



Facile fabrication of nano zerovalent iron – Reduced graphene oxide composites for nitrate reduction in water

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ABSTRACT

Nano zerovalent iron is used to destruct a wide range of organic and inorganic contaminants in water. However, its performance is limited due to rapid aggregation and surface passivation. To minimise aggregation, we fabricated nano zerovalent iron on the reduced graphene oxide sheets using green tea derived polyphenols (hereafter rGO-nZVI-P) or borohydride ions (hereafter rGO-nZVI-B). Both rGO-nZVI-P and rGO-nZVI-B composites were characterised by electron microscopic, molecular spectroscopic and electrochemical methods. The spherical nZVI particulates (e.g. ~4–15 nm diameter) are well dispersed among rGO sheets. Polyphenols act as a capping agent for Fe (0) to prevent its aggregation. The X-ray diffraction and X-ray photon spectroscopic results show an admixture of Fe (0) with rGO and Fe oxides (e.g. FeOOH, Fe₂O₃, and Fe₃O₄ phases). The association of Fe (0) on the reduced graphene oxide matrix is believed to occur via π - π framework thus minimising surface passivation. The reduction efficiency of the nano zerovalent iron composites was determined using nitrate as index ion. When compared with rGO-nZVI-B, the rGO-nZVI-P reduces 70% of 0.8064 mM nitrate within an hour. Although traces of NO and NO₂⁻ are observed, ammonia is the dominant product that accounts for 95% nitrogen mass balance. The nitrate reduction by the rGO-nZVI composites follows pseudo-second-order kinetics. Fe (0) or its oxidation products are environmentally benign. The rGO-nZVI-P also has the potential to destruct excess nitrate in water remediation.

1. Introduction

Nano zerovalent iron (nZVI) readily agglomerates and undergoes rapid oxidation upon exposure to ambient environmental conditions. However, the mechanistic steps of Fe (0) oxidation by various ligands are debated (Gu et al., 2017; Shi et al., 2011). Irrespective of the synthesised method used, bare nZVI particulates inevitably possess core-shells, and they agglomerate into chain-like structures, which eventually result in surface passivation (Guo et al., 2012; Wang et al., 2009a, 2009b). The surface passivation and agglomeration of Fe (0) depends on the nZVI synthesis method. Strong toxic chemical reductants as BH₄⁻ are frequently used for nZVI fabrication. The nZVI fabrication was also made with natural reductants, which are not only

environmentally benign but also inexpensive. Further, the polyphenols derived from green tea holds a great promise as a natural reductant (Khan and Adil, 2018). Polyphenols contain epicatechin, epicatechin gallate, epigallocatechin, and epigallocatechin gallate (EGCG) which are biodegradable. The EGCG makes up about 50–60% of the total polyphenols. Pyrogallol and catechol groups in polyphenols render them hydrophilic antioxidants (Botten et al., 2015). In nZVI particulates fabrication, polyphenols act as a stabiliser, reductant, and a capping agent. However, the nZVI prepared by polyphenols shows surface heterogeneity due to shape, size, and reactivity (Huang et al., 2014; Wang et al., 2014, 2014b). Enhanced agglomeration and rapid oxidation decrease the reactivity of nZVI. Several methods are used to reduce agglomeration. In one way, the surface of the nZVI was modified with surfac-

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tants, cellulose, or starch (Dong et al., 2016; Lefevre et al., 2016). Alternatively, the nZVI particulates were fabricated onto solid substrates such as silica, resins, non-woven fabrics, clays, or membranes to enhance dispersibility (Huang et al., 2014; Wang et al., 2014, 2014b; Zou et al., 2016). In the latter case, most of the chosen substrates were insulators that limit electron transfer. However, graphene or reduced graphene (rGO) transfer electrons via conjugated sp^2 orbitals network. Therefore, the nano zerovalent iron particulates decorated on graphene exhibit enhanced conductivity, high electrolyte contact area, and structural stability, all of which are useful for their applications as a reductant (Kumar et al., 2014; Wang et al., 2010).

This research is aimed at fabricating stable and well-dispersed nZVI on rGO using polyphenols extracted from the green tea (hereafter rGO-nZVI-P). As a control, the Fe (II) and graphene oxide reduction were also achieved using BH_4^- method (rGO-nZVI-B). We used rGO substrate for the production of nZVI by polyphenol reduction method. The nZVI can disperse readily onto the rGO due to its porous layering which minimises particulates agglomeration. The rGO-nZVI composites were characterised by spectroscopic and electrochemical methods to probe reactivity sites. The reduction efficiency of rGO-nZVI-P against rGO-nZVI-B was determined using aqueous nitrate as an index ion.

2. Material and methods

2.1. Materials

Analytical grade chemicals received from Sigma-Aldrich (USA), namely H_2SO_4 (98%), H_2O_2 (30%, v/v), $KMnO_4$ (99.5%), $NaNO_3$ (99.5%), HCl (37 %), $NaBH_4$ (99.0%) and $FeSO_4 \cdot 7H_2O$ (99.0%) was used. Vein graphite and green tea samples were obtained from Sri Lanka (support documentation for details, S-1). All solutions were prepared with ultrapure water ($0.055 \mu S/cm$ at $25^\circ C$).

2.2. Synthesis of graphene oxide (GO)

The GO samples were synthesised according to modified Hummers method (Chen et al., 2013) using 2 g of vein graphite flakes at a given time (S-1.1). The GO particulates were washed with 5 % (v/v) HCl to remove metallic contaminants (Kumar et al., 2017). The acid-washed samples were further washed repeatedly with ultrapure water ($0.055 \mu S/cm$ at $25^\circ C$) until the resultant solution pH was neutral. The solid and solution separation was carried out by centrifugation at 5000 rpm. Graphite has converted into graphite oxide by Hummers treatment. As shown in S-1.1, after successive ultrasonication and centrifugation, the graphite oxide converted into graphene oxide. Accordingly, the presence of GO was determined by XRD and UV-spectroscopic measurements and calculation using Raman spectral data using the constant force model $\omega_G = 1581.6 + \frac{11}{1+n^{1.6}}$ when no coupling between phonon and electrons is assumed (Friedel and Carlson, 1971; Wang et al., 2009, 2009b).

