Potential of zerovalent iron nanoparticles for remediation of environmental organic contaminants in water: a review

Trishikhi Raychoudhury and Traugott Scheytt

ABSTRACT

Zerovalent iron (ZVI) has the potential to degrade different organic contaminants. Nanoscale zerovalent iron (NZVI) can reduce the contaminants even more rapidly due to its small size and large specific surface area (SSA), compared to granular ZVI. The main objective of this paper is to assess and compare the potential of NZVI for degradation of different contaminants in water under specific environmental conditions. As a first step, the potential reactive functional groups/bonds associated with different contaminants are identified and possible reaction mechanisms are discussed. Thereafter, the reaction efficiencies of different organic contaminants with NZVI are compared. Mass of ZVI and reaction time required to transform a certain amount of contaminated water are calculated based on literature data. Sources of contaminants in the environment and their environmental occurrences are discussed to understand the potential locations where NZVI could be applied for removal of different contaminants. Overall it is observed that azo-compounds are readily transformed in the presence of NZVI particles. Reaction efficiencies of ZVI for reduction of nitro-organic compounds are also reasonably high. However, halogenated compounds with high molecular weights or complex structures (i.e., iodinated contrast media, DDT, polychlorinated biphenyls, etc.) show lower reaction rates with NZVI compared to the widely studied chlorinated hydrocarbons (i.e., trichloroethylene).

Key words | azo dyes, explosives, pesticides, pharmaceuticals, reaction time, zerovalent iron

INTRODUCTION

Several studies demonstrated that zerovalent iron (ZVI) has great potential to reduce different types of organic contaminants and heavy metals that are at high oxidation states. Recent studies show that with decrease in ZVI size, the specific surface area (SSA) of the particle increases significantly, which resulted in an increase in reaction rate of ZVI particles (Gillham & O’Hannesin 1994; Tratnyek & Johnson 2006). Therefore, application of nanoscale zerovalent iron (NZVI) for degradation of different organic contaminants and for reduction of heavy metals is becoming a promising remediation technique.

The potential of NZVI for remediation of chlorinated hydrocarbons has been investigated extensively since the 1990s. Most of this research is focused primarily on chlorinated hydrocarbons, based on the fact that several thousands of aquifers are contaminated by those substances (NRC 2005). Environmental persistence of compounds containing a nitro-group is also reported in the literature (Planas et al. 1997; Stackelberg et al. 1997; Rodriguez et al. 2002; USEPA 2002; Pichtel 2012). Several studies have demonstrated that nano or micron sized ZVI particles can degrade different nitro-compounds including nitroaromatic pesticides and explosives under laboratory conditions (Agrawal & Tratnyek 1996; Keum & Li 2004; Naja et al. 2008; Yin et al. 2012). Occurrences of halogenated pesticides (i.e., alachlor, atrazine, DDT) and other compounds with commercial applications (i.e., polychloro biphenyls (PCBs), polybromo diphenyl ethers (PBDEs)) in the environment are reported elsewhere (Biziuk et al. 1996; Spliid & Koppen 1998; Palm et al. 2002). Although some of the pesticides such as DDT are currently banned in most countries worldwide, given that it is not readily biodegradable, trace amounts of it can be found in the environment. Degradation of these compounds by NZVI is also demonstrated in different studies (Wei et al. 2006; Bezbaruah et al. 2009; Poursaberi et al. 2012). Another potential group of environmental...
contaminants are azo dyes (Abramian & El-Rassy 2009)
which can be transformed in the presence of NZVI (Shu
et al. 2007; Wang et al. 2010; Satapanajaru et al. 2011).
Trace amounts of pharmaceuticals and iodinated contrast
media (ICM) are detected in the environment (Steger-
Hartmann et al. 1999; Perez & Barcelo 2007; Plösz et al.
2010; Houeto et al. 2012). Some recent studies have also
focused on reduction of pharmaceutical compounds and
ICM by ZVI under laboratory conditions (Ghauch et al.
2010a, 2010b; Stieber et al. 2011).
Although NZVI can degrade different organic contami-
nants under specific laboratory conditions, one of the major
limitations of NZVI application is its rapid aggregation
(Phenrat et al. 2007). Aggregation of NZVI not only limits
its transport efficiency through porous media but also
reduces its reactivity by transforming it into micron sized
ZVI particles (Tratnyek & Johnson 2006). Many studies
have demonstrated that surface modifications of NZVI by
different polyelectrolytes (or polymers) can increase its col-
loidal stability and thus can improve transport efficiency
through porous media (Saleh et al. 2007; Phenrat et al.
2008; Raychoudhury et al. 2010). However, different labora-
tory scale column transport experiments have demonstrated
that even with surface modification more than 40% of injected NZVI particles are retained within
10 cm of sand packed columns (Phenrat et al. 2008; Ray-
choudhury et al. 2012). Moreover, reactivity of surface
modified NZVI decreases by an order of magnitude (Phenrat
et al. 2009; Zhuang et al. 2011) compared to that of bare NZVI.

Based on the above facts, it could be stated that NZVI
application for remediation of contaminants has many
advantages and several limitations. Reactivity of NZVI
with different contaminants depends on various factors,
such as functional groups associated with the compounds,
characteristics of NZVI particles (i.e., size, surface area, sur-
fase modification, Fe$^0$ content, etc.), physical properties of
contaminants (phase distribution), and environmental con-
ditions (i.e., source of water to be treated, water chemistry
and characteristics of the contaminated sites). Therefore,
it is important to correlate these factors to gain insight
into the suitability of NZVI application for removal of
specific organic contaminants under certain environmental
conditions.

The main objective of this review paper is to evaluate and
compare the potential of NZVI for the degradation of differ-
ent contaminants. As a first step, potentially reactive
functional groups associated with the compounds are identi-
fied and possible interaction mechanisms between selected
organic contaminants and NZVI are discussed. Physical
properties of contaminants (solubility, sorption, hydrophobi-
city, etc.) can influence their phase distribution in the
environment significantly. Suitable techniques and locations
for NZVI application depend on the source of contaminants
and their environmental occurrences. Therefore, physical
properties, sources and environmental occurrences of those
contaminants are discussed. In the next step, the reaction ef-
ciciencies of these contaminants with (nano/micro/granular)
ZVI particles under laboratory conditions are listed from lit-
erature reviews. Subsequently, approximate amount of ZVI
and reaction times required to remediate a unit volume of
contaminated water are calculated based on the given reaction
conditions. We extrapolate the reaction behavior of
different compounds under similar environmental condi-
tions in order to compare their reaction efficiencies. The
potential of NZVI for remediation is evaluated for certain
selected compounds and extended for a wide range of con-
taminants belonging to the same functional groups.

