Nanoscale materials for organohalide degradation via reduction pathways

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Abstract

The unique chemical and physical properties of nanoscale materials have led to important roles in several scientific and technological fields. Environmental chemistry processes have benefitted from the enhanced reactivity of nanoscale particles relative to their bulk counterparts with contaminants. Here, we describe recent advances in the synthesis and characterization of metallic and bimetallic nanoparticles that have been effective toward degrading toxic organohalide contaminants. We then review the degradation mechanisms involved in the reactions of nanoscale particles with organohalides via reduction pathways. We also discuss an emerging area – the degradation of organohalides via multi-electron transfer pathways.

Keywords: multi-electron transfer catalysts; nanoscale materials; organohalide contaminants; reduction; synthesis.

1. Introduction

Organohalides have played important roles in the chemical, agricultural, and pharmaceutical industry as precursors, solvents, or additives. Despite their importance, organohalides have presented serious toxicological and environmental concerns for several decades. Organohalides comprise 44% of the contaminants listed on the US Environmental Protection Agency’s Drinking Water Contaminant Candidate List [1]. They are persistent chemicals that have been suggested as carcinogens, groundwater contaminants, and they have been linked to ozone depletion. Table 1 lists some of the most common organohalide contaminants and their toxicity.

A number of techniques for the remediation of organohalides have been explored including bioremediation [2–9], advanced oxidation technologies [10–15], and permeable reactive barriers [16, 17]. Abiotic reductive transformation using metal particles has attracted much attention in environmental remediation due to the short duration required for complete treatment [18]. Although a number of technologies have been developed for the remediation of organohalides, this review focuses primarily of reduction pathways driven by nanoscale metals, and multi-electron transfer (MET) systems for dehalogenation processes (Figure 1). Zero-valent metals play an important role as reducing agents, thus promoting the reductive dechlorination of organohalides as shown in Figure 2 and described by the following reaction [19, 20]:

\[ \text{M}^{0} + \text{RX} + \text{H}^{+} \rightarrow \text{M}^{2+} + \text{RH} + \text{X}^{-} \]

where X is the halogen.

Zero-valent metals have been found to be highly effective toward dehalogenation processes [21]. There are two mechanisms by which dehalogenation via zero-valent metals occur [22–24]. In the first suggested mechanism, organohalides are adsorbed on the metal surface, followed by direct electron transfer from the metal. The electron reduces the organohalide resulting in release of halogenated ions. In the second suggested mechanism, adsorbed hydrogen generated during the metal corrosion process drives the dehalogenation reaction. In this case, the metal acts as the catalyst [22]. The first suggested mechanism has been found to be the main pathway particularly for metals with high cathodic overpotentials, for example, iron and zinc [23–25].

In the early 1990s, zero-valent iron technology was introduced as a method for remediation of organic contaminants due to iron having a standard reduction potential \( E^0 \) of -0.44 V vs. standard hydrogen electrode (SHE) [26, 27]. Thus, zero-valent iron has become a common technology for treating groundwater polluted by organohalides [28–38]. Zero-valent iron have also been shown to be very effective for the degradation and remediation of a large number of environmental pollutants including organohalides [27–39], heavy metals, nitrates, arsenates, pesticides [40], radio-nuclides [41, 42], and azodyes. Easy access to zero-valent iron, its efficiency, and cost effectiveness have thus led to its increased use for environmental remediation.

