreased to 64.9 mg/L at the 30th min, and interestingly increased again over the next 30 min (Fig. 9a). The change in TDZn concentration over time can be explained by the pH measurements. As depicted in Fig. 9b, the pH of the nitrite solution treated with Zn^0/MOPS increased above 7.7 over the course of the first 30 min, but then gradually fell below 7.5. This can be interpreted as the $Zn(OH)_2$ was most likely formed within the first 30 min when pH was around 7.7, but later it may have been dissolved as a result of decreasing pH. These results confirm the lack of hydroxy-zinc precipitates in the XRD spectra of Zn^0/MOPS sample, shown in Fig. 8.

It is important to indicate that the TDZn concentrations were all measured in AAS after the samples were filtrated through 0.45 μ pore-sized filters. Therefore, the TDZn

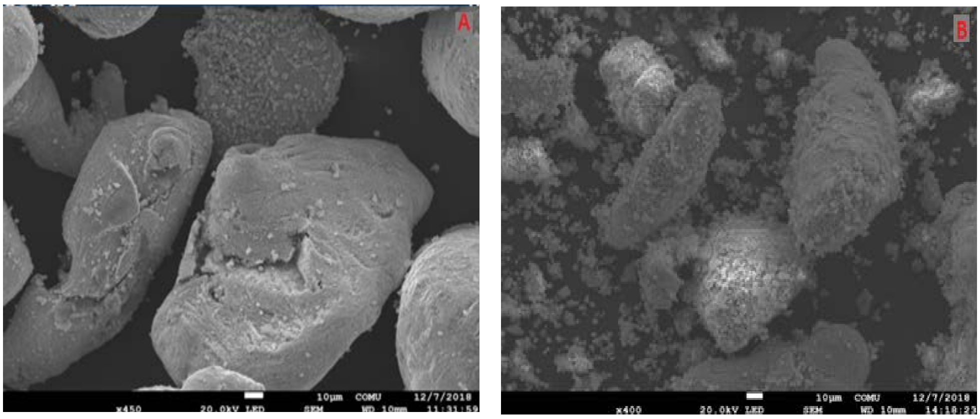

Fig. 8. Scanning electron microscopy images of particles from nitrite solutions treated with Zn^0/MOPS (A) and US/Zn^0/MOPS (B). Zn^0 = 8 g/L, US power = 220.5 W.

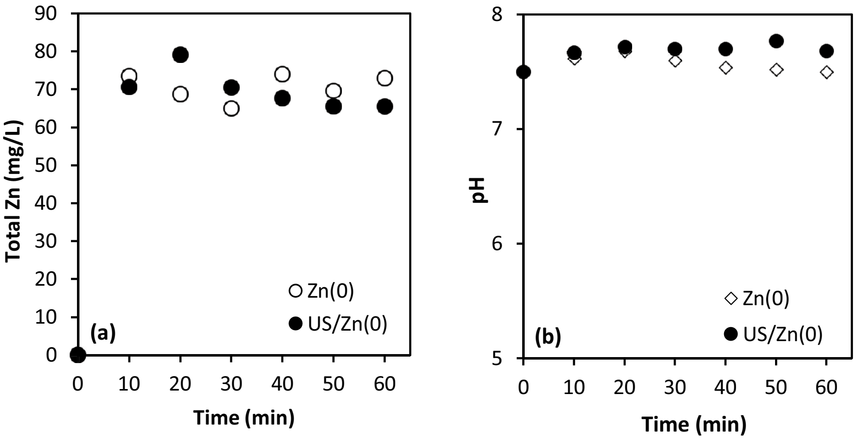

Fig. 9. Changes on total dissolved zinc (TDZn) concentration (a) and pH (b) in nitrite solutions subjected to Zn^0/MOPS and US/Zn^0/MOPS treatments (Zn^0 dose = 8 g/L, US power = 220.5 W).

concentrations given in Fig. 9a do not supposedly include the zinc hydroxide. The $Zn(OH)_2$, however, appeared to exist in the US/Zn^0/MOPS sample throughout the entire treatment. As can be seen in Fig. 9a, the TDZn concentration in the US/Zn^0/MOPS sample increased to 85.5 mg/L within the first 20 min, but then gradually decreased to 65.5 mg/L. The decrease in TDZn concentration after 20 min has been related to the precipitation of Zn^{2+} ions as a result of increasing pH. In contrast to the pH trend observed for Zn^0/MOPS, the pH of US/Zn^0/MOPS sample gradually increased over the 60-min reaction period.