CHARACTERISTICS OF SELECTED ORGANIC
CONTAMINANTS

Interaction mechanism between selected compounds
and NZVI

Application efficiency of NZVI for remediation of organic
contaminants is governed by (i) the reactive functional
groups associated with the compound, (ii) the physical prop-
erties (or phase distributions) of the compound and (iii) the
environmental conditions. In this section possible chemical
and physical interaction mechanisms between selected
organic contaminants and NZVI are discussed.

Possible chemical interaction

Different functional groups and bonds, which can be
involved in chemical reactions with NZVI, are identified
within the selected sets of compounds and presented in
Table 1. To simplify the discussion, the compounds are
classified based on their applications as presented in
Table 1 (and in Tables S1 and S2 in the Supplementary
Material, available online at http://www.iwaponline.com/
wst/068/358.pdf). Those identified reactive compounds are
halogen substituents (Cl, Br, F), nitro (NO$_2$) functional
groups, nitrogen–nitrogen double bonding (N=N) and
carbon–nitrogen bonding (C–N, can belong to any structural
groups, i.e., amides, amines, imidazole, etc.). Possible chemi-
cal interactions between ZVI and some of the selected
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Reactive groups</th>
<th>( \text{M}_w ) (g/mol)</th>
<th>Physical Properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Explosives</strong></td>
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<tr>
<td>1,3,5-trinitro-1,3,5-triazine (RDX)</td>
<td>−NO₂</td>
<td>222.12</td>
<td>Solubility: 42 mg/L (Insoluble)</td>
<td>Pichtel (2012); Kalderisl et al. (2011)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sorption: Moderate to high sorption</td>
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<td></td>
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<td></td>
<td>Hydrophobicity (( \log k_{ow} )): 0.86</td>
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<td>Specific gravity: 1.89 g/cm³</td>
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<tr>
<td>2,4,6 Trinitrotoluene (TNT)</td>
<td>−NO₂</td>
<td>227.13</td>
<td>Solubility: 130 mg/L (Low solubility)</td>
<td>Pichtel (2012); Kalderisl et al. (2011)</td>
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<td></td>
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<td>Sorption: Moderate to high sorption</td>
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<td></td>
<td>Hydrophobicity (( \log k_{ow} )): 1.86</td>
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<td>Specific gravity: 1.5–1.6 g/cm³</td>
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<td><strong>Pesticides</strong></td>
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<tr>
<td>Nitrophenol (2 methyl 4,6 dinitrophenol)</td>
<td>−NO₂</td>
<td>198.13</td>
<td>Solubility: 130 mg/L (Low solubility)</td>
<td>Tuxen et al. (2000); Kenaga (1980)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>Sorption (( \log k_{d} )): 3.43–4.568</td>
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<td></td>
<td>Hydrophobicity (( \log k_{ow} )): 2.12</td>
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<td>Specific gravity: 1.38 g/cm³</td>
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<tr>
<td>Organo phosphorous (Mecharthon, Fenitrothion)</td>
<td>−NO₂</td>
<td>263.21–277.25</td>
<td>Solubility: 30–66 mg/L (Insoluble)</td>
<td>Kenaga (1980)</td>
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<td></td>
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<td>Sorption coefficient (( \log k_{oc} )): 2.67–2.82</td>
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<td>Bioaccumulation: moderate</td>
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<td>Specific gravity: 1.53–1.36 g/cm³</td>
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<tr>
<td>Nitroaniline (Benfluralin, Trifluralin)</td>
<td>−NO₂, −F</td>
<td>335.28</td>
<td>Solubility: Insoluble</td>
<td>Haderlein et al. (1996); Kenaga (1980)</td>
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<td></td>
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<td></td>
<td>Sorption coefficient (( \log k_{oc} )): 3.76–4.14</td>
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<td></td>
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<td></td>
<td>(Sorption is high for nitroaromatics)</td>
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<td>Bioaccumulation: High</td>
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<td>Specific gravity: &gt;1.5 g/cm³</td>
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<tr>
<td>Diphenyl ether (Nitrofen, Bifenox, Oxyfluorofen)</td>
<td>−NO₂, −Cl</td>
<td>284.10–361</td>
<td>Solubility: Insoluble</td>
<td>Haderlein et al. (1996); Kenaga (1980)</td>
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<td>Sorption coefficient (( \log k_{oc} )): 3.892</td>
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<td></td>
<td>(Sorption is high for nitroaromatics)</td>
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<td>Bioaccumulation: High</td>
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<td>Specific gravity: &gt;1.5 g/cm³</td>
<td></td>
</tr>
<tr>
<td>Alachlor</td>
<td>−Cl, −C–N</td>
<td>269.8</td>
<td>Solubility: 242 mg/L (Low solubility)</td>
<td>Kenaga (1980)</td>
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<td></td>
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<td>Sorption coefficient (( \log k_{oc} )): 2.278</td>
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<td></td>
<td>Bioaccumulation: Not very high</td>
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<td>Specific gravity: 1.13 g/cm³</td>
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<tr>
<td>Atrazine</td>
<td>−Cl</td>
<td>215.69</td>
<td>Solubility: 33 mg/L (Insoluble)</td>
<td>Kenaga (1980)</td>
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<td>Sorption coefficient (( \log k_{oc} )): 2.17–2.8</td>
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<td>Bioaccumulation: Not very high</td>
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<td>Specific gravity: 1.23 g/cm³</td>
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<tr>
<td>2,4 Dichlorophenol (DCP)</td>
<td>−Cl</td>
<td>163.01</td>
<td>Solubility: 4,600 mg/L</td>
<td>Lo et al. (1998); Ruelle (2000)</td>
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<td>Sorption (( k_d )): 690–1,580 L/kg</td>
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<td>Hydrophobicity (( \log k_{ow} )): 2.26–3.06</td>
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<td></td>
<td>Specific gravity: 1.38 g/cm³</td>
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<tr>
<td>DDT</td>
<td>−Cl</td>
<td>354.59</td>
<td>Solubility: Insoluble</td>
<td>Kenaga (1980); Ruelle (2000)</td>
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<td></td>
<td>Sorption coefficient (( \log k_{oc} )): 5.16–5.37</td>
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<td></td>
<td>(Very high sorption)</td>
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<td></td>
<td>Hydrophobicity (( \log k_{ow} )): 6.36–7.92</td>
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<td></td>
<td></td>
<td></td>
<td>Specific gravity: 0.99 g/cm³</td>
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<tr>
<td><strong>Organic Dyes</strong></td>
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<tr>
<td>Azo dyes (Acid Orange, Acid Black 24, Red 198, Black 5)</td>
<td>−N = N–</td>
<td>Varies widely</td>
<td>Solubility: Soluble in water</td>
<td>Gupta &amp; Suhas (2009); Mittal et al. (2008)</td>
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<tr>
<td></td>
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<td>Sorption: Sorbed in activated sludge and different waste material</td>
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</table>

