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Scale-up synthesis of zero-valent iron nanoparticles and their applications for synergistic

degradation of pollutants with sodium borohydride

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Abstract

The scale-up synthesis of nZVI (zero-valent iron nanoparticles) was optimized by response surface modeling (RSM). The synthesized nZVI was employed for synergistic degradation of metronidazole (MNZ) or methyl orange (MO) in the presence of sodium borohydride (NaBH₄). Key parameters such as initial MNZ or MO concentration, nZVI concentration, and NaBH₄ concentration for MNZ or MO removal process was optimized using central composite design (CCD). Under the optimized conditions (nZVI concentration: 150 mg/L; NaBH₄:0.1 M; interaction time: 25 min for MNZ and 30 min for MO; and MNZ or MO initial concentration: 40 mg/L), the removal was synergistically increased to 100 % (MNZ) and 98.07±1.1 % (MO). When nZVI was applied without NaBH₄, the removal of MNZ and MO were 50.62±0.28 and 43.72±0.29 %, respectively. In the presence of NaBH₄ alone, the removal of MNZ or MO was 6.5±1.1 % and 4.2±0.7 %, respectively. Addition of NaBH₄ was found to enhance the remediation ability of nZVI. The MNZ or MO degradation followed pseudo-first-order kinetics. The degradation mechanism was studied by UV-visible spectroscopy, XRD, SEM-EDX, FT-IR, and BET analyses. The applicability of the process was tested with MNZ-spiked or MO-spiked lake water and ground water samples.

Keywords: Zero-valent iron nanoparticles; Scale-up synthesis; Metronidazole; Methyl orange; synergistic removal; Degradation mechanism.

1. Introduction

The global increase in the toxic materials burden in environmental media represents a major ecological and human health threat [1, 2]. From this perspective, the utilization of nanomaterials may allows provide an opportunity to reduce the environmental contamination [3]. Subsequently, the broad research attempt of the nanotech–community regarding functionalized nanomaterials has evaluated key properties such as redox capability, sorption, also toxic organic or inorganic entrapment of pollutants [3-5]. Thus far, variations of the nZVI technology are the progressively more promising choice for the remediation of various hazardous and toxic wastes as well as contaminated sites [5-8].

Scaling up of nanomaterials production is one of the important challenges in transitioning from laboratory to the industrial scale [9]. Scale–up of biological and chemical synthesis of nanoparticles has consistently been a challenge. Still there are no reports on a scale–up of synthesis of nZVI; there are few prototypes have been designed in a batch reactor [5, 6]. A batch processes are often imperfect as compared to synthesis in small–scale, because of the low nanoparticle production yield and time intensiveness. A chemical reactor can generate more suitable for a scale–up production of nanoparticles than the batch process. The nZVI technology has turn into an essential research topic in modern years owing to their reducing (remediation) property [5, 10, 11].

Recently, the peer-reviewed literature contains increasing reports regarding the presence and need for treatment of pharmaceuticals and textile wastes in waste waters and surface waters [12, 13] [14]. Pharmaceutical substances are used all over the world for improving the health of humans and animals. Increased and continuous usage of drugs like antibiotics, analgesics and anti–inflammatories have resulted in the increase in the release of these compounds And semi-

degraded metabolites into the aquatic system [15]. Metronidazole is water soluble, nonbiodegradable drug with nitroimidazole ring structure and is used for its antibacterial and antiprotozoal activities. Clearly, the presence of metronidazole in the aquatic environment can be detrimental to the aquatic life and humans [16-18]. Therefore, its removal is necessary as well as a challenge. Nanoscale zero-valent iron particles (nZVI) have been used for metronidazole remediation.

Dyes released from synthesis plants and dye using industries as effluents are significant environmental pollutant due to their non-biodegradable nature. Methyl Orange is a highly toxic, water soluble azo dye that has a complex structure consisting of N=N group and is used in printing, textile, pharmaceutical, paper manufacturing and food industries [19-21]. Several methods like coagulation, chemical oxidation, photochemical degradation, flocculation, membrane separation, floatation, reverse osmosis, and adsorption have been utilized for remediation of dyes in water [22]. Nanoparticles like multiwalled carbon nanotubes, Zinc Oxide nanoparticles, Titania nanoparticles, and nZVI for Methyl Orange removal from aqueous solution in batch studies [23, 24]. Bentonite supported nZVI [20], and bimetallic nZVI/Pd nanoparticles [21] were used by Chen et al. (2011) and Wang et al. (2013) for Methyl Orange removal from aqueous solution in batch experiments.

The current study involves the optimization of scale–up synthesis of nZVI by response surface modeling (RSM) and exploring their applications for degradation of dyes and antibiotics. Metronidazole is a known essential antibiotic drug from the hospital effluents, and MO is an azo dye commonly found in the textile industrial wastes, which cannot be degraded by conventionally degraded by the biological method effectively [18, 25]. In the current study, the synergistic degradation of MNZ or MO using nZVI in the presence of NaBH₄, was attempted.

Since NaBH₄, is already being used for reductive synthesis of nZVI, it was worthwhile to study its possible effects on degradation of pollutants by nZVI. To the best of our knowledge, this heppens to be the first ever study on synergistic action NaBH₄, and nZVI for degerdating the dyes and antibiotics in aqueous solution. The effects of parameters like initial MNZ or MO concentration, nZVI concentration and NaBH₄ concentration on the degradation of MNZ or MO by the nZVI was studied. The mechanism of MNZ or MO degradation using nZVI was also explored.

