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Rabih Saad a, Sonia Thiboutot b, Guy Ampleman b, Wang Dashan c, Jalal Hawari a,⇑

a Biotechnology Research Institute, National Research Council of Canada, 6100 Royalwood Avenue, Montréal, Quebec, Canada H4P2R2
b Defence Research Development Canada, Department of National Defence, Valcartier, Quebec, Canada

c Biotechnology Research Institute, National Research Council of Canada, 6100 Royalmount Avenue, Montréal, Quebec, Canada H4P 2R2

1. Introduction

Trinitroglycerin (TNG) C3H5(ONO2)3, is a versatile chemical widely used in the manufacture of dynamite and in construction and demolition industries. TNG is also known for its clinical properties as a vasodilator to treat angina and heart failure. These seemingly attractive applications of TNG have incited various industries, especially the pharmaceutical and military, to produce the chemical in massive amounts. Large-scale manufacturing of TNG and its wide use in military training led to widespread contamination (Oh et al., 2004). For instance, the chemical has been detected in wastewaters adjacent to Badger Army ammunition plant (Barabo, WI, 180 mg L−1) and Radford Army ammunition plant (Radford, VA, 300–600 mg L−1). Despite its useful applications, TNG is a man made xenobiotic which is toxic to various aquatic and terrestrial organisms including algae, vertebrates and invertebrates (Burton et al., 1993; Oh et al., 2004).

Wastes containing TNG have been incinerated to remove the chemical but this process emits other toxic products (Garg and Castaldini, 1991). Adsorption on granular activated carbon (GAC) is as an effective technology for removing TNG from water (Concurrent Technologies Corporation, 1995), but the chemical remains intact without being degraded. Alternatively, TNG can be hydrolytically degraded under alkaline conditions to produce formate, oxalate, and acetate (Capellos et al., 1984; Tsaplev, 2004; Halasz et al., 2010). However, the use of excess amounts of reactants in these methods creates another disposal problem.

Recently, metal-based reductants such as pyrite (Oh et al., 2008) and nickel (Fuller et al., 2007) were employed to degrade TNG, but degradation often proceeds with slow rates. The recent evolution of nanomaterials is offering great potential for delivering novel and improved water treatment technologies (Shan et al., 2009). Zero-valent iron nanoparticles (ZVINs) have received much recent attention due to their low cost and environmentally benign nature. For example, ZVINs were used in the reductive transformation of nitroaromatics (Bai et al., 2009), nitroamines (Naja et al., 2008, 2009), and trichloroethylene (TCE) (Liu et al., 2005; Zhan et al., 2008; Wang et al., 2010). To our knowledge the degradation of TNG in aqueous solution using ZVINs has not been reported. Thus the main objective of this work is to study the degradation of TNG using ZVINs. Because ZVINs can form aggregates which may

⇑ Corresponding author. Tel.: +1 514 496 6267; fax: +1 514 496 6265.
E-mail address: jalal.hawari@nrc.ca (J. Hawari).
drastically decrease reactivity and mobility, especially during in situ treatment, we stabilized iron nanoparticles by dispersion on the surface of an inert polymer such as nanosilica. Chitosan (Zhu et al., 2006), amorphous silica (Zheng et al., 2008), poly(ethylene glycol) (Wang et al., 2010), polyglycokite (Frost et al., 2010), carboxymethyl cellulose (He et al., 2007; Naja et al., 2008), and poly(acrylic acid) (Schrick et al., 2004) have been used to maintain reactivity by preventing aggregation of the nanometal. In the present study, we prepared nanostructured silica SBA-15 (Santa Barbara Amorphous No. 15), known for its use in catalysis and in drug delivery, and used it as a support to stabilize and keep ZVINs well dispersed. The resulting ZVINs/SBA-15 nanomaterial was then used to degrade TNG in water. We also determined the reusability of ZVINs/SBA-15 for its effective repetitive use in treating TNG-contaminated water.

2. Experimental section

2.1. Chemicals

Tetraethyl orthosilicate (TEOS, purity >98%) was purchased from Sigma–Aldrich (Oakville, ON). Triblock co-polymer P123 (EO_{20}PO_{70}EO_{20}) surfactant was provided by BASF (Mississauga, ON). Ferrous sulfate heptahydrate (99%) and sodium hydroxide (99%) were obtained from Anachemia and EMD (Mississauga, ON), respectively. Sodium borohydride (>98.5%) was purchased from Aldrich (Oakville, ON). TNG dissolved in acetone (1000 mg L\(^{-1}\)) was provided by General Dynamics (Valleyfield, QC). Standard solution of TNG, 1,2-dinitroglycerin (1,2-DNG), 1,3-dinitroglycerin (1,3-DNG), 1-mononitroglycerin (1-MNG) and 2-mononitroglycerin (2-MNG) in acetonitrile (1000 mg L\(^{-1}\)) were purchased from Cerilliant Corporation (Round Rock, TX). All chemicals were as received.