(continued)
### Pharmaceuticals and contrast media

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Reactive groups</th>
<th>$M_w$ (g/mol)</th>
<th>Physical Properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metronidazole</td>
<td>–NO$_2$, –C–N</td>
<td>171.15</td>
<td>Solubility: 9,500 mg/L</td>
<td>Le-Minh et al. (2010); Fang et al. (2011)</td>
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<tr>
<td></td>
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<td></td>
<td>Sorption (log $k_{oc}$): 0.48 (cal.)</td>
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<td></td>
<td></td>
<td></td>
<td>Hydrophobicity (log $k_{ow}$): −0.013</td>
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<tr>
<td>Carbamazepine</td>
<td>–C–N</td>
<td>236.28</td>
<td>Solubility: 17.66 mg/L (Insoluble)</td>
<td>Scheytt et al. (2005a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sorption coefficient (log $k_{oc}$): 2.45–3.74</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>Hydrophobicity (log $k_{ow}$): 2.25</td>
<td></td>
</tr>
<tr>
<td>Diclofenac</td>
<td>–Cl, –C–N</td>
<td>296.15</td>
<td>Solubility: 2.37 mg/L (Insoluble)</td>
<td>Scheytt et al. (2005a)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>Sorption coefficient (log $k_{oc}$): 2.0–3.42</td>
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<td></td>
<td></td>
<td>Hydrophobicity (log $k_{ow}$): 4.02–4.51</td>
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<td></td>
<td></td>
<td>Specific gravity: $\sim$1 g/cm$^3$</td>
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<tr>
<td>Clofibric acid</td>
<td>–Cl</td>
<td></td>
<td>Solubility: 582.5 mg/L</td>
<td>Scheytt et al. (2005b)</td>
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<td></td>
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<td></td>
<td>Sorption coefficient (log $k_{oc}$): 0.9–1.36</td>
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<td></td>
<td></td>
<td></td>
<td>Hydrophobicity (log $k_{ow}$): 2.57–2.88</td>
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<td></td>
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<td></td>
<td>(Highly sorbed in activated sludge)</td>
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<td></td>
<td>Hydrophobicity (log $k_{ow}$): 1.31</td>
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<td></td>
<td>Specific gravity: $\sim$1 g/cm$^3$</td>
<td></td>
</tr>
<tr>
<td>Iopromide</td>
<td>–I,–C–N</td>
<td>791.11</td>
<td>Soluble in water</td>
<td>Carballa et al. (2008); Ternes et al. (2004); Yang et al. (2011)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>Sorption (log $k_{oc}$): 0.72–1.48; (Low)</td>
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<td></td>
<td></td>
<td></td>
<td>Hydrophobicity (log $k_{ow}$): −2.3</td>
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<td></td>
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<td></td>
<td>Specific gravity: 1.26–1.4 g/cm$^3$ (Concentration: 150–370 mg I/mL)</td>
<td></td>
</tr>
<tr>
<td>Ifosfamide</td>
<td>–Cl,–C–N</td>
<td>261.09</td>
<td>Soluble in water</td>
<td>Ternes et al. (2004)</td>
</tr>
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<td></td>
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<td></td>
<td>Sorption (log $k_{oc}$): 0.15–1.3; (Low)</td>
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<td></td>
<td></td>
<td></td>
<td>Hydrophobicity (log $k_{ow}$): 0.86</td>
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</table>

### Other selected organic compounds with commercial application

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Reactive groups</th>
<th>$M_w$ (g/mol)</th>
<th>Physical Properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3,4 Polybrominated diphenyl ether</td>
<td>–Br</td>
<td>406.89</td>
<td>Solubility: Insoluble</td>
<td>Palm et al. (2002)</td>
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<tr>
<td>(PBDE)</td>
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<td>Sorption (log $k_{oc}$): 4.46–5.32 (cal.)</td>
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<td></td>
<td>Hydrophobicity (log $k_{ow}$): 5.52–6.72</td>
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<td>Specific gravity: $&gt;$1 g/cm$^3$</td>
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<tr>
<td>2,3,4, Polychlorinated biphenyl (2,3,4 PCB)</td>
<td>–Cl</td>
<td>257.54</td>
<td>Solubility: 5.5 mg/L (Insoluble)</td>
<td>Shiu &amp; Mackay (1986); Ruelle (2000)</td>
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<td></td>
<td></td>
<td></td>
<td>Sorption (log $k_{oc}$): 4.58–4.64 (cal.)</td>
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<td></td>
<td>Hydrophobicity (log $k_{ow}$): 5.68–5.77</td>
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<td>Specific gravity: $&gt;$1 g/cm$^3$</td>
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<tr>
<td>Nitrobenzene (NB)</td>
<td>–NO$_2$</td>
<td>123.06</td>
<td>Solubility: 190 mg/L, Adsorption coefficient (log $k_{oc}$): 1.85</td>
<td>Kenaga (1980)</td>
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<td></td>
<td></td>
<td></td>
<td>Bioaccumulation: negligible</td>
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<td></td>
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<td>Specific gravity: 1.2 g/cm$^3$</td>
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<tr>
<td>Trinitroglycerin</td>
<td>–NO$_2$</td>
<td>227.08</td>
<td>Solubility: 1,250–1,950 mg/L</td>
<td>Pichtel (2012)</td>
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<td>Sorption (log $k_{oc}$): 1.42 (cal)</td>
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<td>Hydrophobicity (log $k_{ow}$): 1.62</td>
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<td></td>
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<td>Specific gravity: 1.59 g/cm$^3$</td>
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### Halogenated organic solvent

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<th>Compounds</th>
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<th>$M_w$ (g/mol)</th>
<th>Physical Properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halogenated hydrocarbon (i.e, TCE, PCE)</td>
<td>–Cl</td>
<td>Varies</td>
<td>Solubility: Low to moderate solubility</td>
<td>Cohen &amp; Mercer (1993)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sorption: Varies</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hydrophobicity: High</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Specific gravity: $&gt;$1 g/cm$^3$</td>
<td></td>
</tr>
</tbody>
</table>

Notes: $M_w$: Molecular weight. $^b$(cal.): Calculated value of log ($k_{oc}$), based on the equation: 
$\log(k_{oc}) = 1 \times \log(k_{ow}) - 0.21$ (Scheytt et al. 2005b).
compounds are discussed here. The interaction mechanisms between NZVI and the specific compounds are considered as an example for a wide range of compounds belonging to the same functional group.