2.3. UV spectroscopy of rGO

Polyphenols extracted from the green tea were added to GO suspension to yield reduced graphene oxide (rGO-GT). The solution colour changed from brownish-yellow to black was monitored to determine the progress of the reaction. The rGO/rGO-GT were washed thoroughly with deionised water until the pH of the washed solution was neutral (Wang et al., 2011). A UV spectroscopic method was used to determine rearrangements of π electronic conjugation in rGO-GT and rGO (UV 201, Thermo Scientific, USA).

2.4. Synthesis of rGO-nZVI composites

rGO-nZVI composites under facile conditions were synthesised using BH_4^- or green tea derived polyphenols. A 200 mL of 0.25 M $FeSO_4 \cdot 7H_2O$ dissolved was mixed rGO suspension under vigorous shaking for 1 h. In

the synthesis of rGO-nZVI-B, a 50 mL of 1 M sodium borohydride solution was added dropwise to rGO and $FeSO_4 \cdot 7H_2O$ suspension stirred for 24 h. Alternatively, for the preparation of rGO-nZVI-P, 200 mL polyphenol extract was added to the rGO/ $FeSO_4 \cdot 7H_2O$ suspension and stirred for 24 h. The black materials resulted from both routes were washed to a neutral pH. The freshly prepared rGO-nZVI composites (rGO-nZVI-P or rGO-nZVI-B) were separated, vacuum dried, and stored at $4^\circ C$. The hydrated rGO was also ultrasonicated for 20 min and stored at $4^\circ C$.

2.5. Characterisation of rGO-nZVI composites

The rGO-nZVI composites were characterised with spectroscopic and electrochemical methods. X-ray diffractograms of rGO-nZVI-P and rGO-nZVI-B were obtained for phase identification and particle size estimation. An X-ray diffractometer at 20 kV and 30 mA was operated using $Cu-K_\alpha$ radiation at $\lambda = 0.154$ nm (Rigaku Ultima IV, Japan). The mean diameter of the crystallites was estimated by the Scherrer equation (Kumar et al., 2019a);

$$D = \frac{0.94\lambda}{\beta \cos \theta}$$

where D is the mean size of the crystalline substrate, λ is the wavelength of $Cu-K_\alpha$ radiation, β is the line broadening at half the maximum intensity of the Bragg peak corrected for instrumental line broadening, 0.94 is a shape factor (Scherrer constant), and θ Bragg angle. Transmission electron microscopy (TEM) images were obtained on a JEM-200CX 139 electron microscope operated at 200 kV. FTIR spectra were recorded in transmission mode for the characterisation of surface sites with an IR spectrometer equipped with a DTGS detector (iS50 Thermo Scientific, USA). All spectra were obtained at 4 cm^{-1} resolutions in the $400\text{--}4000 \text{ cm}^{-1}$ spectral range. The Raman measurements of the rGO-nZVI composites were obtained by Raman spectrometer with at 532 nm laser excitation (Lumenera BRUKER SENTERRA, Germany). The electrons transfer of rGO-nZVI composites were examined by cyclic voltammetry using modified glassy carbon electrodes as detailed in the S-1.2.

2.6. X-ray photon spectroscopic (XPS) analysis

All XPS measurements were carried out by an XPS (5000 VersaProbe II ULVAC-PHI Inc., Japan) system equipped with a scanning microprobe X-ray source (monochromatic Al K_α 1486.7 eV X rays), an electron flood gun, a floating ion gun generating low energy electrons (1.1 eV), and low energy Ar ions (8 eV) for charge compensation at isolating samples (dual beam technique), respectively. A small amount of well-dried and fine sample was evenly distributed and pressed against a conducting Cu tape fastened onto a sample holder mounted on the manipulator. During the experiment, the base pressure in the experimental chamber was $\sim 5 \times 10^{-10}$ mbar, and all photoemission data was acquired in the normal emission mode from well-outgassed samples. The angle between the sample surface and analyser was set at 45° . Survey scans were recorded with an X-ray source power of 31 W and pass energy of 187.85 eV. Narrow scans of the elemental lines were recorded at 23.5 eV pass energy, which yields an energy resolution of 0.69 eV FWHM at the Ag $3d_{5/2}$ line of pure Ag. All spectra were referenced to C 1s (hydrocarbon) at 284.8 eV. Data analysis was performed using the embedded peak resolving program (ULVAC-PHI MultiPak ver. 9.5, Japan).

2.7. Classical surface properties

The specific surface area of the rGO-nZVI composites was determined with the Brunauer–Emmett–Teller (BET) method, (Quanta chrome Instruments version 11.0). Before specific surface area determination, the samples were degassed at $300^\circ C$ for 6 h using 99.998% Ar to remove water, and other surface sorbed impurities, and yield clean surfaces for surface area measurements. The specific surface area of rGO-nZVI-B was $31.2 \text{ m}^2 \text{ g}^{-1}$, while for rGO-nZVI-P, it was $16.1 \text{ m}^2 \text{ g}^{-1}$. The zero point of

charge (pH_{ZPC}) of the rGO-nZVI composites was determined by proton surface titration. A 2 g L^{-1} composite materials were separately equilibrated in NaCl for 1 h under N_2 (99.996%) purging. The initial pH of the composite suspension was ~ 5.4 . The suspension pH was raised to pH 10 with 0.05 M NaOH. The acid titrations were carried out with auto titrator systems to pH 4.