2. Experimental

2.1 Materials

Ferrous sulfate (FeSO₄·7H₂O) and EDTA ($C_{10}H_{14}N_2Na_2O_8·2H_2O$) were obtained from Sisco Research Laboratories Pvt. Ltd., India. Sodium borohydride (NaBH₄) obtained from SD Fine Chemicals, Mumbai, India. Metronidazole obtained from the Sigma–Aldrich, Methyl orange ($C_{14}H_{14}N_3NaO_3S$) was acquired from Hi–Media Laboratories, Mumbai, India. The chemicals used in this study were of analytical grade, and with deionized water the solutions were prepared.

2.2 Scale-up synthesis of nZVI particles in chemical reactor

The synthesis of nZVI particles procedure was described in our previous report [6]. Briefly, FeSO₄ and disodium salt of EDTA were prepared and mixed, and then, NaBH₄ was added at a speed of 1–2 drop sec⁻¹ into the mixture in a nitrogen atmosphere at 60 °C under vigorous and continuous stirring. The solution turned black due to precipitation of nano zerovalent iron; the solution was filtered, and nZVI nanoparticles were rinsed with absolute ethanol

three times and dried over night at 100° C. The experimental volume is 200 ml (1:1 ratio of FeSO₄ and NaBH₄).

The experimental conditions for synthesis of nZVI particles were optimized by Box–Behnken Design [6] (BBD) of Response surface modeling (RSM). The process was optimized by varying the concentration of the variables which directly affects the yield percentage of the synthesized nZVI. The parameters considered were concentrations of FeSO₄ (0.05 to 0.15 M), NaBH₄ (0.1 to 0.75 M) and temperature (30 to 60 °C).

Here, yield percentage was considered as the response in conducted series of experiments. Yield percentage was calculated by using the formula:

$$Yield (\%) = \frac{Experimental weight of product nZVI}{Theoretical weight of product iron} \times 100$$
(1)

Where, experimental weight is the dry weight of synthesized nZVI; theoretical weight is the % of iron content of the precursor material (FeSO₄).

The optimized experimental condition of the synthesis of nZVI was carried out in a 2.5 L chemical reactor.

2.3 Characterization of nZVI particles

The structure and crystallinity of the nZVI was analysed using powder X–ray diffraction (XRD) (D8 Advance diffractometer, Bruker, Germany). The average crystalline size calculated using Debey–Scherrer's formula [26].

$$D = \frac{\kappa\lambda}{\beta\cos(\theta)} \tag{2}$$

The nZVI size distribution was calculated by Dynamic Light Scattering (DLS) (Horiba, SZ–100, Japan) in Milli–Q water. UV–visible spectral investigation of synthesized nZVI particles was determined using UV–vis spectrophotometer (UV1750, Shimadzu Corporation,

Kyoto, Japan). SEM image of the nZVI was analysed by scanning electron microscopy (FESEM–SUPRA 55 – Carl Zeiss, Germany). The surface elemental analysis of synthesized nZVI and reacted with MNZ or MO were conducted using Energy Dispersive X–ray spectroscopy (FESEM–SUPRA 55 – Carl Zeiss, Germany). Surface area of the nZVI reacted and un–reacted with MNZ or MO was analyzed by BET (Micromeritics, TriStar III, USA). The surface chemical characteristics of the synthesized nZVI reacted and un–reacted with MNZ or MO were analyzed by Fourier Transform Infra–Red Spectrometer (IR Affinity–1, Shimadzu, Japan).

2.4. Batch experiments for removal of MNZ or MO using nZVI

2.4.1 Optimization of parameters for removal of MNZ or MO using nZVI using RSM

The degradation of MNZ (metronidazole) and Methyl orange (MO) using nZVI in the presence of sodium borohydride experimental conditions was optimized using RSM modeling [Central Composite Design (CCD)] [27]. Degradation of MNZ or MO experiments were conducted in a conical flask (250 mL), in which the experiments the volume of the solution was 100 mL. The three major factors (initial MNZ or MO concentration, nZVI concentration, and concentration of NABH₄) were taken for the optimization of MNZ or MO degradation, where the pH (pH–7) of MNZ or MO solution and experimental temperature (25 °C) was kept constant to imitate the natural environment. At prescribed time intervals, 5 mL of samples were taken out and immediately centrifuged. The MNZ absorbance was measured by using UV–vis spectrophotometer at wavelength 314 nm. The MO absorbance was measured by using a UV–vis and reaction temperature 27 °C.

2.4.2 Measurement of the removal percentage and removal capacity

The removal percentage of MNZ or MO has been calculated by the following equation [20]:

Removal (%) =
$$\frac{(C_0 - C_e)X100}{C_0}$$
 (3)

The amounts of MO or MB removal capacity [qe (mg/g)] at equilibrium was calculated by the expression [28]:

$$qe = \frac{(C_0 - C_e)XV}{W} \tag{4}$$

where C_0 and C_e (mg/L) are the MNZ or MO initial and equilibrium concentrations, respectively; V (L) is the volume of solution; and W (g) is the weight of nZVI used.

2.4.3 Kinetic study

The similar equilibrium experiment method was used for kinetic tests, aqueous samples were collected at selected time intervals and the MNZ or MO concentrations were measured. The kinetics of MNZ or MO removal with nZVI was determined using pseudo first–order, pseudo second–order, Elovich, and Intraparticle diffusion kinetic models [6]. The correlation coefficients (r^2) values were close or equal to 1, expressing the agreement between experimental data and the model predicted values. A relatively high r^2 value denotes that the model successfully explains the kinetics of MNZ or MO removal [29].