During degradation of halogenated organic compounds (i.e., trichloroethylene (TCE), PCBs, DDT, PBDEs, etc.), electrons are released due to Fe\(^0\) oxidation in the presence of water. Consequently, halide ions are substituted by protons in the presence of electrons (Wang & Zhang 1997; Liu et al. 2005). Numerous studies have suggested that the nitro-groups (–NO\(_2\)) associated in nitroaromatic compounds such as nitrobenzene (NB), trinitrotoluene (TNT) or nitroaromatic pesticides (i.e., me-parathion, nitrofen), are reduced to the amino groups (–NH\(_2\)) by proton transfer (Agrawal & Tratnyek 1996; Keum & Li 2004). However, degradation of different nitro-organic compounds generally depends on the structure of the compounds and the priority of the amino groups relative to the other substitutions. For example, Fang et al. (2011) have suggested that there could be different reduction pathways such as (i) nitro-reduction (into amino), (ii) cleavage at the carbon–nitrogen bond or (iii) denitration of the NO\(_2\) group during metronidazole degradation by NZVI. Naja et al. (2008) suggested 1,3,5 trinitro 1,3,5 triazine (RDX) reduction follows both denitration and nitro-reduction pathways. On the other hand, mainly stepwise denitration was observed for trinitroglycerin reduction by NZVI (Oh et al. 2004). In all these redox reactions the main source of electrons is Fe\(^0\) oxidation and protons are donated from water. The nitrogen–nitrogen double bond (N = N) is typically observed in azo dyes. Freyria et al. (2011) have observed that the nitrogen–nitrogen double bond is partially transformed into hydrazone by internal proton transfer. While Cao et al. (1999) suggest that in the first step the azo double bond is destroyed due to reduction, and subsequently with further protonation (protons donated from water and electrons released from Fe\(^0\)) aromatic amine is produced. Limited studies are found on azo dye transformation pathways in the presence of NZVI. There are possibilities that some of these dyes may lose their color due to variation of pH within the system. For some of the pharmaceutical compounds (and for certain ICM), transformations are observed by cleavage reaction at the carbon–nitrogen (C–N) bond (Stieber et al. 2011).

Possible physical interaction

Physical sorption of the contaminants on the iron surfaces can be attributed to the observed value of contaminant degradation rates. For example, Roy et al. (2005) have demonstrated that tropaeolin (azo dye) is adsorbed on the iron surface prior to its degradation. They suggest that the negatively charged sulfonate functional group is responsible for the sorption of tropaeolin on the iron surface. The possibility of metronidazole sorption on the metal surface is also suggested in the literature (Fang et al. 2011).

Physical properties of selected compounds

To understand the potential of NZVI for removal of environmental contaminants, it is also important to know in which form they are persistent in the environment. The fate of organic contaminants in the environment depends on their physicochemical properties such as aqueous solubility, sorption, hydrophobicity etc. and on the environmental conditions (Merkel & Planer-Friedrich 2008). Therefore, physical properties of different contaminants are presented in Table 1 and discussed below.

From Table 1 it can be noted that nitro-organic explosives (i.e., RDX and TNT) and pesticides (i.e., benfluralin, nitrofen, oxyfluorfen, me-parathion, etc.), considered in this study, show poor solubility and have low to moderate hydrophobicity. Sorption of these explosives varies widely depending on the chemistry of the soil and groundwater. These compounds might act as a continuous source of contamination by slow desorption due to ion exchange in the presence of certain cations (Kenaga 1980; Tuxen et al. 2000; Kalderisl et al. 2011). Other chlorinated herbicides such as alachlor, atrazine, and-DDT have low water solubility with high hydrophobicity and sorption (Kenaga 1980; Lo et al. 1998; Ruelle 2000). It suggests that these compounds are immobile in the environment and can accumulate in biomass. Azo compounds (N = N) are generally soluble in water and can be released easily into the environment (Mittal et al. 2008; Gupta & Suhas 2009). Among different pharmaceuticals, metronidazole (NO\(_2\)) and ICM (halogen substituent), discussed in this paper, are soluble in water and have low hydrophobicity and sorption coefficients (Ternes et al. 2004; Carballa et al. 2008; Fang et al. 2011). Carbamazepine and ciprofloxacin (C–N bond) have low to moderate hydrophobicity and sorption coefficients (Scheytt et al. 2005b, 2005a, Le-Minh et al. 2010), suggesting that there is risk associated with these compounds if they are released into the environment. Diclofenac and clofibric acid (halogen substituent, C–N bond) are moderately soluble in water at low pH. However, with increase in pH the solubility of these compounds increases due to ionization and in the range of environmental pH (6–9) both of these compounds are highly soluble. Sorption of these pharmaceuticals
varies widely depending on the soil composition (Scheytt et al. 2005b, a). Among other organic compounds with different commercial applications, PBDEs and PCBs (halogen bond, CAP 2006) exhibit poor solubility with high sorption and hydrophobicity. It suggests that they are immobile in the environment and may have significant bioaccumulation (Shiu & Mackay 1986; Ruelle 2000; Palm et al. 2002). Nitrobenzene has poor water solubility whereas trinitroglycerin (NO₂) has high water solubility. Sorption and hydrophobicity of both the compounds are comparatively low, which suggests that these compounds would be mobile in the environment (Kenaga 1980; Pichtel 2012).