2.2. Preparation of ZVINs and ZVINs/SBA-15

Zero-valent iron nanoparticles (ZVINs) were prepared as described by Liu et al. (2005). FeSO\(_4\)·7H\(_2\)O (8 g) was dissolved in 400 mL of methanol/deoxygenated water solution (30% v/v), maintaining pH at 6.1 with NaOH (5 M). Twenty milliliters of sodium borohydride (2.1 M) was added dropwise to the mixture while stirring. The resulting suspension was centrifuged at 8000 rpm for 20 min, washed several times with aqueous methanol solution (50% v/v) and kept in 50 mL methanol aqueous solution under argon until further use.

Nanostructured silica SBA-15 was prepared as previously reported by Wang and Liu (2005). First the surfactant P123 (20 g) was dissolved in 2.0 M HCl and stirred with TEOS (37.5 g) for 20 h at 40 °C then heated for 24 h at 100 °C under static conditions. SBA-15 was filtered, washed and dried at room temperature over-night. Subsequently, SBA-15 was heated at 540 °C for 5 h to remove the P123 (Zhao et al., 2005).

ZVINs/SBA-15 nano assembly was prepared by treating SBA-15 (1 g) with FeSO\(_4\)·7H\(_2\)O (1.2 M) as described by Xiang et al. (2009). The iron-impregnated SBA-15 (1 g) was suspended in 10 mL deionized water and treated with 20 mL of NaBH\(_4\) (2.4 M) to reduce Fe(II) to metallic Fe. The resulting black particles were centrifuged, washed twice with aqueous methanol solution (50% v/v) and freeze dried before use. The concentration of nanoiron in ZVINs/SBA-15 was determined using a thermostatic UV–VIS spectrophotometer at 562 nm. ZVINs/SBA-15 (100 mg) was agitated in concentrated HCl solution (2 mL) for 1 h. Diluted samples were filtered through a Millex-HV 0.45-μm syringe and analyzed as described by Gibbs (1979). The iron concentration, analyzed as Fe(II), was 9.96 mg/100 mg of ZVINs/SBA-15.

2.3. Characterization of ZVINs and ZVINs/SBA-15

BET (Brunauer–Emmett–Teller) surface analysis was performed on a TRISTAR II 3020 surface analyzer (Micromeritics Analytical Services, GA) using the multipoint method. Each material was degassed at 200 °C for 2 h and nitrogen adsorption–desorption isotherms determined at 77 °C. Total pore volume was evaluated from the amount of nitrogen adsorbed at P/P\(_0\) = 0.99 (P = applied pressure, P\(_0\) = system initial pressure).

X-ray diffraction (XRD) patterns were recorded using Cu K\(_\alpha\) radiation (wavelength 1.5406 Å) on a Siemens (D5000) diffractometer operated at 40 kV and 30 mA. Powder diffraction patterns were obtained between 1° and 10° or 1° and 80° with a scan speed of 1° min\(^{-1}\).

Transmission electron micrographs (TEM) were recorded using a Philips CM20 200 kV electron microscope equipped with a Gatan UltraScan 1000 CCD camera and an energy dispersive X-ray spectrometer INCA Energy TEM 200. Samples for TEM analysis were prepared by suspending the nanoparticles in ethanol and sonicating for several minutes. One drop of the suspension was placed onto a 300 mesh carbon-coated TEM copper grid and dried in air. The dried specimen was loaded into the specimen holder and examined with the equipment under 200 kV. Bright field images were taken with the CCD camera at different magnifications on different areas of the specimen.