2.8. Nitrate reduction by rGO-nZVI composites

The rGO-nZVI composites were used to reduce nitrate in water. The experimental procedures are documented elsewhere (Ratnayake et al., 2017). In a typical experimental setup, a 200 mL batch solution was prepared in 0.01M NaCl using 5 g L^{-1} rGO-nZVI-B or rGO-nZVI-P at pH ~ 5.6 and 25°C . The reactor system was continuously purged with Ar. At a given point, the solution was spiked with nitrate to yield 0.8064 mM, and at pre-defined times a known volume of suspension was filtered (0.22 μm membrane filters) into 2.5 mL tubes for nitrate and nitrite detection by ion chromatography (Shimadzu CDD 10A VP, Japan) in triplicate. Empirical rates of nitrate reduction by rGO-nZVI composites were developed from the experimental data.

2.9. Nitrate reduction in well water by rGO-nZVI composites

The spatial distribution of nitrate in well waters in Nettiyagama village (Sri Lanka) was also compiled (Fig. 8-S: support documentation). Well water with the highest nitrate (94 mg/L NO_3^-) was sampled to evaluate the efficiency of rGO-nZVI catalysts for nitrate destruction. The experimental procedure is the same as stated in Section 2.8, except as received natural well water was used in place of nitrate test solutions. TDS and pH measurements were carried out with a pH/EC/TDS/ORP meter (EXTECH, 341350A, USA). We used a photometer to determine hardness, nitrate and alkalinity in water with the manufacturer supplied test kits (MD 600, Lovibond, Germany).

3. Results and discussion

3.1. UV-vis spectroscopy of graphene derivatives

The reduction of GO $\rightarrow$ rGO by polyphenol is observed in UV-vis spectroscopic data (Wang et al., 2011). When compared to polyphenol, the reduction of GO $\rightarrow$ rGO by BH_4^- is relatively straightforward. As shown in Fig. 1-S GO shows maximum absorption at 230 nm with a shoulder (at 300 nm) due to aromatic C-C and C=O, $\pi-\pi^*$ and $n-\pi^*$ electron transitions, respectively (Mhamane et al., 2011). As the GO $\rightarrow$ rGO reduction proceeds, the colour of the solution changes from brownish-yellow $\rightarrow$ black. The peak observed at 230 nm for GO red-shifted to 273 nm, which confirms the restored graphene structure. The new peak at 205 nm confirms the presence of polyphenol (Wang et al., 2011) adsorbed on rGO. The reduction of peak intensity at 273 nm is due to the overlapping of adsorbed polyphenol and rGO spectrums.

3.2. X-ray diffraction and TEM characterisation

The X-ray diffraction peaks at $2\theta = 44.34^\circ$, 65.26° (Fig. 1-A: rGO-nZVI-P), 44.43° , and 65.11° (Fig. 1-A: rGO-nZVI-B) confirm the presence of $\alpha\text{-Fe}$ (0) BCC phase in the core (Kassae et al., 2011). The basal peak at $2\theta = 26.72^\circ$ corresponds to organised graphite sheets in rGO-nZVI-P with 0.33 nm inter-layer spacing (Fig. 2-S). During the graphite $\rightarrow$ GO oxidation, the peak at $2\theta = 26.72^\circ$ has disappeared, and a new one appears at $2\theta = 11.46^\circ$ with enhanced interlayer spacing (i.e., 0.76 nm). The absence of the peak at $2\theta = 11.46^\circ$ suggests GO $\rightarrow$ rGO conversion by exfoliation (Guo et al., 2012) (Fig. 2-S). As shown in Fig. 1-B-I and B-II, the diffraction patterns for rGO-nZVI-B matches well with that of the iron oxide (Wang et al., 2009, 2009b), and they further confirmed by XRD results. The shell structure is composed of mixed iron oxides/hydroxides with a layer thickness around 2–7 nm. However, the outer

layering is sporadic around metallic Fe cores (Petala et al., 2013). The Fe (0) is highly reactive, and upon exposure to the ambient atmospheric conditions, they readily oxidised into core-shell structures. The relative proportions of oxidation states of iron in the mixed-layer coatings are highly variable, and they depend on the reductants used in the material fabrication (Li et al., 2006). In the presence of rGO, the nZVI particulates are decorated with a coating that protects the core Fe (0) from further oxidation. Due to the presence of Fe (0), the electron diffraction patterns of rGO-nZVI-P are more complex than the rGO-nZVI-B. The preparation methods of nZVI exert significant influence on the physical and chemical properties of the particulates and operation parameters (Li et al., 2006).

As shown in TEM images (Fig. 1-C), the graphene sheets form stable configurations as corrugation, bending, and folding (Yadav et al., 2016; Wang et al., 2014a, 2014b). Most nZVI particulates are spherical with diameters in the range ~ 4 to ~ 15 nm, which are well dispersed within rGO layers (Fig. 1-D). This unique arrangement inhibits Fe (0) rapid oxidation and agglomeration (Peik-see et al., 2014). However, in the case of BH_4^- reduction, Fe (0) tends to agglomerate on the rGO surface (rGO-nZVI-B). Polyphenols act as a capping agent for Fe (0) to prevent its aggregation. According to published data (Wang et al., 2009, 2009b), fully oxidised nZVI particles are relatively small (diameter 4–10 nm) while core-shell particles are relatively large and include a Fe core (~ 18 nm). When compared to rGO-nZVI-P, the relative proportion of Fe (0) in rGO-nZVI-B is low. In the latter case, under ambient conditions, the exterior portions of Fe (0) particulates readily convert into amorphous Fe (OH)₂ or Fe (OH)₃ with specific surface area (Wang et al., 2014, 2014b). Therefore, the specific surface area of the rGO-nZVI-P (16 $\text{m}^2 \text{g}^{-1}$) should be less than the rGO-nZVI-B (32 $\text{m}^2 \text{g}^{-1}$).