The pseudo first order, pseudo second order, Elovich model, and Intraparticle diffusion model equations are expressed in eq (5), (6), (7), and (8) respectively.

$$ln\frac{q_{e}-q_{t}}{q_{e}} = -K_{L}t\tag{5}$$

$$\frac{t}{q_t} = \frac{1}{2K'q^2e} + \frac{t}{q_e} \tag{6}$$

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln(t)$$
(7)
$$q_t = k_{id} t^{0.5}$$
(8)

Where K_L -removal rate constant of Lagergen (L/min); K'- rate constant adsorption of pseudosecond order (mg/g), qe and qt are the amounts of MNZ or MO degrade (mg/g) at equilibrium and time t respectively; α -initial adsorption rate (mg/g. min); β -desorption constant (g/mg); Rpercent MNZ or MO adsorbed; t-contact time (h); kid–Intraparticle diffusion rate constant (h⁻¹); The linear plots pseudo first order [log (qe–qt) vs t] and pseudo second order [linear plot t/qt vs t], Elovich model [qt vs ln (t)], and intra–particle diffusion model [qt vs t^{0.5}] yields a linear relationship of and reaction from which K_{L} , K', α , β , and kid can be calculated from the slope and intercept of the plot, respectively [29, 30].

2.5. MNZ or MO removal in environmental water matrices (lake and ground water)

Water samples were taken from different locations at Vellore. The ground water and lake water samples were collected from Sipcot and VIT University Vellore respectively. The removal of MNZ or MO spiked environmental water samples were carried out at the optimized conditions.

2.6. Statistical analysis

All the experiments were carried out in triplicate, Using Design Expert 9 and one-way ANOVA software was carried out to ensure the results statistical significance.

3. Results and discussion

3.1 Optimization of scaled up synthesis process of nZVI

The BBD was used for optimizing the experimental conditions for synthesis of nZVI particles. The successive experimental runs and ANOVA are shown in Table 1A, B. The F–value of Model 53.84 implied that the model was significant. The values of "Prob > F" < 0.05 showed that the terms of the model are significant. The values > 0.1 indicated that the model terms are not significant. The standard deviation of the experimental design was found to be 1.41, R²–0.98. The mean and C.V % of the experimental design were observed to be 74.00 and 1.90 (adjusted R^2 –0.96; predicted R^2 –0.87; adequate precision 23.87).

The predicted R^2 (0.87) was in agreement with the adjusted R^2 (0.96); i.e. < 0.2 difference. A ratio greater than 4 for the adequate precision (measures signal to noise ratio) is desirable. An experimental design ratio of 23.87 denotes an adequate signal. This model may be used to navigate the design space.

Fig. 1 showed the three–dimensional (3D) response of the counter image and also the effect of varying factors like temperature, FeSO₄, and NaBH₄ concentration in the scale-up synthesis of nZVI. Fig. 1A demonstrates that an increase in the concentration of FeSO₄ and NaBH₄ causes an increase in the yield percentage at constant temperature (60 °C). When constant NaBH₄ concentration (0.75 M) was used by varying FeSO₄ concentration and temperature, the results demonstrated that an increase in the concentration of FeSO₄ and temperature resulted in an increase in the yield percentage (Fig. 1B). When FeSO₄ concentration (0.1 M) was maintained constant by varying NaBH₄ concentration and temperature, the yield percentage was increased with increase in the NaBH₄ concentration and temperature as shown in Fig. 1C.

The results proved that the $FeSO_4$ and $NaBH_4$ concentrations and temperature played an important role in the synthesis of nZVI. With increase in concentration of $FeSO_4$ (0.05 to 0.15)

M) at constant NaBH₄ concentration (0.75 M) and temperature (60 °C), the yield percentage was observed to be increased due to availability of sufficient amount of reducing agent in the solution. Similar concentrations were used for small-scale synthesis of nZVI as mentioned in an earlier report [6]. With a decrease in NaBH₄ concentration at constant FeSO₄ (0.1 M) concentration and temperature (60 °C), the yield percentage was observed to be decreased, probably owing to the insufficient amount of reducing agent available for synthesis. It is well known that NaBH₄ is a strong reducing agent, which plays an important role in nZVI synthesis [6]. Therefore, NaBH₄ concentration was considered as an important factor in nZVI synthesis. With increase in temperature (30–60 °C), the yield percentage was found to be increased at constant FeSO₄ (0.1 M) and NaBH₄ (0.75 M) concentration. Through previous studies, it can be proved that with increase in temperature, there will be more formation of nanoparticles [31, 32]. Similar to the earlier reports that use a maximum temperature of 50 °C for nZVI synthesis, in our experiments, we have used a maximum of 60 °C [6].

From the above results from BBD, the optimized experimental conditions were found to be 0.13 M FeSO₄, 0.05 M EDTA, 0.75M NaBH₄, and a temperature of 60 °C. The maximum nZVI yield was found to be 86.08±1.8 %. Small–scale synthesis in flask and large–scale synthesis of nZVI in chemical reactor showed similar characterization data as shown in Table S1 (supplementary information). XRD analysis confirmed the formation of nZVI, and the 2θ peaks (44.74 [6], 46.78) showed similar crystalline structures in both synthesis process. By using DLS and BET analyses, the mean particle size and surface area of nZVI were found to be similar in both synthesis processes. The SEM and EDX results showed comparable surface characteristics and iron weight percentage. By analyzing these results, small scale and large scale synthesis of

nZVI showed a similar result in size and nZVI formation. The scale–up synthesis of nZVI in a chemical reactor can be suggested to produce large quantities of nZVI.

Due to reducing property of nZVI, it has been frequently used as a sorbent for environmental remediation [7, 11]. To further study the applicability of synthesized nZVI for environmental remediation in the present work, the removal of antibiotic (metronidazole) and azo dye (methyl orange) from aqueous solution was performed.