2.4. Degradation of TNG by ZVINs and ZVINs/SBA-15

Batch degradation experiments of TNG were performed at room temperature in 20 mL serum bottles sealed with Teflon-coated septa. To each bottle we added 10 mL of an aqueous solution of TNG (3.5 μmol) and the equivalent of ZVINs (0.5 g L\(^{-1}\)) taken as unstabilized ZVINs or stabilized as ZVINs/SBA-15 (50.2 mg of freeze-dried ZVINs/SBA-15). The solution was made anaerobic by purging the headspace with argon for 10 min or kept under aerobic conditions. The pH of the TNG aqueous solution was kept at either 5.6 or adjusted to 4 with HCl (0.01 M) or to 9 with NaOH (0.01 M). Three control experiments were performed: (i) a control containing ZVINs in water with no TNG to determine ZVINs stability in water, (ii) a control containing nanostructured silica support SBA-15 with TNG aqueous solution to study the reactivity of SBA-15 with TNG, and (iii) a control containing FeSO\(_4\) with TNG aqueous solution to evaluate the reactivity of Fe(II) towards TNG. All bottles were placed on a rotary shaker at 250 rpm. At different time intervals (5, 10, 15, 20, 60, 120 and 240 min) triplicate bottles were sacrificed for analysis. Aliquots of the aqueous solutions (5 mL) were withdrawn, filtered through a Millex-HV 0.45-μm syringe and analyzed for TNG and its products (see below).

The reusability of ZVINs/SBA-15 was conducted under anaerobic conditions by mixing an aqueous TNG solution (3.5 μmol) with ZVINs/SBA-15 (0.5 g L\(^{-1}\) of ZVINs) in 50 mL serum bottles sealed with Teflon-coated septa. The mixture was stirred for 3 h and centrifuged at 3700 rpm for 20 min. The clear aqueous phase was decanted and the remaining precipitate washed twice with 20 mL of aqueous methanol (50% v/v). Fe(II) in the washed ZVINs/SBA-15 material was reduced with sodium borohydride (2.4 M) to regenerate Fe\(_0\), considered responsible for TNG degradation, as described above. ZVINs/SBA-15 was washed with aqueous methanol (50% v/v) before being repeatedly used to degrade fresh batches of TNG. Five TNG degradation cycles were conducted using the same ZVINs/SBA-15 batch.

2.5. Chemical analysis

TNG, 1,2-DNG, 1,3-DNG, 1-MNG and 2-MNG were analyzed by HPLC equipped with a Ion-310 column (6.5 mm × 15 mm)
genomic, Los Angeles, CA) and UV detection. Sulfuric acid solution (96 μM) was the mobile phase at a flow rate of 0.6 mL min⁻¹ for 45 min. The injection volume was 50 μL and detection was done at 205 nm.

Glycerol was measured using an HPLC (Waters, Milford, MA, USA) equipped with an electrochemical detector (Waters, Milford, MA, USA). The separation was made on a Dionex IonPac AS15 column (4.6 x 250 mm). The mobile phase was a KOH solution (5 mM) at a flow rate of 0.4 mL min⁻¹. Injection volume was 10 μL.

Nitrite, nitrate and ammonium were analyzed using ion chromatography as described by Balakrishnan et al. (2004).

3. Results and discussion

3.1. Characterization of ZVINs and ZVINs/SBA-15

The BET surface areas of ZVINs, SBA-15 and ZVINs/SBA-15 were 82.8, 747.0 and 275.1 m² g⁻¹, respectively. The specific surface area of ZVINs (82.8 m² g⁻¹) exceeded those obtained previously by Choe et al. (2001) and Naja et al. (2008), i.e. 31.4 and 42.6 m² g⁻¹, respectively. Choe et al. (2001) reported that washing might affect the total available sites for nitrogen adsorption during BET analysis, causing changes in the specific surface areas. In our case no modifications in the ZVINs synthesis were made and changes in surface area may have been caused by the washing step. The decrease in the observed specific surface area of ZVINs/SBA-15 (275.1 m² g⁻¹) compared to SBA-15 (747.0 m² g⁻¹) was attributed to occupation of the SBA-15 surface with iron nanoparticles. The porosity of ZVINs, SBA-15 and ZVINs/SBA-15 as determined by nitrogen adsorption/desorption was 0.11, 0.80 and 0.65 cm³ g⁻¹, respectively. The slight decrease in the porosity of ZVINs/SBA-15 (0.65 cm³ g⁻¹) as compared to SBA-15 (0.80 cm³ g⁻¹) was possibly caused by blocking some of the pores in SBA-15 by iron nanoparticles.