It is clear that both MOPS and ultrasound played important roles in the activation of zinc particles. The MOPS buffer has a potential to donate hydrogen protons (H^+) for oxidation–reduction reactions, and also minimizes negative charges around metallic particles so that negatively charged species like Cr(VI) and possibly NO_2^- can be better adsorbed on the particle surface [27]. In addition, because the MOPS buffer keeps the pH neutral, the oxidation of metallic particle can be lowered. But despite all these positive effects of MOPS, the Zn^0 particles did not successfully reduce nitrite ions in the absence of ultrasound. This is because just a formation of a thin oxide layer around the zinc particle can be enough to inactivate it, and at pH around 7 with MOPS the emergence of such a thin oxide film ($Zn(OH)_2$) was inevitable. Since the zinc hydroxide is a quite stable solid with a solubility product (K_{sp}) of $10^{-17.2}$ at 25°C [28], its dissolution or removal from the particle surface was not successful either by MOPS or ultrasound. Such a difficulty in cleaning oxide surfaces by ultrasound for different metallic particles including iron and zinc has been also reported in other studies [18,29]. For example, Lee et al. [18] used sodium persulfate ($Na_2S_2O_8$) to increase the ultrasonic activation of zero-valent zinc (Zn^0) for the removal of methyl orange. In another study, sulfuric acid (H_2SO_4) was used to enhance the nitrate reduction capacity of Fe^0 under ultrasonic irradiation [29]. In these studies, both chemical were used to minimize the surface passivation of Zn^0 and Fe^0 particles in an aim to boost their ultrasonic activation. A similar physicochemical effect was also observed in our study. When MOPS buffer and ultrasound were used together, surface reactivation of zinc particles was achieved, thereby oxidizing Zn^0 to $Zn(OH)_2$ while efficiently converting nitrite to nitrogen gas.

4. Conclusion

Ultrasound and MOPS buffers were employed to enhance zinc activation for nitrite removal. Neither ultrasound nor MOPS alone provided sufficient nitrite removal by Zn^0, but their combination acted synergistically on Zn^0 activation, resulting in a nitrite reduction greater than 99.5%. The reduction rate of nitrite increased with increasing zinc powder dose, ultrasonic power and processing time, but decreased with increasing initial nitrite concentration. The synergy of the combined system has been attributed to the surface cleaning effect of ultrasound and MOPS buffer. The Zn^0/MOPS/US treatment seems to be a promising reductive process as it produces a non-toxic reduction and easily separable oxidation products (N_2 and $Zn(OH)_2$) both of which do not require any further advanced treatment.

Supplementary materials

Supplementary information related to this article is available online from Desalination Publications or from the author.

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Supplementary information

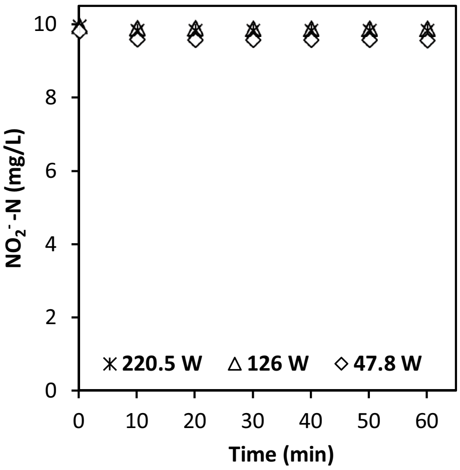

Fig. S1. Removal of nitrite by ultrasound at different ultrasonic powers.