3.3. Vibration spectroscopic data

The Raman spectrum of nZVI is virtually featureless. The weak band shows at 700 cm^{-1} is due to partial oxidation of the Fe (0) (Jabeen et al., 2013). The Raman spectra of rGO-nZVI-B and rGO-nZVI-P are simple and contain G, D, 2G, and 2D bands characteristic of crystalline carbon structures (Fig. 2-A). Graphite or high-quality graphene shows a D band at 1351 cm^{-1} with weak intensity. The D-band is due to the breathing mode of the distorted sp^2 C rings that requires a defect or an adjacent graphene edge for activation; it results from transverse optical phonons around the K point of the Brillouin zone (Wang et al., 2014, 2014b; Lespade et al., 1984). The intensity of the D band directly proportional to defect density and the highest value is shown in rGO-nZVI-B ($\frac{I_D}{I_G} = 0.851$). The G-band corresponds to the doubly degenerated E_{2g} phonon at the Brillouin zone. In rGO-nZVI-P, the G band due to first-order scattering of E_{2g} phonon of sp^2 C in rGO occurs at 1535 cm^{-1} . However, in rGO-nZVI-B, the G band has shifted from $1535 \rightarrow 1587 \text{ cm}^{-1}$ due to the rGO oxidation (Chen et al., 2013). In both instances, the rGO phase is present, and the D band intensity of graphite increases with the oxidation.

Upon conversion of GO to rGO, both G and D bands broaden and shift. The intensities of G and D bands are higher in rGO-nZVI-B ($\frac{I_D}{I_G} = 0.851$) than rGO-nZVI-P ($\frac{I_D}{I_G} = 0.853$), which suggest the abundance of isolated rGO domains (Li et al., 2014; Wang et al., 2009, 2009b). The 2D overtone at 2679 cm^{-1} determines the multi-layering in graphene. The presence of mono-layering in graphene signifies by the 2D band at 2679 cm^{-1} . The D band broadens and blue shift evidence multi-layering of graphene (Li et al., 2014; Wang et al., 2009, 2009b). In rGO-nZVI-B, the band at 2680 cm^{-1} indicates mono-layering in graphene structure, whereas a multi-layering structure is observed in rGO-nZVI-P. However, the presence of functional groups such as carbonyl, carboxyl, hydroxyl, and epoxides in GO inhibits layer stacking and further enhance the attachment of metal oxide nanomaterials (Kumar et al., 2019b). The confirmatory evidence for the presence of rGO monolayers required high-resolution transmission spectroscopic measurements (Chen et al., 2012;

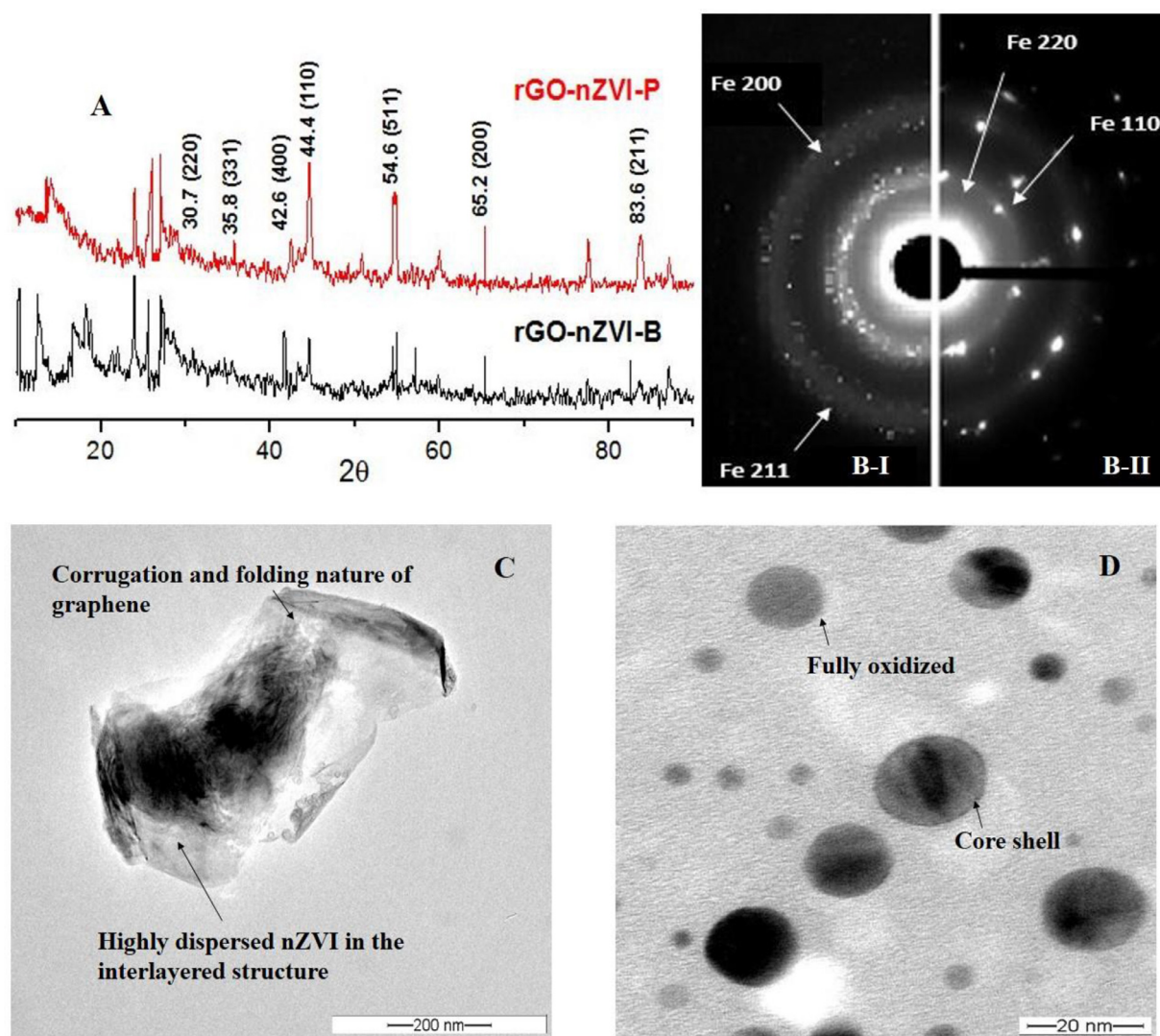


Fig. 1. (A–D): (A). X-ray diffractograms of rGO – nZVI-B and rGO – nZVI-P. (B). Low energy diffraction patterns rGO-nZVI-P (B-I) and rGO-nZVI-B (B-II). (C). Corrugation and folding morphology of rGO, (D). nZVI core shells and oxidised particulates.