**Environmental occurrences of selected compounds and possible methods of NZVI application**

Suitable techniques of NZVI application for removal of different organic contaminants depend on their environmental occurrences (i.e., groundwater, wastewater, drinking water). Therefore, sources and occurrences of selected organic compounds in the environment are pointed out in Table S1 (Supplementary Material, available online at http://www.iwaponline.com/wst/068/358.pdf). Trace amounts of different explosives, pesticides, pharmaceuticals, and other selected organic compounds with commercial applications are detected in the subsurface groundwater (Table S1). Widely accepted approaches for in situ remediation of groundwater contaminated with organic contaminants are either by targeting the source zone by direct injection of NZVI slurry (Zhang 2003; He et al. 2010) or by creating a single or a series of ZVI permeable reactive barriers in front of the contaminated plume (Noubactep & Care 2010; Crane & Scott 2012). However, the efficiency of each of the techniques depends on the characteristics of the contaminated sites.

Significant soil phase persistence of different pesticides (nitro aromatic or halogenated), PCBs, and nitro-aromatic explosives are also detected in the environment (Table S1). Considering this fact, several studies have focused on the application of ZVI for removal of different pesticides and explosives from the soil phase (Shea et al. 2004; Naja et al. 2009; Sing & Bose 2012). Azo dyes, pharmaceuticals, contrast media, and trinitroglycerin are released into the environment from industrial effluents or wastewater treatment plants (Table S1). The motivation behind several studies is to explore the possibility of removing these compounds from wastewater treatment plants using NZVI particles (Ghauch et al. 2010b, 2011b; Shu et al. 2010; Satapanajaran et al. 2011). For example, azo dye removal efficiencies, either by NZVI suspensions in the anaerobic batch systems or by NZVI supported cation exchange resin columns, are investigated in different studies (Cao et al. 1999; Zhao et al. 2008; Shu et al. 2010).

Some of the pharmaceuticals and pesticides are also detected in tap water (Table 1). Thus, another possible technique, which can be explored further, is application of NZVI into domestic filter media (Noubactep & Care 2010). This concept has been proposed and investigated especially for arsenic removal for drinking water quality control (Zhu et al. 2009).

To address the water chemistry, generally, the pH level in natural water lies within a range of 6–9 (Scholl & Harvey 1992). The range of ionic strength (IS) in groundwater and drinking water can vary within 10⁻⁴ to 10⁻² M (Yang et al. 2007). The level of dissolved oxygen (DO) in groundwater is generally in the low range compared to that of drinking water. Overall, DO ranging between 0.1 and 10 mg/L can cover the entire regime of natural water DO (Datry et al. 2004). Water chemistry in wastewater is controlled by influent loadings and operational criteria.

**REACTIVITY OF SELECTED CONTAMINANTS WITH ZVI**

In this section, reaction efficiencies of ZVI with different compounds, reported in the literature, are discussed. Details of laboratory experimental conditions, ZVI/compound ratios used in different studies, and first order reaction rate coefficients are specified in Table S2 (Supplementary Material, available online at http://www.iwaponline.com/wst/068/358.pdf). The compatibility between environmental conditions, where the contaminants occur, in which conditions they could be treated and laboratory experimental conditions is discussed. The approximate reaction time for remediation of organic contaminants is calculated based on first order reaction kinetics as shown in Equation 1 (Johnson et al. 1996). Environmental concentrations of different contaminants vary widely in the range of a few ng/L to a few hundred mg/L (Table S1). However, in this calculation, a fixed initial contaminant concentration (C₀) of 100 mg/L is assumed for all the contaminants to get a fair comparison of reaction efficiencies between different contaminants. The permissible concentration of contaminant (Cₗimit) was fixed to 5 μg/L.

\[
\frac{dC}{dt} = -k_{obs} \times C
\]
Here, $C$ is the contaminant concentration (ML$^{-3}$) at time $t$, $t$ is time (T), $k_{\text{obs}}$ is first order reaction rate coefficient (T$^{-1}$). The mass of ZVI required to remediate 1 L of contaminated water is calculated using simple arithmetic based on the ZVI/contaminant ratio (Table S2) and presented in Figure 1(a). The calculated reaction time for remediating different contaminants is presented in Figure 1(b). These calculations are performed to compare ZVI application efficiencies for different contaminants.

Reaction conditions and rates for degradation of different organic compounds by ZVI are discussed in the following section. In different studies different types of ZVI are used. The reaction efficiency of ZVI is highly dependent on the characteristics of the particle such as size, SSA, age, Fe$^0$ content of ZVI, etc. (Nurmi et al. 2005; Liu & Lowry 2006; Sarathy et al. 2008). Nano-particles can reduce the contaminants at a much higher rate compared to granular particles, due to their larger SSA (Tratnyek & Johnson 2006). The SSA of NZVI varies widely in the range of 12–140 m$^{2}$/g (Table S2), whereas the SSA of micron sized ZVI is less than 1 m$^{2}$/g (O’Carroll et al. 2012). Considering this fact, while comparing reaction rates of different compounds, we also discuss the differences in SSAs of ZVIs used in different studies (Table S2, Figure 1(c)).

**Halogenated organic solvent**

During the last two decades, NZVI application efficiency for remediation of chlorinated hydrocarbons has been investigated widely. Different chlorinated hydrocarbons that are degradable by NZVI are reported in the literature (Li et al. 2006; He et al. 2010; Zhao et al. 2011; O’Carroll et al. 2012). Among various contaminants, degradation and remediation of TCE (and tetrachloroethylene (PCE)) under various conditions are reported most frequently (Wang & Zhang 1997; Zhang 2003; Liu et al. 2005; Liu & Lowry 2006). Therefore, in this paper TCE degradation by NZVI is selected as a benchmark to compare degradation efficiencies of other organic contaminants by ZVI.

Our calculations, based on TCE degradation rate as listed in Table S2 (Liu et al. 2005), suggest that 43 g of NZVI can remediate ($C_0 = 100$ mg/L to $C_{\text{limit}} = 5$ µg/L) 1 L of TCE contaminated water in 10.23 hours. In this reaction, freshly synthesized NZVI was used, which contained 97% Fe$^0$ and the SSA of the particles was 36.5 m$^{2}$/g (size range 30–40 nm). The reaction efficiency of NZVI depends upon the characteristics of the particles. For example, in the same study, when commercial ZVI nanoparticles (RNIP) were used with a SSA of 23 m$^{2}$/g (size range 40–60 nm) and Fe$^0$ content of 52%, the reaction rate was also reduced significantly. Our calculation (Figure 1) suggests that RNIP requires 76.4 hours to remediate the same amount of TCE contaminated water. If a smaller proportion of RNIP (RNIP/TCE = 1.2) is used for the reaction, then the required mass (0.12 g) of the nanoparticles reduces over two orders of magnitude. However, the reaction rate decreases significantly and the time required for a complete reaction is 153.5 days (or 3,199 hours).