With advances in nanoscale science, an interest in using zero-valent iron nanoparticles for environmental remediation emerged in the late 1990s [43–45]. Compared with conventional granular iron particles, nanoscale zero-valent iron particles, nanoscale zero-valent iron particles provide a larger surface area to volume ratio and, hence, enhanced reactivity could successfully decrease the site clean-up time and consequently the remediation cost [46]. Furthermore, zero-valent iron nanoparticles can be engineered more easily relative to conventional granular iron particles, thus providing an advantage for in situ applications.
<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical structure</th>
<th>MCL&lt;sup&gt;a&lt;/sup&gt; (mg/l)</th>
<th>LD&lt;sub&gt;50&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (mg/kg)</th>
<th>Used metallic or bimetallic NPs</th>
<th>Possible health effects</th>
</tr>
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<tbody>
<tr>
<td>3,3',4,4'-Tetrachlorobiphenyl</td>
<td><img src="image.png" alt="Chemical Structure" /></td>
<td>0.0005</td>
<td>1010</td>
<td>Fe, Fe/Al, Fe, Fe/Ni, Pd, Pd/Fe, Ni/Fe</td>
<td>Skin changes, thymus gland problems, immune deficiencies, reproductive or nervous system difficulties, increased risk of cancer</td>
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<td>Carbon tetrachloride</td>
<td><img src="image.png" alt="Chemical Structure" /></td>
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<td>2800</td>
<td>Fe/Al, Fe/Fe/Cu</td>
<td>Liver problems, increased risk of cancer</td>
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<tr>
<td>Hexachlorobenzene</td>
<td><img src="image.png" alt="Chemical Structure" /></td>
<td>0.0005</td>
<td>3500</td>
<td>Fe, Fe/Pd/Fe, Fe/Cu, Ni/Fe</td>
<td>Liver or kidney problems, reproductive difficulties, increased risk of cancer</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td><img src="image.png" alt="Chemical Structure" /></td>
<td>0.005</td>
<td>2402</td>
<td>Fe, Ni/Fe, Fe/Pd, Fe/Pd</td>
<td>Liver problems, increased risk of cancer</td>
</tr>
<tr>
<td>p-Nitrochlorobenzene</td>
<td><img src="image.png" alt="Chemical Structure" /></td>
<td>0.005</td>
<td>420</td>
<td>Fe, Pd, Ni/Fe</td>
<td>Affects central nervous system</td>
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</tbody>
</table>
### Table 1 (continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical structure</th>
<th>MCL&lt;sup&gt;a&lt;/sup&gt; (mg/l)</th>
<th>LD&lt;sub&gt;50&lt;/sub&gt; (mg/kg)</th>
<th>Used metallic or bimetallic NPs</th>
<th>Possible health effects</th>
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<tr>
<td>O-Nitrochlorobenzene</td>
<td><img src="image1" alt="Structure" /></td>
<td>–</td>
<td>219</td>
<td>Fe</td>
<td>Affects central nervous system</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td><img src="image2" alt="Structure" /></td>
<td>–</td>
<td>1276</td>
<td>Pd/Fe</td>
<td>Highly toxic, mutagenic, and possibly carcinogenic</td>
</tr>
<tr>
<td>Tetrabromobisphenol</td>
<td><img src="image3" alt="Structure" /></td>
<td>&gt;5000</td>
<td></td>
<td>Fe/Ag</td>
<td></td>
</tr>
<tr>
<td>Monochloroacetic acid</td>
<td><img src="image4" alt="Structure" /></td>
<td>0.06&lt;sup&gt;c&lt;/sup&gt;</td>
<td>55</td>
<td>Pd/Fe</td>
<td>Increased risk of cancer</td>
</tr>
<tr>
<td>Benzyl chloride</td>
<td><img src="image5" alt="Structure" /></td>
<td>–</td>
<td>1231</td>
<td>Ag/Au</td>
<td>Irritant to skin, eyes, and mucous membranes Affects central nervous system</td>
</tr>
</tbody>
</table>
### Table 1 continued

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical structure</th>
<th>MCL&lt;sup&gt;a&lt;/sup&gt; (mg/l)</th>
<th>LD50&lt;sup&gt;b&lt;/sup&gt; (mg/kg)</th>
<th>Used metallic or bimetallic NPs</th>
<th>Possible health effects</th>
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<td>0.0002</td>
<td>88</td>
<td>Pd/Fe, Fe, Pd</td>
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<tr>
<td>Decabromodiphenyl ether</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>–</td>
<td>500</td>
<td>Ni/Fe, Fe</td>
<td>Possible human carcinogen</td>
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<tr>
<td>Pentachlorophenol</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>0.001</td>
<td>27</td>
<td>Pd/Fe, Ni/Fe</td>
<td>Liver or kidney problems, increased cancer risk</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>0.005</td>
<td>3835</td>
<td>Ni/Fe, Pd/Fe</td>
<td>Liver, kidney, or circulatory system problems</td>
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<td><em>cis</em>-1,2-Dichloroethene</td>
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<td>0.07</td>
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<td>Ni/Fe</td>
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<tr>
<td>Vinyl chloride</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>0.002</td>
<td>500</td>
<td>Ni/Fe, Fe</td>
<td>Increased risk of cancer</td>
</tr>
<tr>
<td>Name</td>
<td>Chemical structure</td>
<td>MCL&lt;sup&gt;a&lt;/sup&gt; (mg/l)</td>
<td>LD50&lt;sup&gt;b&lt;/sup&gt; (mg/kg)</td>
<td>Used metallic or bimetallic NPs</td>
<td>Possible health effects</td>
</tr>
<tr>
<td>-----------------------</td>
<td>--------------------</td>
<td>-------------------------</td>
<td>--------------------------</td>
<td>--------------------------------</td>
<td>----------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Chloroform</td>
<td></td>
<td>0.08&lt;sup&gt;d&lt;/sup&gt;</td>
<td>36</td>
<td>Fe, Fe/Ni</td>
<td>Causes blood, kidney, and liver problems. Also affect the central nervous system</td>
</tr>
<tr>
<td>Dichloroacetic acid</td>
<td></td>
<td>0.06&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2820</td>
<td>Pd/Fe</td>
<td>Increases risk of cancer</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td></td>
<td>0.06&lt;sup&gt;c&lt;/sup&gt;</td>
<td>400</td>
<td>Pd/Fe</td>
<td>Increases risk of cancer</td>
</tr>
<tr>
<td>2,4,6-Trichlorophenol</td>
<td></td>
<td>–</td>
<td>820</td>
<td>Pd/Fe</td>
<td>Highly toxic, mutagenic, and possibly carcinogenic</td>
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<tr>
<td>Monochlorobenzene</td>
<td></td>
<td>0.01</td>
<td>2290</td>
<td>Ni/Fe</td>
<td>Liver or kidney problems, increased cancer risk</td>
</tr>
<tr>
<td>Atrazine</td>
<td></td>
<td>0.003</td>
<td>3090</td>
<td>Fe, Pt</td>
<td>Cardiovascular system or reproductive problems</td>
</tr>
</tbody>
</table>