Sun et al., 2017). However, without high-resolution TEM data, we cannot express the light areas of rGO sheets as monolayers (Kumar et al., 2016).

In the FTIR spectrum of crystalline graphite, no specific bands do appear, but weak bands around 2200 cm^{-1} are due to aromaticity within the non-crystalline graphite matrix (Friedel and Carlson, 1971; Țucureanu et al., 2016) (Fig. 2-B). In GO, the graphite structure still remains with increased inter-layer distance (graphite = 0.33 nm GO = 0.76 nm). The GO is composed of sp^3 -hybridized carbons (with hydroxyl and ether/epoxy functional groups arranged on both sides of the surface) and sp^2 -hybridized carbons (with carbonyl and carboxyl functional groups ion basal and edge structures). The rGO derived nZVI nanocomposites are enriched with functional groups. The broadband at $3000\text{--}3600\text{ cm}^{-1}$ region relates to H-bonded O–H stretching vibrations of –COOH, physisorbed water, or structural –OH in GO. However, the discrimination of –OH present in –C–OH and H_2O is not possible from our data. The band at 1724 cm^{-1} corresponds to stretching of –C=O in –COOH, or easily convertible functional groups as anhydride or lactone preferentially located along the periphery of the GO sheets. The band at 1724 cm^{-1} disappeared upon the reduction of $\text{GO} \rightarrow \text{rGO}$ and $\text{Fe(II)} \rightarrow \text{Fe(0)}$ by either BH_4^- or polyphenols. In GO, the band at 1620 cm^{-1} attributes

to bending modes of –OH groups from physisorbed water. In rGO, the shoulder bands at $\sim 1630\text{ cm}^{-1}$ and 1400 cm^{-1} are assigned to aromatic and –C–C– stretching. The GO structure contains a large proportion of –COOH groups in different H-bonded local environments. The band at 1047 cm^{-1} ascribed for H-bonded –COOH deformations. The band at 1047 cm^{-1} increased when polyphenol is used in the Fe (0) and GO reductions.

The broad doublet around $3200\text{ to }3350\text{ cm}^{-1}$ corresponds to H-bonded –OH vibrations in phenolic and carboxylic groups of polyphenols. The band at 2810 cm^{-1} indicates the vibrations of –C–H present in phenolic and graphene structures. The absence of band at 1724 cm^{-1} in both rGO-nZVI-B and rGO-nZVI-P spectrums confirms $\text{GO} \rightarrow \text{rGO}$ conversion. The shoulder band at 980 cm^{-1} is due to bending vibrations of –C–H in rGO and is prominent due to the formation of admixture with graphite and rGO. The band at 598 cm^{-1} indicates the presence of Fe_xO_y phase on graphene sheets (Fig. 2-B). The shoulder peak at 1400 cm^{-1} due to –COOH symmetric stretching has developed as a discrete band upon $\text{GO} \rightarrow \text{rGO}$ conversion. The invariant behaviour of IR bands around $3000\text{--}3500\text{ cm}^{-1}$ and 1047 cm^{-1} indicates surface adherence of C–O bonds onto defects or graphene sheets. The association of Fe (0) on rGO matrix is possibly occurred via π – π framework is shown in Fig. 3.

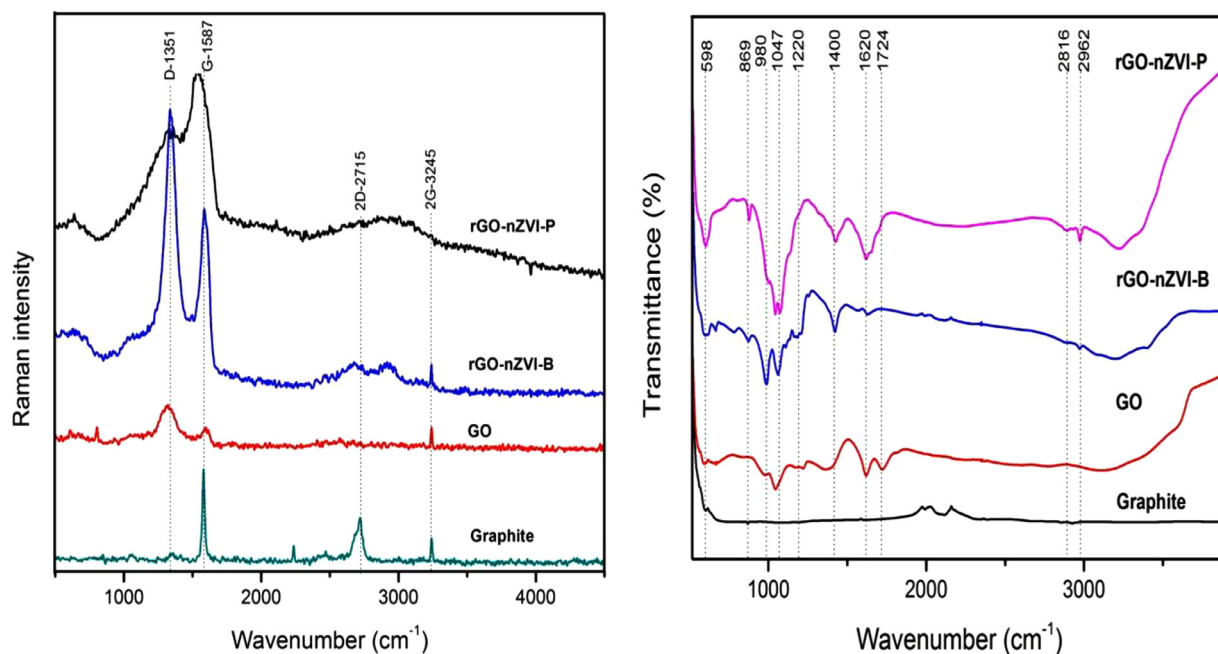


Fig. 2. (A–B): (A). Raman spectra of graphite, GO, rGO-nZVI-B, and rGO-nZVI-P (B). FTIR spectra of graphite, GO, rGO-nZVI-B, and rGO-nZVI-P.