3.2 Statistical optimization of MNZ or MO removal

The removal of MNZ and MO using nZVI was done in separate batch experiments. CCD was performed to identify the best conditions for removal of MNZ or MO using nZVI in the presence of NaBH₄, enabling the statistical evaluation of the aspects that significantly influence the removal of MNZ by nZVI. The experimental data for MNZ or MO removal by nZVI in the presence of NaBH₄ are shown in Table 2A, B. From the CCD model, the analysis of variance (ANOVA) results for MNZ or MO removal are shown in Table 3A, B. The CCD model F–values for removal of MNZ or MO using nZVI in the presence of NaBH₄ was found to be 1621.31 (MNZ) and 544.85 (MO), which means that the CCD model is significant. The "Probability >F" value was >0.05, which shows that present method is statistically significant for the removal of MNZ by nZVI in the presence of NaBH₄. The equations (9, 10) were produced by the analysis of regression through the correlation coefficients (\mathbb{R}^2) of MNZ (0.99) and MO (0.99), and p<0.0001 for MNZ or MO removal using nZVI in the presence of NaBH₄.

 $R1=66.63-13.40A+14.60B+13.33C-0.59AB+1.61AC-0.16BC+4.45A^{2}-6.56B^{2}-3.62C^{2} \quad (9)$ $R1=63.84-8.16A+10.69B+20.10C-2.37AB+4.11AC-3.19BC+5.69A^{2}-1.05B^{2}-5.49C^{2} \quad (10)$

where, R1-percentage of MNZ or MO removal using nZVI, A- initial concentration of MNZ or MO, B- concentration of nZVI, and C- NaBH₄ concentration. The result of factors on the removal of MNZ or MO (R1) was correlated by the coefficient values of A, B, and C independently.

For MNZ removal by nZVI in the presence of NaBH₄, the coefficient of variation (CV) was observed to be 1.13%. The "predicted R^2 " of 0.99 is in agreement with the "adjusted R^2 " of 0.99; i.e. the difference is < 0.2. Accordingly, the coefficient of variation (CV) was observed to be 1.91%, and the "predicted R^2 " of 0.98 is in agreement with "adjusted R^2 " of 0.99 for MO removal by the nZVI in presence of NaBH₄. The CV for both nanoparticles was observed to be < 10%, which represents the reliability and precision of the experimental design. A ratio greater than 4 for adequate precision (measures signal to noise ratio) is desirable. The ratio of MNZ (31.70) and MO (89.92) denotes an adequate signal for MNZ or MO removal by nZVI. The results recommended that the CCD model may be employed to pilot the design space.

The relationship between independent and dependent variables is illustrated in three-dimensional representations of the response surfaces (Fig. 2). A decrease in the removal (%) of MNZ or MO was observed with increase in the concentration of initial MNZ or MO concentration [100 to 18.43 ± 1.2 % (MNZ) and 98.07 ± 1.1 to 17.69 ± 0.9 % (MO)]. The higher values of MNZ or MO removal efficiencies were obtained by the increase in nZVI and NaBH₄ concentration (Fig. 2). At 25-min reaction time for MNZ and 30 min for MO, the maximum removal of MNZ and MO was 100 % and 98 %, respectively. The consequence of surface interaction involving nZVI and MNZ or MO removal efficiencies were appreciate the MNZ or MO initial concentrations (40–150 mg/L) and NaBH₄ (0.05–0.1 M), whereas the concentration of nZVI (150 mg/L) was set as constant (Fig. 2A, B).

The increased NaBH₄ concentration also leads to enhancement of MNZ or MO removal percentage. The maximum removal of MNZ or MO >98 % was determined at constant NaBH₄ concentration 0.1 M. Similarly, a decrease in the removal of MNZ or MO was observed upon increasing the initial MNZ or MO concentrations above 40 mg/L in the solution. Fig. 2C, D shows the surface interaction between nZVI and NaBH₄, which was studied by varying the nZVI concentrations (50–150 mg/L) and NaBH₄ concentrations (0.05–0.1 M) at a constant initial MNZ or MO concentration (40 mg/L). The removal percentage of MNZ or MO was gradually enhanced with increase in nZVI dosage and NaBH₄ concentration. The cause of surface interaction between nZVI and MNZ or MO was observed by varying the initial concentrations of MNZ or MO (40-150 mg/L) and nZVI (50-150 mg/L), whereas the NaBH₄ concentration (~0.1 M) was kept constant (Fig. 2E, F). The removal percentage of MNZ or MO was observed to be increased as the nZVI concentration increases; furthermore, maximum response was achieved at 150 mg/L for MNZ or MO removal. Similarly, a decrease in the MNZ or MO removal was noted upon increasing the initial MNZ or MO concentration above 40 mg/L in the solution. Maximum removal was attained at an initial concentration of MNZ or MO: 40 mg/L and 150 mg/L of nZVI and 0.1 M of NaBH₄.

Using nZVI alone, the MNZ or MO removal experiments were conducted according to the design expert software, and their corresponding results are listed in Table S2A, B (supplementary information). The quadratic equations for prediction of the optimum point were obtained according to the CCD and input variables as follows:

For MNZ removal

 $R1{=}{+}10.47{+}7.06{*}A{-}13.86{*}B{-}5.58{*}AB{+}1.90{*}A^{2}{+}11.80{*}B^{2}$

For MO removal

R1=+16.59+5.77*A-14.52*B-5.60*AB+0.44*A²+3.72*B²

where R1 is the MNZ or MO removal efficiency (R %), and A and B represent the nZVI concentration and MNZ or MO concentrations, respectively. ANOVA suggests that the model equation derived by RSM could be used to describe the MNZ [Table S2C (supplementary information)] or MO [Table S2D (supplementary information)] removal by nZVI. It is well-known that a corresponding variable is more significant if its absolute p-value is smaller than 0.05. The three-dimensional representations of the response surface plots illustrated the relationship between independent and dependent variables. The maximum removal of MNZ and MO was obtained by the increase in nZVI concentration [Fig. S1A (supplementary information)]. The decreased initial MNZ or MO concentrations also led to enhancement in the removal percentage [Fig. S1B (supplementary information)].