Fig. 1 represents XRD of ZVINs, SBA-15 and ZVINs/SBA-15 showing diffraction peaks that corresponded to a body-centered cubic of α-Fe₆ nanoparticles (Fig. 1a). The peak at 2θ = 44.76° corresponded to a (1 1 0) plane while the weak peak at 65.16° corresponded to a (2 0 0) plane (Frost et al., 2010). XRD analysis of the ZVINs/SBA-15 (Fig. 1b,c) confirmed the presence of α-Fe₆ and showed a major peak at 2θ = 1.0° together with two additional peaks at 1.7° and 1.9°, characteristic of the hexagonal structure of SBA-15 (Fig. 1c) (Wang and Liu, 2005). The wide angle diffractogram of pure silica SBA-15 (Fig. 1d) did not contain the two peaks (2θ = 44.76° and 65.16°) characteristic of ZVINs.

Fig. 2 shows representative TEM images of ZVINs, SBA-15 and ZVINs/SBA-15. ZVINs appeared as spherical aggregates (Fig. 2a), while SBA-15 occurred as an ordered microstructure with a hexagonal array of mesopores (Fig. 2b). In the case of ZVINs/SBA-15 the

![Fig. 1. X-ray diffraction of: (a) ZVINs, (b) ZVINs/SBA-15, (c) SBA-15 small angle and (d) SBA-15 wide angle.](image)

![Fig. 2. Transmission electron micrographs (TEM) of: (a) ZVINs, (b) SBA-15 and (c) ZVINs/SBA-15.](image)
iron nanoparticles were well dispersed on the nanosilica surface (Fig. 2c). Particle size distribution (Fig. S-1) determined by measuring the diameter of 100 particles in different regions of a given TEM grid was in the range of 1–100 and 1–60 nm for ZVIN and ZVIN/SBA-15, respectively. More than 80% of the iron nanoparticles in ZVIN/SBA-15 exceeded the SBA-15 pore diameter (≈8–10 nm) (Fig. S-1b), suggesting that most of the ZVINs are located on the SBA-15 outer walls. In addition, the difference in particle size distribution between ZVIN and ZVIN/SBA-15 suggests that Si–OH groups on SBA-15 might affect the size of iron nanoparticles. To our knowledge this is the first report describing the synthesis of the nanomaterial ZVIN/SBA-15, although composites such as Fe2O3/SBA-15 has been synthesized and used to degrade phenol (Xiang et al., 2009).

3.2. Degradation kinetics of TNG

Fig. 3 shows that degradation of TNG (3.5 μmol) with ZVINs (0.5 g L⁻¹) proceeded in two phases, a rapid 5-min phase (74% of TNG degraded), followed by a slower phase that continued to the end of the experiment (20 min). Oh et al. (2008) showed that a much larger amount of pyrite (20 g L⁻¹) was needed to degrade 89% of TNG (3.1 μmol) in 32 d. Fuller et al. (2007) similarly reported that 10 g L⁻¹ of nickel were needed to degrade 0.15 μmol of TNG in 24 h. The rapid degradation of TNG in our case was attributed to the surface area (82.0 m² g⁻¹) of the nanometal (Wanaratna et al., 2006; Zheng et al., 2008).

When TNG (3.5 μmol) was treated with ZVIN/SBA-15 containing the same amount of ZVIN (0.5 g L⁻¹) as in the above experiment, 100% of the TNG was degraded in less than 5 min (Fig. 3). Faster degradation of TNG using ZVIN/SBA-15 compared to ZVINs could be attributed to the higher reactivity of ZVINs due to the discrete dispersion of the nanometal particles on the nanosilica surface. Moreover, the specific surface area of ZVIN/SBA-15 (275 m² g⁻¹) was much larger than that of the unstabilized ZVINs (82.0 m² g⁻¹). Recently Naja et al. (2008) reported that ZVINs stabilized on carboxymethylcellulose (CMC) degraded RDX 40 times faster than unstabilized ZVINs.

The molar stoichiometry of the reaction between Fe⁰ and TNG was 12 Fe⁰:1 TNG (Oh et al., 2004). Because nanoiron (89 μmol) was used in excess of TNG (3.5 μmol) we presumed that changes in Fe⁰ is negligible, and thus, the degradation process should obey pseudo-first-order kinetics (Eq. (1)) (Xu and Zhao, 2007; Bai et al., 2009):

\[
\ln \left( \frac{C_{\text{TNG}}}{C_{\text{TNG}0}} \right) = k_it
\]