3.4. X-ray photon spectroscopy (XPS)

Details of the XPS spectrums of rGO-nZVI-P and rGO-nZVI-B are shown in Figs. 3-S to 5-S, and only the spectral evidence corresponds to Fe (II) $\rightarrow$ Fe (III) conversion is discussed. Fig. 5-S (A) shows the resolved Fe (0) peaks correspond to Fe 2p_{3/2} and Fe 2p_{1/2} of rGO-nZVI-P and rGO-nZVI-B at (711.5 eV, 725 eV) and (710.8 eV, 723 eV), respectively. The Fe 2p_{3/2} and Fe 2p_{1/2} peak shifts are due to Fe (0) $\rightarrow$ Fe (III) conversion (Kumar et al., 2017). The characteristics Fe (0) peak shows at 707 eV or 706.8 eV for rGO-nZVI-B or rGO-nZVI-P, respectively (Guo et al., 2012). As shown in Fig. 5-S (B and C), the anionic oxygen in Fe_xO_y shows a peak around 529–530 eV (Guo et al., 2012; Li et al., 2011). The peaks observed at 530 and 531 eV are due to anionic oxygen in rGO-nZVI composites. However, the origin of surface oxygens cannot be resolved from the nature of the data presented.

3.5. Nitrate reduction in water

The reduction efficiency of nitrate by rGO-nZVI-P or rGO-nZVI-B was determined around pH 5.6. When compared to rGO-nZVI-B, the rGO-nZVI-P shows enhanced reactivity for nitrate reduction (Fig. 5-A). Always, the dominant nitrate reduction product by rGO-nZVI composites is ammonium ion, which accounts for over 95 % of N-mass balance. Nitrite and nitrogen oxides are present in small quantities initially. However, no nitrite accumulation is shown (Microbes et al., 2004). When kinetic measurements were made with nitrite or nitrate and Fe (0), it was shown that the rate of nitrite reduction by Fe (0) is over ten-fold faster than of nitrate (Microbes et al., 2004). In the nitrite/Fe (0) system, only 50% of N was accounted for ammonium ion conversion (Scherer, 2002). Mainly the ammonium production seems to occur via nitrite reduction pathway. The nitrate reduction by NO or N₂ pathways is not significant (Goto and Fujie, 2001; Han et al., 2016) shown in the CV data (Fig. 6-S. A and B, Fig. 7-S), the Fe (0), Fe (II) and Fe (II)-polyphenol species are active in nitrate reduction by rGO-nZVI composites (Fig. 4). In the presence of Fe (II), however, the nitrate reduction does not occur in homogeneous solution (Liu and Wang, 2019), and it is essentially surface-mediated. The pH_{zpc} values of rGO-nZVI-P and rGO-nZVI-B are 6.2 and 6.9, respectively. When pH $\sim$ 5.6, the surface of rGO-nZVI composites is positively charged, and NO₃⁻ forms an outer-sphere surface complex without a

ligand exchange. The Fe (0) and C include an array of micro-galvanic cells with a relatively large potential difference (Liu and Wang, 2019) which drives larger electron flow from rGO-nZVI-P or rGO-nZVI-B compared to nZVI. The transfer of electrons occurs readily to nitrate ions via surface attached OH⁻ conduits. The experimental data suggest ammonium as a major product, while N₂, NO and NO₂⁻ present in the system in traces. Accordingly, the nitrate reduction seems occurring via nitrite into ammonium, as shown in Fig. 4.

3.6. Nitrate reduction kinetics

Nitrate reduction by rGO-nZVI composites occurs via multi-electron transfer routes. Therefore, the development of a mechanistic model to account for nitrate reduction kinetics is quite challenging. Therefore, to quantify NO₃⁻ reduction by rGO-nZVI composites, an empirical kinetic model was developed using the initial rate determination method (Fig. 5-A). The nitrate reduction by nZVI composites at pH 5.6 follows second-order kinetics by the model shown below:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$

where Q_t and Q_e are [NO₃⁻] at a given time t and [NO₃⁻] at a maximum reduction, respectively. The k_2 represents the empirical rate constant for nitrate reduction. When initial [NO₃⁻] = 0.8062 mM, the reduction rate is highest in the rGO-nZVI-P composite. The rate constants are determined as 2.1039 and 2.9347 for rGO-nZVI-P and rGO-nZVI-B, respectively.

3.7. Reusability of nZVI composites

The Fe (0) in polyphenol/rGO composite is well dispersed, which results in enhanced efficiency of nitrate reduction at initial [NO₃⁻] = 0.8062 mM and pH 5.6. The reusability of the substrates for nitrate reduction was also examined. Always when compared to rGO-nZVI-B, the rGO-nZVI-P showed superior performance for nitrate reduction. The efficiency of nitrate reduction by nZVI is optimal around pH $\sim$ 2 and decreases rapidly at neutral pH. However, in the presence of rGO, the nitrate reduction by rGO-nZVI-P was optimal around pH 5.6. In rGO-nZVI composites, rGO acts as an electrode in the array of Fe (0)