Up to date NZVI suspensions have been applied at several contaminated sites for remediation of chlorinated contaminants (Zhang 2003; He et al. 2010; Mueller et al. 2012). Concentrations of NZVI slurries that were injected at different sites varied over the range of 1–30 g/L (Mueller et al. 2012). Efficiency of NZVI based in situ remediation techniques is highly dependent on existing field conditions. It is reported that in several contaminated sites 40–90% chlorinated hydrocarbons had been removed over time after injecting NZVI (Zhang 2003; Mueller et al. 2012). However, there is a concern related to the ecotoxicity of NZVI (or bimetallic-NZVI) for its application in groundwater. Gilbert et al. (2007) suggest that oxidized NZVI can adsorb contaminants and can act as a carrier in the natural environment. On the contrary, Zhang (2003) suggests that NZVI can facilitate the growth of bacteria, which can indirectly enhance TCE remediation over long periods by facilitating biodegradation.

**Explosives**

Our calculation, based on the data given in Table S2, suggests that only 1.64 g of bare NZVI is required per liter of water to bring down RDX concentration from 100 mg/L to 5 µg/L in 8 hours (Figure 1). Average size and SSA of NZVI used in that study were in the range of 32 ± 7 nm and 42.6 m$^{2}$/g, respectively. For TNT reduction, our calculation based on the reaction details reported in Zhang et al. (2010) suggests that 6.6 g of NZVI per liter of water is required. The time required for TNT degradation is approximately 32 hours. SSA and size of NZVI used in that study were in the range of 40–60 m$^{2}$/g and 1–60 nm, respectively.

It can be observed that, although the SSA of NZVI used in both studies is similar, the amount of NZVI or time required for complete degradation is almost four times higher for TNT compared to that of RDX. Differences in reaction rates could be attributed to the fact that experimental conditions and reaction pathways for those two systems were different. For example, Naja et al. (2008) have
Figure 1 | (a) Mass of zerovalent iron required. (b) Reaction time for remediation of 1 L water contaminated by different organic compounds. Here remediation refers to the reduction of initial contaminant concentration ($C_0 = 100 \text{ mg/L}$) to final contaminant concentration ($C_{\text{final}} = 5 \mu\text{g/L}$). (c) Specific surface area (SSA) of zerovalent iron used in different studies for reduction of different organic compounds.
conducted the reaction with a pH value of 5.9–6.1 and a temperature of 25 °C, whereas TNT degradation was performed with a pH value of 3.96 and a temperature of 40 °C. Zhang et al. (2010) show that with increase in pH or with decrease in temperature the reaction rate decreases further, which suggests that TNT reaction conditions were more favorable than TCE reaction conditions. Naja et al. (2008) suggest that RDX reduction follows both denitration and nitro-reduction pathways, whereas nitro-reduction is the only pathway for TNT degradation. Differences in reaction pathways are probably influencing the degradation efficiencies more significantly in these cases. However, it could be stated that both compounds show good reactivity with NZVI.

**Pesticides**

**Nitroaromatic pesticides**

Experiments on the reactivity of zerovalent iron powder (ZVIP) with different types of nitroaromatic pesticides (Table S2) were performed by Keum & Li (2004). The pH (6.5) in the laboratory experimental conditions was maintained within the groundwater pH range (6–9), however the temperature (35 °C) was much higher than normal groundwater temperature. In some of the diphenyl ethers or nitroaniline pesticides, both halogen substituents (–Cl or –F) and nitro-group are present. However, in their study mainly reduction of the nitro-group was observed.

From our calculations (Figure 1) it could be observed that 36, 30, and 35 g of ZVIP can remediate (from $C_0 = 100$ mg/L to $C_{\text{limit}} = 5 \mu$g/L) 1 L of benfluralin, me-parathion and nitrofen contaminated water in 76.4, 52.2, and in 39.8 hours, respectively. In Figure 1(a) and 1(b), it appears that larger amounts of ZVI and longer times are required to remediate nitro-pesticides than to remediate nitro-explosives. However, it is important to note first that for nitro-pesticides the reaction was performed with ZVIP. The SSA ($<1 \text{ m}^2/\text{g}$) of ZVIP used by Keum & Li (2004) would be orders of magnitude lower than the NZVI used in other studies (40–50 $\text{m}^2/\text{g}$). Secondly, in Keum & Li (2004), ZVIP was exposed in air for 10 days prior to conducting the reactivity experiments. On the other hand, most of the studies presented here were conducted under controlled conditions under the nitrogen or argon atmosphere. Exposure to air (and aging) of ZVI is one of the major factors that reduce Fe$^0$ content in ZVI and thus its reactivity (Liu & Lowry 2006; Sarathy et al. 2008; Wang et al. 2009; Kim et al. 2012).

**Halogenated pesticides**

Among chlorinated pesticides the degradation rate of alachlor by NZVI is much higher compared to that of atrazine and DDT (Bezbaruah et al. 2009). Alachlor reduction efficiency is comparable with TCE degradation efficiency (Liu et al. 2005). The required amount of NZVI to remediate alachlor is approximately four times less (10 g) than to remediate TCE (45 g), however, the TCE reduction rate is approximately 3 (RNIP) to 20 (NZVI) times higher compared to the alachlor reduction rate (Table S2, Figure 1). The SSA of NZVI (25 $\text{m}^2/\text{g}$) used in Bezbaruah et al. (2009) is comparable to the SSA of NZVI (or RNIP, 23–36 $\text{m}^2/\text{g}$) used for TCE degradation (Liu et al. 2005).

Ghauch (2001) performed reactivity experiments with different halogenated and non-halogenated pesticides (Dicamba, Picloram and Benomyl) and ZVIP. In this study, rapid degradation of atrazine by ZVIP was found, however, a high ZVIP/pesticide ratio (16,000:1 to 20,000:1) was used. This suggests that around 1.6–2 kg of ZVIP is required to remediate 1 L of contaminated water.