Since nZVI is a strong reducing agent, [5, 6, 33] it was also reported as a well–known sorbent for removing contaminants [5]. As the MNZ or MO concentration increases, there will be more oxidation of Fe^0 , which can lead to loss of reactivity and results in the decrease of MNZ or MO removal efficiency [18, 20]. Further, the increase in removal efficiency was observed at fixed MNZ or MO (40 mg/L) and nZVI (150 mg/L) concentration by increasing the NaBH₄ concentration This was due to the regeneration of nZVI particles, which led to the increase in reaction sites on the surface of nZVI [18]. In addition, there was a decrease in the removal efficiency observed at constant nZVI and NaBH₄ concentration by increasing the initial MNZ or MO concentration, presumably due to the limited availability of limited reaction sites on the nZVI surface [6, 21, 33].

3.3 Optimized conditions for batch removal study

The optimal conditions for maximum removal of MNZ or MO using nZVI in presence of NaBH₄ were found to be following; initial MNZ or MO concentration: 40 mg/L; nZVI concentration: 150 mg/L; NaBH₄ concentration: 0.1M; interaction time: 25 min for MNZ and 30 min for MO. Under these optimized conditions, the removal percentage of MNZ and MO was found to be 100 and 98.07 %, respectively, and the removal capacity was observed to be 266±4.7 (for MNZ) and 261±3.1 (for MO) mg/g, respectively. Compared to previous studies, the degradation of MNZ or MO using nZVI [20, 33, 34] in the present study showed high removal (%) at low concentrations of nZVI as mentioned in Table 4.

The optimal experimental conditions for the removal of MNZ or MO using nZVI alone were determined using the desirability function by the Design expert software. The optimum conditions were found to be nZVI concentration: 150 mg/L and initial concentration of MNZ or MO: 40 mg/L, which provide maximum MNZ and MO removal efficiencies of 50.62 ± 0.28 and 43.72 ± 0.29 %, respectively.

In the presence of only NaBH₄, the removal percentages of MNZ or MO were only 6.5 ± 1.1 and 4.2 ± 0.7 %, respectively. These results indicated that nZVI in the presence of NaBH₄ had a synergistic effect on the MNZ or MO removal in aqueous solutions.

3.4 Kinetic study

The effect of contact time on removal of MNZ or MO was investigated at constant nZVI (150 mg/L) and NaBH₄ (0.1 M) concentrations by varying the initial concentrations of MNZ or MO solutions (40, 80, 120, 160 mg/L). The interaction time was checked for a period of 35 min. As the reaction time increased to 25 min for MNZ and 30 min for MO, the removal percentage of MNZ or MO was found to be maximum, and additionally, an equilibrium state was attained

for MNZ and MO, respectively. No further increase in removal percentage (a maximum of 100 % for MNZ and 98 % for MO) was observed beyond the time points (Fig. 3A, B). In the case of MO degradation, the color of solutions turned to colorless at 30 min after interaction with nZVI in the presence of NaBH₄ (Fig. 3C, D). The fast removal of MNZ or MO was observed at an initial stage, which is due to the availability of a large number of reaction sites on the nZVI. Until the point that equilibrium was attained, the MNZ or MO removal rate gradually decreased due to the reduction in the MNZ or MO gradient concentration between nZVI and aqueous phases. Pseudo-first-order, pseudo-second-order, elovich, and intraparticle diffusion were used to study the mechanism and rate of reaction for the removal process. The calculated results fit the kinetic models as presented in Table 5 and Fig. S2 (supplementary information). The correlation coefficients (R²) values (>0.98) of the pseudo-first-order model was higher than that of the pseudo-second-order model, indicating that the removal kinetic data of MO on nZVI was well described by the pseudo-first-order model. Farzadkia et al. (2015) and Chen et al. (2011) reported MNZ removal by nanoparticles and MO removal by nZVI particles, [20, 35] which concluded that the kinetic model of pseudo-first-order may strongly rely on the nZVI concentration. The experimental results confirmed that the high removal percentage, removal capacity, and rapid kinetics reaction for MNZ or MO removal using nZVI make it a competent tool for MNZ or MO removal in other environmental matrices and contaminated sites.

3.5 Characterization of nZVI before and after reaction with MNZ or MO

The XRD results of nZVI synthesized in the chemical reactor showed a sharp 2 θ peak at 46.78°, which confirmed the presence of nZVI [JCPDS no. 00-006-0696] [8]. From the XRD analysis, the crystalline size (D) was found to be 18nm. The XRD analyses of nZVI and MNZ or

MO reacted with nZVI are shown in Fig. 4A, B, C. The evident 20 peak at 44.94° also indicated the presence of nZVI (Fig. 4A). The nZVI after reaction with MNZ or MO (Fig. 4B, C) indicated the presence of Fe₂O₃ (20: 35.68° and 55.62°), Fe₃O₄ (20: 35.45° and 65.76°), MNZ peaks (**) [36], and MO peaks (*). After interaction with MNZ or MO, the appearance of Fe (II) and Fe (III) peaks confirmed the occurrence of redox reactions between Fe⁰ and MNZ or MO. This is in concordance with other studies, where nZVI particles were used as a reductant [37-39]. The average crystalline size of nZVI was found to be 18 nm, and the average crystalline size of nZVI was increased after interaction with MNZ (38 nm) or MO (52 nm).