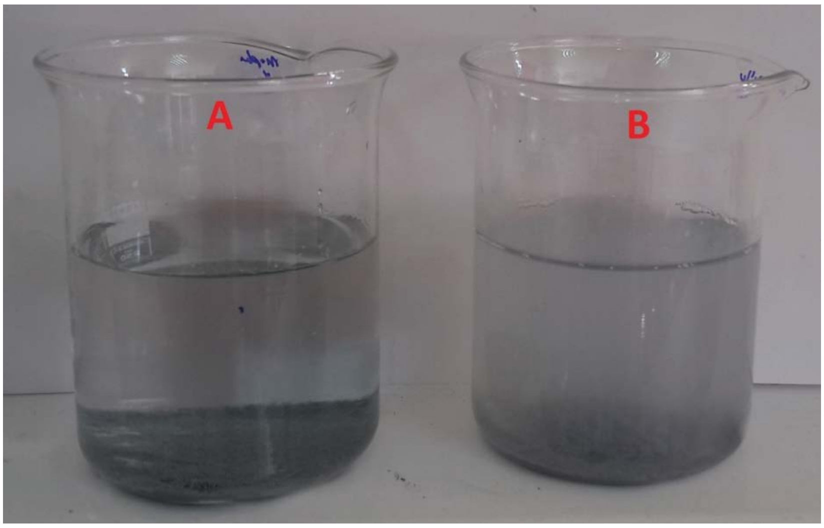

Fig. S2. Nitrite solutions treated with Zn^0/MOPS (A) and Zn^0/MOPS/US (B). Zn^0 = 8 g/L, US power = 220.5 W.

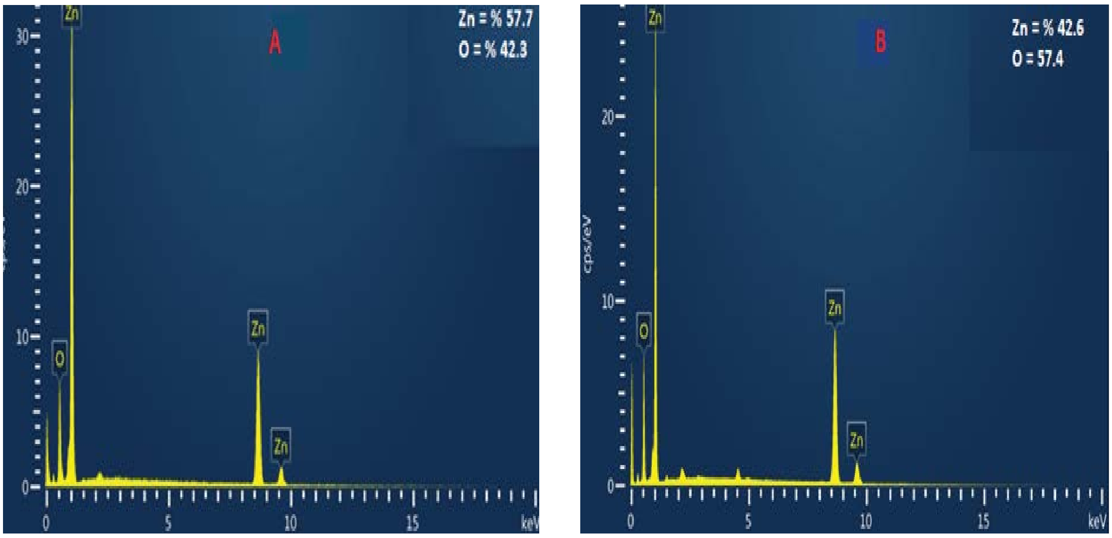

Fig. S3. Surface elemental distribution of solid particles recovered from the nitrite solutions processed with Zn^0/MOPS (A) and US/Zn^0/MOPS/US (B) (Zn^0 dose = 8 g/L, US power = 220.5 W).