Dichlorophenol (DCP) degradation by bimetallic NZVI was demonstrated in different studies (Wei et al. 2006; Jia & Wang 2012). Remediation (from $C_0 = 100$ mg/L to $C_{\text{limit}} = 5 \mu$g/L) of DCP by bimetallic NZVI required 30 g of Pd/NZVI per liter of water. The SSA of Pd/NZVI used in that study was 12.4 $\text{m}^2/\text{g}$. It is important to note that the reactivity of NZVI increases by orders of magnitude with increasing percentage of Pd (Zhuang et al. 2011; O’Carroll et al. 2012), however, ecotoxicity of Pd is becoming a major concern (Kielhorn et al. 2002).

**Azo dyes**

Recent literature has reported on azo dyes and NZVI reactivity (Shu et al. 2007; Satapanajaru et al. 2011; Zhang et al. 2012). Most of the studies show that a comparatively small proportion of NZVI is required to transform azo dyes and the reaction rate is rapid (Table S2). Our calculations suggest that only 3.3, 0.5 and 0.5 g of NZVI can remediate Acid Black 24, Black 5 and Red 198 within 0.36, 8.5 and 7.68 hours (Figure 1(b)), respectively. The SSA of NZVI used for reduction of Black 5 and Red 198 was around 13.97 $\text{m}^2/\text{g}$, whereas the SSA of NZVI was as high as 140 $\text{m}^2/\text{g}$ when used for reduction of Acid Black 24. The faster rate of Acid Black 24 decolorization compared to other azo dyes was probably facilitated by the high SSA of NZVI used in that study. A high rate of azo dye
transformation might also be attributed to the physical sorption of it on the NZVI surface (Roy et al. 2003).

**Pharmaceutical compounds and iodinated contrast media**

**Metronidazole**

Recently, a few studies have reported on metronidazole and NZVI reactivity (Fang et al. 2011; Chen et al. 2012). Our calculation, based on the reaction condition given in Fang et al. (2011), suggests that 0.125 g of NZVI can remediate \((C_0 = 100 \, \text{mg/L} \text{ to } C_{\text{limit}} = 5 \, \mu\text{g/L})\) 1 L of metronidazole contaminated water within 0.2 hours. The SSA of NZVI used in their study was 35 m²/g, which is in the same range as that used for TCE degradation (Liu et al. 2005). Although the SSAs of the particles used in both studies are in the same range, the metronidazole reduction rate is two orders of magnitude higher than the TCE degradation rate. On top of that, the proportion of NZVI used for metronidazole reduction is almost 345 times less compared to that used for TCE degradation (Liu et al. 2005).

Metronidazole shows excellent reactivity with NZVI, which may also be attributed to its physical sorption on the iron surface. Moreover, there is concern related to the formation and precipitation of corrosion products on the NZVI surface. Chen et al. (2012) observed that the size of NZVI increases from 20–60 to 80–120 nm after reacting with metronidazole. They suggested the possibility of accumulation of corrosion products on the surface of NZVI, which can reduce the rate of reaction over time.

**Diclofenac and contrast media**

Reactivity of pharmaceuticals such as diclofenac, clofibrionic acid and contrast media with ZVI are demonstrated in a few recent studies (Ghauch et al. 2010a, 2010b, 2011; Stieber et al. 2011). From our calculations (Figure 1), it is observed that 400 g of ZVI is required to remediate \((C_0 = 100 \, \text{mg/L} \text{ to } C_{\text{limit}} = 5 \, \mu\text{g/L})\) diclofenac contaminated water in 50 hours. Degradation efficiency is even lower for clofibrionic acid (Ghauch et al. 2010b). However, it can be noted that micron sized (SSA < 1 m²/g) ZVI was used in these studies. Our calculations also suggest that 40 and 20 g of ZVI are required to remediate ifosfamide and iopromide in 27.5 and 72.4 hours, respectively. The size of granular ZVI particles used in this study ranges between 0.125 μm and 3 mm. At low pH (pH = 3), the reaction efficiency of contrast media and granular ZVI (SSA = 0.67 m²/g) is a little higher than the TCE reduction rate by RNIP (SSA = 23 m²/g). However, above pH 5, negligible reaction with contrast media and ZVI was reported.

**Ciprofloxacin and carbamazepine**

Ciprofloxacin-ZVI reaction conditions and efficiency are similar to iompride-ZVI reaction conditions (Stieber et al. 2011). Carbamazepine-ZVI reactivity in the presence of H₂O₂ was reported by Ghauch et al. (2011b). It is difficult to isolate and comment on carbamazepine-ZVI reactivity independently, when H₂O₂ is also present in the system. However, considering the fact that carbamazepine also has a carbon–nitrogen (C–N) bond, the cleavage reaction at the carbon–nitrogen bond may be expected in the absence of H₂O₂.

**Other selected compounds with commercial applications**

**Nitro-organic compounds**

Nitrobenzene (NB) reduction by granular or micron sized ZVI has been reported in different studies (Tong et al. 2011; Ling et al. 2012; Yin et al. 2012). Reaction conditions and reaction rate reported in Yin et al. (2012) are listed in Table S2. In their study, they have observed that with a comparatively lower proportion of ZVI (ZVI/NB = 20–120), zero order reaction kinetics can explain the data better than first order reaction kinetics. However, at a higher ratio of ZVI (ZVI/NB = 200), first order reaction kinetics \((2.66 \times 10^{-4} \, \text{s}^{-1})\) have a better fit to the data. In that study, they used 50 μm sized ZVI with a SSA of 0.4 m²/g. Our calculation (based on their data) suggests that 4 g of ZVI can remediate \((C_0 = 100 \, \text{mg/L} \text{ to } C_{\text{limit}} = 5 \, \mu\text{g/L})\) 1 L of NB contaminated water in 44 hours. If the amount of ZVI is increased to 20 g/L, then the reaction rate also increases and the calculated reaction time is 10.3 hours. In another study, Agrawal & Tratnyek (1996) have observed first order decay \((5.8 \times 10^{-4} \, \text{s}^{-1})\) of NB by granular ZVI (particle size: mesh 20–30, a temperature of 15 °C), which has a SSA of 0.038 m²/g. In spite of the fact that the SSA of ZVI is an order of magnitude less in this study, the NB reduction rate coefficient is two times higher than that reported in Yin et al. (2012). This observation could be attributed to the fact that in Agrawal & Tratnyek (1996) the ratio of ZVI/NB \((=18,000)\) was kept approximately three orders of magnitude higher than that used in Yin et al. (2012). Removal efficiency of NB by different forms of NZVI, i.e., either embedded in mesoporous carbon or
immobilized by PEG/nylon is investigated in recent studies (Tong et al. 2011; Ling et al. 2012). Tong et al. (2011) demonstrated that around 69% of NB is degraded in 20 min by immobilized NZVI. After an initial time period, the reaction rate decreases due to the formation and accumulation of ferrous (Fe(II)) ions.