Table S3 (supplementary information) demonstrates that the average particle size of nZVI before interaction to be 114 nm, and that after interaction, the average particle size was found to be 394 nm with MNZ and 664 nm with MO. From BET analysis, the nZVI surface area was calculated as 87 m²/g after interaction with MNZ ($21 \text{ m}^2/\text{g}$) or MO ($15 \text{ m}^2/\text{g}$). A decrease in the surface area of nZVI was observed. The particle size was increased due to the binding of degradation-related components of MNZ or MO on the surface of nZVI. This was confirmed by the BET studies performed in the available literature, which showed that an increase in the size of the particle will cause a decrease in the surface area [8].

When MNZ reacted with nZVI in the presence of NaBH₄, the MNZ absorbance peak at 314 nm decreased with increase in time from 5 to 35 min as shown in Fig. 3A. In case of MO, the absorbance peak was recorded at 464 nm, and this peak was also observed to decrease over time. Also, an increase in the absorbance peak at 248 nm (Fig. 3B) showed that the degradation of MO was occuring. This was also signified by the change from colored to colorless solution over a reaction time of 30 min upon interaction with nZVI in the presence of NaBH₄ (Fig. 3C, D).

The SEM results show that as-syntesized nZVI [Fig. S3A (supplementary information)] was spherical in shape with an average particle size of 30 nm. After interaction with MNZ or MO, the surface was observed to be rough and existed as aggregates as shown in Fig. S3B, C (supplementary information). The EDX results of nZVI showed a 78 weight percentage of iron content in the sample with trace elements shown in Fig. S3D (supplementary information), which indicated that the synthesized nano-iron is in zero state i.e nZVI. Fig. S3E, F (supplementary information) shows the elemental composition of nZVI after exposure to MNZ or MO. After interaction with MNZ or MO, the atomic percentages of carbon, nitrogen, and oxygen [Fig. S3E, F (supplementary information)] were increased due to the presence of degraded components of MNZ or MO on the nZVI surface [19]. Thus, the EDX result established the involvement of nZVI in the MNZ or MO removal process.

Fig. 5 shows the FT–IR spectra of nZVI particles before and after interaction with MNZ or MO, from which a remarkable change in the absorption bands of the functional groups was observed. The broad peaks at 3328 cm⁻¹ suggested the presence of hydroxyl group (–OH) and the peaks at 2365 cm⁻¹ were due to C–H stretching band [40]. The peaks at 1418 cm⁻¹ denoted the presence of C–O (stretching vibration) group [41]. The FT–IR spectra were recorded for nZVI before and after interaction with MNZ or MO (Fig. 5). An increase in absorbance at 3328 cm⁻¹ (hydroxyl), 1418 cm⁻¹ (carbonyl), 1039 cm⁻¹ and 876 cm⁻¹ were noted, which was due to the complexation of MNZ or MO [34].

From the above results, a possible removal mechanism of MNZ can be proposed that MNZ degrades into 1–(2–hydroxyethyl)–2–methyl–5–imidazole or 1–(2–hydroxyethyl)–2–methyl–5–aminoimidazole, 2–methyl–5– nitroimidazole [34]. The nitro reduction and hydroxyethyl cleavage or N–denitration are the pathways considered in the MNZ degradation

process with nZVI surface that result in the generation of electrons and hydrogen species [42, 43].

In the case of MO, the degradation results in the formation of sulfanilic acid and aromatic amines [20]. This is due to the cleavage of azo N = N bond by Fe⁰ to form hydrazine–like N–H particular bonds, which consume H⁺ and lead to increase in pH. On the other hand, the instant reaction of Fe⁰ with water to produce Fe²⁺, OH, and H₂ can also cause pH increase in solutions [19, 20]. In nZVI–MO system, the fluctuation of pH from 12 to 9.07 was observed within 20 min of interaction. Consequently, the decrease in pH of the system was found to be 7.45 in 30 min. This was attributed to the utilization of H⁺, resulting in an alkaline state for Fe²⁺ upon reacting with OH to form Fe(OH)₂ in the solutions [20]. Fig. 6 shows the schematic representation of the nZVI scale-up synthesis and possible ways of metronidazole and methyl orange degradation using nZVI.

3.6 MNZ or MO removal in environmental water matrices

The application of nZVI in the removal of MNZ or MO was studied by performing the experiment in environmental water matrices. The removal percentage of MNZ was evaluated in ground water (GW) and lake water (LW) taken from Sipcot and VIT Lake, Vellore, India, and was spiked with 40 mg/L of MNZ or MO. In GW and LW, 88.75 ± 0.6 and $79.74\pm1.2\%$ of MNZ removal, respectively, were achieved by nZVI (150 mg/L) in the presence of NaBH₄ (0.1M). The MO removal percentages of 81.54 ± 1.3 and $71.01\pm1.2\%$ were observed by nZVI (150 mg/L) in the presence of NaBH₄ (0.1M) in MO-spiked GW and LW, respectively. The removal percentage of MO or MNZ calculated in spiked environmental water samples was found to be decreased by 10 to 20 % in contrast with the experimental outcome quantified in distilled deionized water.

However, a decline in the removal percentage calculated in natural samples was observed. This decrease was due to the existence of natural colloids in the environmental water samples [6, 8]. Thus, the results suggested that the synthesized nZVI can be employed in MNZ or MO removal in different aqueous samples, even though a lesser removal percentage was observed as compared to the MNZ or MO removal percentage in distilled deionized water.