where \(C_{\text{TNG}}\) is the initial TNG concentration (μmol L⁻¹), \(C_{\text{TNG}0}\) is the TNG concentration at any time (μmol L⁻¹), \(k_i\) is the pseudo-first-order rate constant (min⁻¹) and \(t\) is the sampling time (min). \(k_i\) can be expanded to \(k_{\text{norn}}[\text{Fe}^0]\) where \(k_{\text{norn}}\) is the surface-area normalized rate constant (L h⁻¹ m⁻²), \([\text{Fe}^0]\) is the specific surface area of Fe⁰ (m² g⁻¹) and \([\text{Fe}^0]\) is the Fe⁰ concentration (g L⁻¹). \(k_i\) was obtained by linear regression of \(\ln \left( \frac{C_{\text{TNG}}}{C_{\text{TNG}0}} \right)\) versus time. The high values of correlation coefficients \(R^2\) (Table S1) confirmed that the TNG degradation rate followed pseudo-first-order kinetics. The pseudo-first-rate constant for ZVIN/SBA-15 reaction with TNG (0.83 ± 0.04 min⁻¹) was almost 4-fold that of unstabilized ZVINs (0.23 ± 0.02 min⁻¹). The surface-area normalized rate constants \(k_{\text{norn}}\) reported in this study (0.33 L h⁻¹ m⁻² for ZVINs and 0.36 L h⁻¹ m⁻² for ZVIN/SBA-15) exceeded by 10²–10⁶ fold those reported for TNG degradation using granular cast iron (\(k_{\text{norn}} = 0.8 \times 10^{-2} \text{ L h}^{-1} \text{ m}^{-2}\) (Oh et al., 2004) or pyrite (\(k_{\text{norn}} = 0.57 \times 10^{-3} \text{ L h}^{-1} \text{ m}^{-2}\)) (Oh et al., 2008).

We found that ZVINs (0.5 g L⁻¹) efficiently degraded TNG (3.5 μmol) in 20 min under anaerobic (100% of TNG degraded) and aerobic (84.0% of TNG degraded) conditions. The decrease in reactivity in the presence of air can be attributed to oxidation of nanoiron (Naja et al., 2008). Subsequent studies were conducted in batch experiments under anaerobic conditions. Controls containing FeSO₄ and TNG or SBA-15 and TNG without ZVINs showed that neither Fe(II) nor SBA-15 degraded TNG.

3.3. Degradation products

Fig. 4 summarizes the reductive transformation of TNG with Fe⁰ and the evolution of intermediate and final products. Fig. 4a shows a ratio of 1,2-DNG:1,3-DNG close to 2, indicating a denitration that favors the primary carbon of TNG. Fig. 4a also shows that 1-MNG and 2-MNG were produced concurrently, with 1-MNG being the dominant isomer (1-MNG/2-MNG close to 3). None of the detected intermediates (1,2-DNG, 1,3-DNG, 1-MNG and 2-MNG) persisted in the system, rather they all transformed further to eventually produce NO₂⁻, NH₄⁺ and glycerol (Fig. 4b). At the end of the experiment which lasted 240 min, the initial 3.5 μmol of TNG employed in the reaction was accounted as 5.40 μmol of NO₂⁻, 5.18 μmol of NH₄⁺, and 3.57 μmol of glycerol, representing a nitrogen mass balance of ~100.7% and a carbon mass balance of ~102%.

According to Oh et al. (2004), reductive denitration of TNG by Fe⁰ should follow the sequence of equations below:

\[
\text{C}_3\text{H}_5(\text{ONO}_2)_3 + 2\text{e}^- + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_5(\text{ONO}_2)_2\text{OH} + \text{NO}_2^- + \text{OH}^-
\]

(2)

\[
\text{C}_3\text{H}_5(\text{ONO}_2)_2\text{OH} + 2\text{e}^- + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_5(\text{ONO}_2)\text{OH}_2 + \text{NO}_2^- + \text{OH}^-
\]

(3)

\[
\text{C}_3\text{H}_5(\text{ONO}_2)\text{OH}_2 + 2\text{e}^- + \text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_5(\text{OH})_3 + \text{NO}_2^- + \text{OH}^-
\]

(4)

\[
\text{NO}_2^- + 6\text{e}^- + 6\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + 8\text{OH}^-
\]

(5)

\[
\text{C}_3\text{H}_5(\text{ONO}_2)_3 + 24\text{e}^- + 21\text{H}_2\text{O} \rightarrow \text{C}_3\text{H}_5(\text{OH})_3 + 3\text{NH}_4^+ + 27\text{OH}^-
\]

(6)