Saad et al. (2010) showed that NZVI (SSA = 82 m²/g) can degrade trinitroglycerin at a rapid rate \((3.8 \times 10^{-3} \text{ s}^{-1})\). Our calculation suggests that only 0.63 g of NZVI can remediate \((C_0 = 100 \text{ mg/L to } C_{\text{limit}} = 5 \mu \text{g/L})\) trinitroglycerin contaminated water within 0.72 hours. Overall, it can be observed that ZVI can degrade nitro-compounds (NB or trinitroglycerin) rapidly. However, there are challenges due to precipitation of corrosion products on the Fe(0) surface that can reduce the reaction rate over time (Agrawal & Tratnyek 1996; Huang & Zhang 2006).

### Halogenated compounds

Several studies explore the reaction efficiencies of NZVI for PCBs or PBDEs reductions (Wang & Zhang 1997; Lowry & Johnson 2004; Zhuang et al. 2011). Wang & Zhang (1997) showed that laboratory synthesized NZVI particles (size range 1–100 nm, SSA = 33.6 m²/g) can degrade PCB more

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**Table 2 | Potential of NZVI for removal of organic contaminants belonging to certain functional groups**

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<tr>
<td>Explosives</td>
<td>–</td>
<td>Very low water solubility, persistence in soil phase is high. Good reactivity with NZVI. Remediation by NZVI sorbed soil can be explored.</td>
<td>Compounds belonging to this group: moderate reactivity with NZVI is expected.</td>
<td>Compounds belonging to this group: low to moderate reactivity with NZVI is expected.</td>
</tr>
<tr>
<td>Pesticides</td>
<td>–</td>
<td>Occurrence in soil phase is higher. Reaction with ZVI is moderately high. Removal by NZVI sorbed in soil can be explored.</td>
<td>Compounds belonging to this group: low to moderate reactivity with NZVI is expected.</td>
<td>Low solubility, moderate to high sorption. Low reaction efficiency with NZVI.</td>
</tr>
<tr>
<td>Azo dyes</td>
<td>Soluble in water. Transformed rapidly in the presence of NZVI.</td>
<td>Compounds belonging to this group: high reactivity with NZVI is expected.</td>
<td>–</td>
<td>Compounds belonging to this group: low to moderate reactivity is expected.</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>–</td>
<td>Low sorption, highly reactive with NZVI. NZVI application in treatment plant for removal of these compounds is more suitable.</td>
<td>Low to moderate reactivity with NZVI.</td>
<td>Solubility is moderate. Sorption is moderate to low. Low reactivity with ZVI. Reaction with NZVI can be explored.</td>
</tr>
<tr>
<td>Contrast media</td>
<td>–</td>
<td>–</td>
<td>C-N bond reacts faster with NZVI compared to halide ion substitution.</td>
<td>Soluble in water, low sorption and negligible biodegradation. Moderately reactive at low pH, however not reactive above certain pH value.</td>
</tr>
<tr>
<td>Other organic compounds with commercial applications</td>
<td>Compounds belonging to this group: very high reactivity with NZVI is expected</td>
<td>Solubility varies, highly reactive with NZVI.</td>
<td>Compounds belonging to this group: moderate reactivity with NZVI is expected</td>
<td>Solubility varies, sorption is high, main persistance is in soil and food. Reaction efficiency with NZVI is low.</td>
</tr>
<tr>
<td>Halogenated organic solvents</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Low solubility. Act as constant source for groundwater contamination. Moderate to low reactivity with NZVI.</td>
</tr>
</tbody>
</table>
efficiently than commercially available ZVI nanoparticles. However, in their study they have used a high NZVI (50 g/L) concentration (NZVI/PCB = 10,000:1). Lowry & Johnson (2004) conducted reactivity studies with NZVI (size range 50–50 nm and SSA = 36.5 m²/g) and different PCBs. In their study, the reported value of pseudo first order dechlorination rates for 2,3,4 PCB (8.5 × 10⁻⁹/s) is in close proximity the degradation rate (2.3 × 10⁻⁸/s) of that reported in Zhuang et al. (2011). From our calculation based on the data given in Zhuang et al. (2011), it is observed that almost 13.65 years are required to remediate (C₀ = 100 mg/L to Cₚ = 5 µg/L) 1 L of 2,3,4 PCB contaminated water even though the NZVI/2,3,4 PCB ratio is maintained as high as 4,000:1 (400 g NZVI per liter of water, Figure 1(b)). The size and SSA of NZVI used in that study were in the range of 50–70 nm and 16 m²/g, respectively.

PBDE (2,3,4 BDE) degradation by NZVI particles (size range: 50–70 nm and SSA = 16 m²/g) was also studied by Zhuang et al. (2011). Our calculation suggests that 400 g of NZVI is required to remediate 1 L of 2, 3, 4 BDE contaminated water in 33 days (or 809 hours). Most of the above studies have demonstrated that palladized NZVI can improve PCB or PBDE degradation efficiency significantly.

**CONCLUSION**

As a conclusion, the potential of NZVI application for removal of different organic contaminants in different scenarios (i.e., groundwater, wastewater, etc.) is summarized in Table 2. From our observations it could be concluded that azo compounds are highly interactive with NZVI. There is scope to explore the application efficiency of NZVI for azo dye removal in industrial effluents and in wastewater treatment plants.

All the nitro-organic compounds including explosives, pesticides, pharmaceuticals and commercial compounds show good reactivity with ZVI. Selected nitroaromatic compounds, mainly used as explosives or pesticides, show high sorption. Therefore this raises the possibility to explore the combined effect of sorption and chemical reduction, by introducing NZVI coated sand, for removal of nitroaromatic contaminants.

The degradation efficiency of compounds containing a carbon–nitrogen bond is expected to be moderately high, if NZVI particles are used. There is scope to explore the potential of NZVI application for treating different types of pharmaceuticals in wastewater treatment plants.

Chlorinated hydrocarbons (i.e., TCE, carbon tetrachloride) are moderately reactive with NZVI. Reaction efficiencies of other chlorinated compounds with higher molecular weights or with complex structures (DDT, ICM, PCBs, PBDEs) are much lower than that of commonly studied chlorinated hydrocarbons (i.e., TCE).

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