4. Conclusions

The scale–up synthesis of nZVI was successfully optimized by RSM. The synergistic removal of MNZ or MO using nZVI in the presence of NaBH₄ was investigated using CCD. Results showed that the removal of MNZ or MO increased with increase in the nZVI concentration and decreased with increase in the MNZ or MO initial concentration. The removal percentage of MNZ or MO using nZVI in the presence of NaBH₄ was found to be enhanced in comparison to either nZVI or NaBH₄ alone. The synthesized nZVI was successfully employed for MNZ or MO removal in MNZ-spiked or MO-spiked environmental water samples. Further, the scaling up of the synthesis process of nZVI can be utilized for the MNZ or MO removal through *in situ* remediation processes using permeable reactive barriers (PRB) technology and/or by *ex–situ* "pump and treat" processes.

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Compliance with ethical standards

In this study, neither human participants nor animals were involved.

Conflict of interest

The authors declare that they do not have any conflict of interest.

CCCCCCC N

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Figure captions

Fig. 1. Scaling up the synthesis process of nZVI response surface plots (**A**) showing the effect of FeSO₄ and NaBH₄ concentrations at constant temperature (60 °C) (**B**) showing the effect of FeSO₄ concentration and temperature at constant NaBH₄ concentration (0.75 M) (**C**) showing the effect of NaBH₄ concentration and temperature at constant FeSO₄ concentration.

Fig. 2. The response surface plots: **(A)** Effect of MNZ and NaBH₄ concentration on MNZ removal and **(B)** Effect of MO and NaBH₄ concentration on MO removal at 150 mg/L of nZVI. **(C)** Effect of nZVI and NaBH₄ concentration on MNZ (40 mg/L) removal, **(D)** Effect of nZVI and NaBH₄ concentration on removal of MO (40 mg/L), **(E)** Effect of MNZ and nZVI concentration on removal of MO at constant NaBH₄ concentration (0.1 M), **(F)** Effect of MO and nZVI concentration on removal of MO at constant NaBH₄ concentration (0.1 M)

Fig. 3. UV-vis spectrophotometry analysis at different time intervals:

A) MNZ reacted with nZVI **B**) MO reacted with nZVI **C**) MO solution **D**) MO solution after reaction with nZVI

Fig. 4. XRD image: (A) nZVI particles, (B) MNZ reacted nZVI, (C) MO reacted nZVI

Fig. 5. FT-IR spectra of nZVI, MNZ reacted nZVI, MO reacted nZVI

Fig. 6. Schematic representation of the nZVI scaling up the synthesis process of nZVI and possible ways of MNZ and MO degradation using nZVI

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using nZVI

Table 3 ANOVA for Response Surface Quadratic model for removal of A) MNZ using nZVI B)

MO using nZVI

Table 4 Comparison of MNZ or MO Removal (%) of nZVI As Reported with the Current Study

Table 5 Kinetic study of MNZ and MO Removal Using nZVI

	Factor 1:	Factor 2:	Factor 3:	
Run	FeSO ₄ (M)	NaBH ₄ (M)	Temperature(°C)	nZVI Yield (%)
1	0.1	0.425	45	72.11±2.1
2	0.05	0.425	30	76.61±1.5
3	0.15	0.425	30	75.65±1.8
4	0.05	0.1	45	68.90±2.2
5	0.05	0.425	60	83.50±1.1
6	0.15	0.75	45	81.85±1.1
7	0.1	0.75	60	86.08±1.8
8	0.1	0.1	30	58.88±1.9
9	0.05	0.75	45	83.76±1.8
10	0.1	0.1	60	68.60±1.4
11	0.15	0.1	45	59.34±1.6
12	0.1	0.75	30	81.17±1.3
13	0.15	0.425	60	73.15±1.7

Table 1A

Table 1B

	Sum of	10	Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	957.45	9	106.38	53.84	< 0.0001	Significant
A-FeSO ₄	64.87	1	64.87	32.83	0.0007	
B-NaBH ₄	743.82	1	743.82	376.47	< 0.0001	
C-temperature	45.22	1	45.22	22.89	0.0020	
AB	14.63	1	14.63	7.41	0.0297	
AC	22.04	1	22.04	11.16	0.0124	
BC	5.78	1	5.78	2.93	0.1308	
A^2	25.25	1	25.25	12.78	0.0090	
B^2	5.06	1	5.06	2.56	0.1536	
C^2	29.99	1	29.99	15.18	0.0059	
Residual	13.83	7	1.98			
Lack of Fit	13.83	3	4.61			
Pure Error	0.000	4	0.000			
Cor Total	971.28	16				
Std. Dev.	1.41		R-Squared	0.98		
Mean 74	1.00		Adj R-Square	ed 0.96		
C.V. %	1.90		Pred R-Squar	ed 0.87		

PRESS 221.29 Adeq Precision 23.87

D	MNZ concentration	nZVI concentration	NaBH ₄	MNZ
Kun	(mg/L)	(mg/L)	Concentration (M)	removal (%)
1	40	150	0.01	78.68±0.7
2	120	100	0.055	67.60±1.2
3	200	150	0.01	46.92±2.5
4	120	100	0.13	78.69±2.2
5	40	50	0.1	71.87±1.2
6	40	150	0.1	100
7	200	50	0.01	18.43±1.2
8	200	50	0.1	48.92±1.3
9	120	15.91	0.055	23.12±1.2
10	254.54	100	0.055	56.06±2.2
11	120	100	0	44.55±1.9
12	40	50	0.01	46.43±1.8
13	120	184.09	0.055	72.70±1.2
14	200	150	0.1	76.06±2.2
	No.			