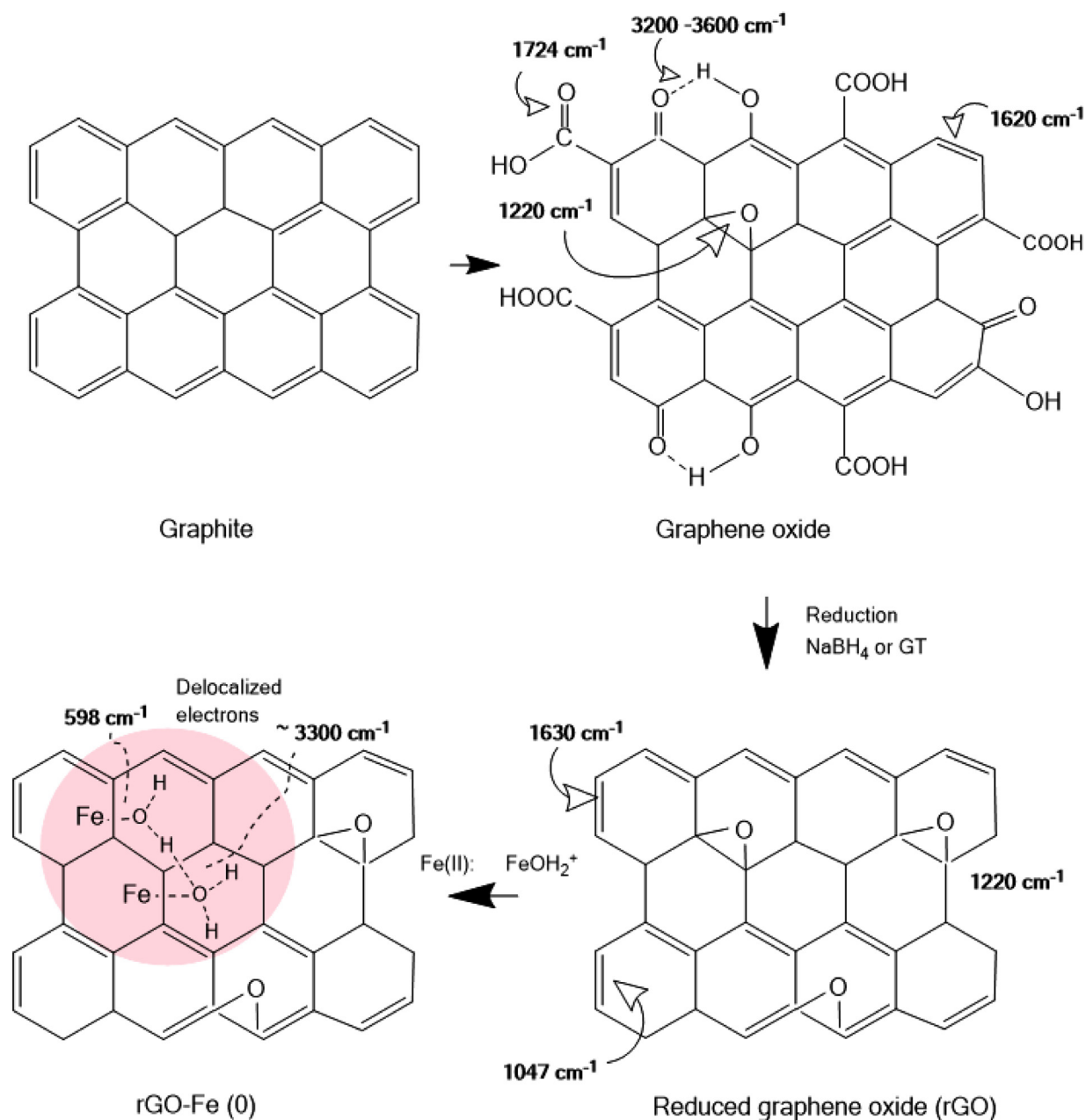


Fig. 3. A postulated model for the association of Fe (0) with rGO. The Fe (0) adhesion on rGO believes via π - π stacking.

and C galvanic cells, which increases electron flux. However, rGO-nZVI-B, most of the nZVI particulates are covered with an insulating oxide layer, which limits electrons transfer to some extent. In the case of rGO-nZVI-P, this effect is minimised, which enhances electrons flux. When compared to rGO-nZVI-B, the enhanced efficiency of nitrate reduction by rGO-nZVI-P is ascribed due to higher electrons flux. The improved reduction efficiency of nitrate by rGO-nZVI-P is ascribed due to the following factors; a. the large proportions of electrons are released from rGO-nZVI-P by the Fe (0) and C galvanic cell, b. surface water splitting at the surface generating H⁺. The large potential difference created by Fe (0) and C galvanic cells drives a more significant number of electrons than corrosion, and water splitting at the surface site creates H⁺ both favour nitrate reduction (Liu and Wang, 2019). Although nZVI is dispersed well in the rGO surface, in rGO-nZVI-B, most of the nZVI particulates are covered with an oxide layer that limits efficient electrons transfer to nitrate (Fig. 5B). The efficiency of rGO-nZVI-P is declined by about 2% with repeated use for five days.

3.8. Application to nitrate-rich natural well water

In a batch experiment, rGO-nZVI-B or rGO-nZVI-P was used to destruct nitrate in a well water sample used for human consumption (Fig. 8-S: support documentation). As in Table 1-S (support documentation), the nitrate concentration of our water sample exceeds the WHO limit (e.g. 50 mg/L nitrate, WHO, 2017) specified for drinking water by about two folds. Over 55% nitrate in the well water can be eliminated by rGO-nZVI-P treatment. Concurrently, over 40% TDS reduction in water can also achieve. However, when rGO-nZVI-B is used, only 43% of nitrate was destructed; however, no decrease in TDS was observed. The divalent cations seem to complex with polyphenolic compounds present in rGO-nZVI-P. Although nitrate is enforceable water quality parameter, TDS is non-enforceable. However, excess TDS renders water unpalatable. Therefore, TDS control is desirable first, to increase water palatability. The rGO-nZVI-P can use as a starting material for concurrent removal of TDS and nitrate in water. However, the mechanism of the reduction