As Eq. (6) shows, the complete denitration of the 3.5 μmol TNG used in the reaction to produce glycerol and ammonium ion required 84 μmol of electrons. Since one mole of Fe⁰ yields 2 mol of electrons, the 5 mg Fe⁰ used in the present study represented 178 μmol of electrons, twice the amount required to transform the 3.5 μmol of TNG to glycerol and ammonium. However as Fig. 4b shows, reaction 4 was incomplete in our case and approximately 50% of NO₂⁻ remained intact and the rest was reduced to NH₄⁺. The incomplete reduction of NO₂⁻ to NH₄⁺ was attributed to the lack of electrons.
caused by the agglomeration of iron nanoparticles as mentioned earlier. Interestingly, Fig. 4c shows that when we used the stabilized ZVINs/SBA-15 instead of ZVINs, all of the initially produced NO$_3^-$ from TNG reduction was transformed completely to NH$_4^+$ in 240 min. Fig. 4c also shows that glycerol was the final carbon product of TNG and formed quantitatively. During TNG degradation with ZVINs/SBA-15, the pH solution reached 8.9 but did not exceed 7.6 in the case of ZVINs. A control containing TNG (3.5 µmol) without ZVINs/SBA-15 at pH 9 did not show any significant degradation of the nitrate ester. When TNG (3.5 µmol) was allowed to react with ZVINs/SBA-15 (0.5 g L$^{-1}$ of ZVINs) at either pH 4, 5.6 or 9 the disappearance of TNG was more favorable under neutral or slightly acidic conditions (Fig. 5). Alkaline conditions (pH 9) seemed to retard TNG degradation with ZVINs/SBA-15. Similar findings were reported for the RDX degradation with ZVINs at pH2 (Singh et al., 1999).

![Figure 5](image_url)  
**Fig. 5.** Effect of pH on degradation of TNG (3.5 µmol) with ZVINs/SBA-15 (containing 0.5 g L$^{-1}$ of ZVINs). Error bars represent standard deviations for triplicate analysis.

![Figure 6](image_url)  
**Fig. 6.** (a) X-ray diffraction (XRD) of ZVINs/SBA-15 after five successive cycles of reaction with TNG. The ZVINs/SBA-15 nano assembly was washed with aqueous methanol solution and treated with NaBH$_4$ following each cycle. (b) Transmission electron micrograph (TEM) of ZVINs/SBA-15 after five successive cycles of reaction with TNG. The ZVINs/SBA-15 nano assembly was washed with aqueous methanol solution and treated with NaBH$_4$ following each cycle.
3.4. Sustained reactivity of ZVINs/SBA-15

To determine whether the ZVINs/SBA-15 reactivity can be sustained, we treated ZVINs/SBA-15 (0.5 g L$^{-1}$) with TNG (3.5 μmol) in water for five successive cycles. We found that TNG removal was nearly 100% in every cycle. XRD analysis of the washed material (Fig. 6a) showed that ZSA-15 preserved its ordered hexagonal structure because the Bragg peaks at about 2θ = 1.0°, 1.7 and 1.9° were not changed. Moreover, the peak at 2θ = 44.76° corresponding to α-Fe nanoparticles responsible for TNG degradation also remained intact. Furthermore, TEM analysis of ZVINs/SBA-15 (Fig. 6b) revealed that the nano assembly preserved its ordered mesostructure with clear dispersion of ZVINs on the surface of SBA-15 after five successive applications, indicating that the nano assembly sustained its reactivity towards TNG.

4. Conclusion

The present study demonstrated that ZVINs/SBA-15, ZVINs stabilized on a nanosilica surface, can effectively and quantitatively transform TNG to two benign products, ammonium cation and increased its surface area allowing accessibility of the TNG to iron entrapped within the nanosilica structure. Kinetic studies showed that degradation of TNG with Fe$^0$ was faster with ZVINs/SBA-15 ($k_1$ = 0.83 min$^{-1}$) than with ZVINs ($k_1$ = 0.228 min$^{-1}$). The corresponding surface-area normalized rate constants were 0.36 L h$^{-1}$ m$^{-2}$ for ZVINs/SBA-15 and 0.33 L h$^{-1}$ m$^{-2}$ for ZVINs. Reusability studies showed that ZVINs/SBA-15 sustained its reactivity during five successive degradation cycles. Due to the low cost of iron and silica and the benign nature of the reagents used and products formed, ZVINs/SBA-15 shows promise as a cost effective and environmental friendly remediation technology for cleaning up water contaminated with TNG.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.08.012.

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