Table 2A

Dum	MO concentration	nZVI concentration	NaBH ₄ concentration	MO removal
Kull	(mg/L)	(mg/L)	(mg/L)	(%)
1	120	100	0	33.11±1.4
2	40	50	0.1	76.92±1.2
3	200	150	0.1	84.72±1.8
4	40	150	0.1	98.07±1.1
5	120	100	0.055	63.66±1.2
6	120	100	0.130	81.49±0.9
7	40	50	0.01	38.00±0.8
8	200	50	0.1	73.70±1.2
9	120	15.91	0.055	44.40±1.7
10	254.54	100	0.055	66.66±1.3
11	120	184.09	0.055	77.77±1.1
12	200	150	0.01	42.11±1.9
13	200	50	0.01	17.69±0.9
14	40	150	0.01	71.28±1.8

Table 2B

Table	3A
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G	Sum of	Df	Mean	T V-l	p-value	
Source	Squares	DI	Square	F value	Prob > F	
Model	6916.37	9	768.49	1612.31	< 0.0001	significant
A-MNZ	1587.26	1	1587.26	3330.11	< 0.0001	
B-nZVI	2911.19	1	2911.19	6107.78	< 0.0001	
C-NaBH ₄	2058.06	1	2058.06	4317.89	< 0.0001	
AB	2.81	1	2.81	5.90	0.0380	
AC	20.74	1	20.74	43.52	< 0.0001	
BC	3.73	1	3.73	7.83	0.0208	
A^2	155.36	1	155.36	325.95	< 0.0001	
B^2	596.69	1	⁺ 596.69	1251.88	< 0.0001	
C^2	120.97	1	120.97	253.80	< 0.0001	
Residual	4.29	9	0.48			
Lack of Fit	1.64	4	0.41			
Pure Error	2.64	5	0.53			
Cor Total	6920.66	18				

Std. Dev.	0.69	R-Squared	0.9994
Mean	61.18	Adj R-Squared	0.9988
C.V. %	1.13	Pred R-Squared	0.9963
PRESS	25.90	Adeq Precision	165.03

AA A 0.9994 A 0.9963 Ision 165.03

Table	3B
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Same	Sum of	Df	Mean	F	p-value	
Source	Squares	DI	Square	Value	Prob > F	
Model	6991.72	9	776.86	544.85	< 0.0001	Significant
A-MO	588.30	1	588.30	412.61	< 0.0001	
B-nZVI	1560.94	1	1560.94	1094.78	< 0.0001	
C-NaBH ₄	4680.62	1	4680.62	3282.79	< 0.0001	
AB	45.11	1	45.11	31.64	0.0103	
AC	135.38	1	135.38	94.95	< 0.0031	
BC	81.48	1	81.48	57.14	< 0.0041	
A^2	265.78	1	265.78	186.41	< 0.0001	
B^2	15.39	1	15.39	10.79	0.0094	
C^2	279.24	1	279.24	195.85	< 0.0001	
Residual	12.83	9	1.43			
Lack of Fit	12.83	$\bar{4}$	3.21			
Pure Error	1.030	5	0.210			
Cor Total	7004.55	18				

Std. Dev.	1.19	R-Squared	0.9982
Mean	62.53	Adj R-Squared	0.9963
C.V. %	1.91	Pred R-Squared	0.9833
PRESS	117.08	Adeq Precision	89.924

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Table 4

Sl. no.	Sorbent used	Sorbent dosage	рН	Temp. (°C)	Contaminant conc. (mg/L)	Removal (%)	Interaction time (min)	Ref.
		(mg/L)				X		
1	nZVI	330	5.6	27	MNZ-80		90	[34]
2	rectorite– supported nZVI	500	_	_	MNZ-40	97	20	[33]
	bentonite				2			
	_						10	
3	supported	500	6.5	30	MO-100	79.46	10	[20]
	nZVI				*			
	rectorite-			X				
4	supported	500	_	<hr/>	MO-40	93	20	[33]
	nZVI)				
			\bigcirc	Room				
6	nZVI	150	7.0	temperatur	MNZ-40	100	25	Current Study*
			*	e				-
				Room				
7	nZVI	150	7.0	temperatur	MO-40	98	30	Current Study*
				e				
	* showi	ing current	study re	sult				

Table 5

Kinetic	Parameters	MNZ concentration (mg/L)				MO concentration (mg/L)			
models		40	80	120	160	40	80	120	160
pseudo–	K_L /min	0.048	0.0578	0.0686	0.0879	0.0328	0.0575	0.0646	0.0765
first– order	r ²	0.985	0.995	0.989	0.992	0.995	0.983	0.987	0.978
pseudo-	K' (g/mg min)	0.229	0.769	1.13	1.24	0.114	0.203	0.469	0.755
second– order	r^2	0.886	0.852	0.892	0.921	0.825	0.811	0.875	0.912
	α (mg/g min)	2.64	3.89	5.32	7.33	1.183	3.5	5.72	6.22
elovich model	β (g/mg)	0.0954	0.132	0.188	0.212	0.076	0.167	0.178	0.202
	r ²	0.956	0.948	0.972	0.964	0.911	0.945	0.992	0.995
intra–	k _{id} (mg/g min ^{0.5})	0.92	0.88	0.65	0.54	0.51	0.36	0.35	0.26
diffusion	r^2	0.961	0.952	0.954	0.96	0.992	0.961	0.995	0.987



Figure 1

Figure 2







Figure 4







Figure 6



Highlights

- Synergistic degradation of antibiotic and azo dye using nZVI with NaBH₄
- Enhanced removal in presence of sodium borohydride compared to nZVI alone
- The mechanism of degradation of metronidazole and methyl orange was studied •
- The applicability of the nZVI in real water matrixes was explored •

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