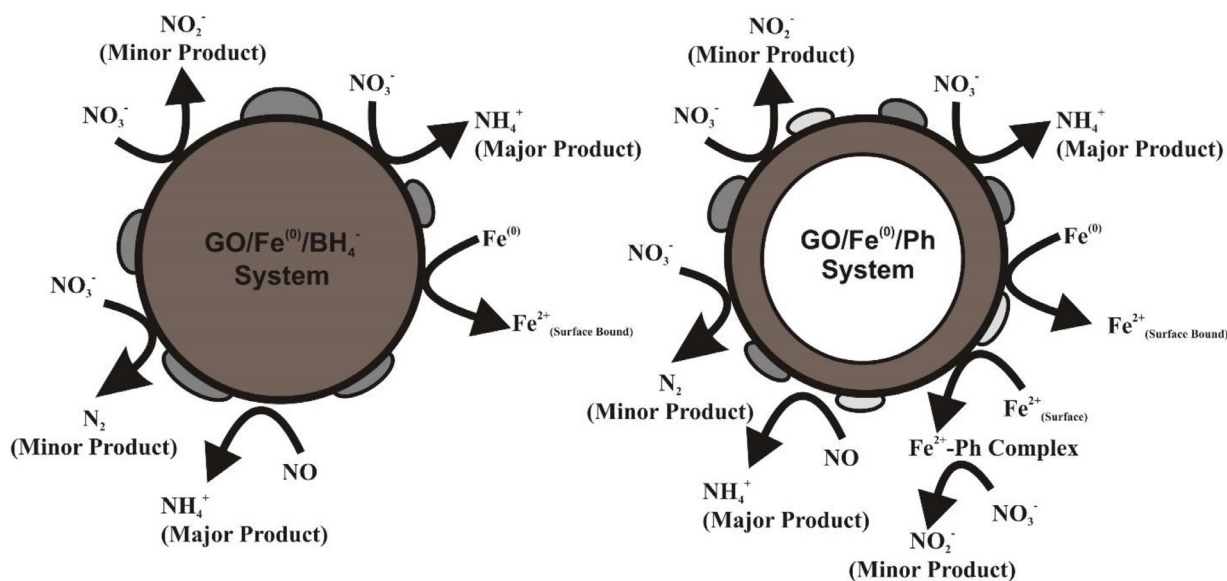


Fig. 4. Postulated nitrate reduction pathways. $\text{NO}_2^-/\text{NO}_3^-$ E^0 0.843 V; NO/NO_3^- E^0 0.952 V; N_2/NO_3^- E^0 1.241 V, $\text{NH}_4^+/\text{NO}_3^-$ E^0 0.878 V, $\text{NH}_4^+/\text{NO}_2^-$ E^0 0.890 V.

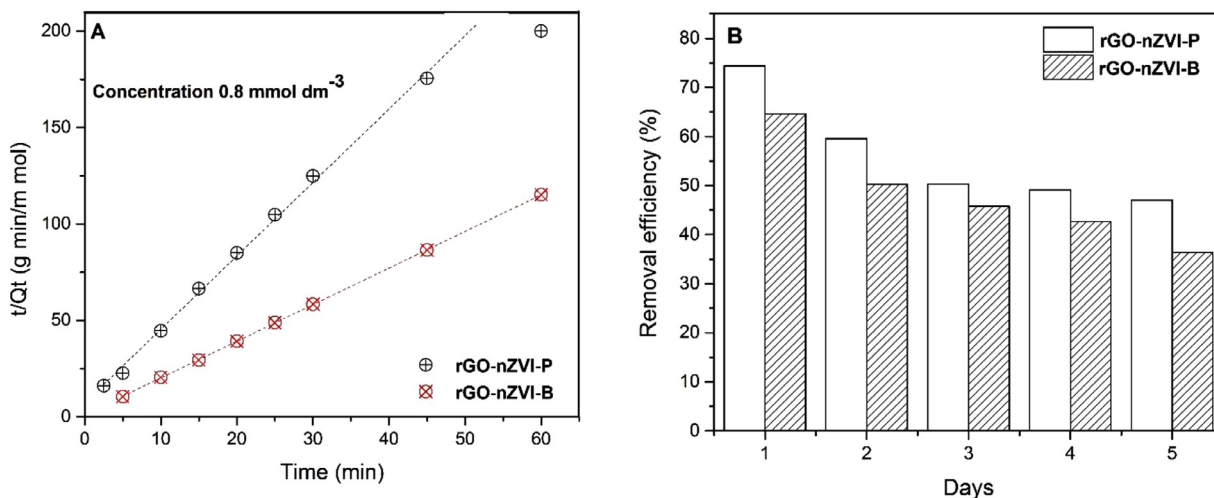


Fig. 5. (A–B): (A). Pseudo Second-order kinetic model for the removal of excess nitrate using rGO – nZVI composites and T 25 °C. (B) Nitrate removal efficiency on repeated use of rGO-nZVI substrates. Initial solution composition $[\text{NO}_3^-]_{\text{initial}} = 0.8062 \text{ mM}$ $[\text{rGO-nZVI}] = 5 \text{ g L}^{-1}$, pH 5.6.

of divalent ions by rGO-nZVI substrates, and detailed characterisation of the spent catalyst warrants further research.

4. Conclusions

The synthesis of Fe⁰ on rGO matrix by polyphenol has resulted in nZVI with enhanced stability (rGO-nZVI-P). The rGO-nZVI-P is suitable to destruct nitrate from water. The nitrate reduction occurs efficiently at near-neutral pH yielding ammonia as the main product (~95%). The incorporation of nZVI amidst rGO is believed via π - π stacking. Further research warrants into *in situ* conversion of ammonium produced by nitrate reduction into chloramines for safe water disinfection. The rGO-nZVI-P has a promise in drinking water treatment due to its ability to reduce nitrate and TDS in natural water concurrently.

Author contributions

JU. Halpegama: investigation and writing original draft; PMCJ Bandara: investigation (nitrate reduction), L. Jayarathne: investigation; A. Bandara: data curation and conceptualisation (FTIR) Chen-Yu. Yeh:

resources; Jiann-Yeu Chen: investigation (XPS); C. Kuss: supervision (electrochemistry); U. Dahanayake: investigation (electron microscopy); AC Herath: investigation (electrochemistry); SK Weragoda: investigation (nitrate kinetics); Xing Chen: conceptualisation, formal analysis R. Weerasooriya: supervision and funding acquisition, writing-revision editing.

Declaration of Competing Interest

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

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envadv.2020.100024.

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