*(Table 1 continued)*
<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical structure</th>
<th>MCL$^c$ (mg/l)</th>
<th>LD$^{50}$ (mg/kg)</th>
<th>Used metallic or bimetallic NPs</th>
<th>Possible health effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,4-Trichlorobenzene</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>0.07</td>
<td>756</td>
<td>Fe/Pd</td>
<td>Changes in adrenal glands</td>
</tr>
</tbody>
</table>

MCL is the maximum contaminant level in the drinking water, according to US Environmental Protection Agency, Drinking Water Contaminants, US Environmental Protection Agency, www.EPA.gov.

LD$^{50}$ values are for oral exposure in rats, extracted from MSDS of each substance. MCL values are for total haloacetic acids (monochloroacetic, dichloroacetic, and tribromoacetic acids).

MCL is for total trihalomethanes (chloroform, bromoform, bromodichloromethane, and dibromochloromethane).

**Figure 1** Metallic, biometallic, or functionalized nanoscale materials can be used in the dehalogenation of organohalides (RX) to less toxic products (RH).

**2. Synthesis**

**2.1. Synthesis of metallic nanoparticles**

The chemical and physical properties and reactivity of nanoparticles are dependent on their size, shape, and morphology. Thus, synthetic procedures that produce well-defined nanoparticles with controlled dispersity are significant toward understanding the properties and applications of nanoscale materials. In this section, we provide an overview on the common methods for synthesis of metallic and bimetallic nanoparticles that are relevant toward degradation of organohalide pollutants (Table 2) [47, 48]. We also compare some of the advantages and disadvantages for the described methods.

Several articles have recently appeared in the literature that review general synthetic procedures for metal nanoparticles [49–68]. The formation of nanoparticles involves two important processes, nucleation and growth, and significant details on the mechanism for nanoparticle formation have been described [69–79]. The initial nucleation process occurs through homogenous, heterogeneous, or secondary nucleation in a supersaturated solvent [62]. The nucleation process is followed by growth of the nuclei via molecular
addition. Molecular addition causes the concentration of the target element to drop below the critical point, resulting in an end to the nucleation process. However, the growth process continues until the concentration of the precipitates reaches equilibrium. The unity of the size of nanoparticles takes place due to the difference in free energy ($\Delta G$) of the driving force within nanoparticles of different size. Smaller particles have larger free energy relative to larger particles. This difference in free energies results in faster growth for the smaller particles. It should be noted that under these conditions, the reaction should be stopped or more reactant should be added to the system to retrieve the depletion of its concentration due to particle growth. Alternatively, Ostwald ripening occurs, whereby the larger particles continue growing, as a result of generation of smaller particles. Formation of smaller particles is kinetically favored, whereas the formation of larger particles is thermodynamically favored. The process continues until the smaller particles completely dissolve in the solvent.

In 1992, Bönneman et al. [80] expressed that the synthesis of metal nanoparticles requires at least three parameters: a metal precursor, a stabilizer, and a reducing agent. Stabilizers are important in the synthesis of nanoparticles, as they control the particle size and shape while reducing the tendency to aggregate. In general, desired metal nanoparticles can be obtained by carefully choosing and manipulating these three substrates. Eq. (1) demonstrates a general reaction for synthesizing metal nanoparticles.

$$MX_n(NR_4)_m+(n-m)\text{Red} \rightarrow M_{(n-m)}(NR_4)^{m}\text{Red}^+X^- + m(NR_4)^+X^-$$

where $M$ represents a group VII, IX, or X transition metal, $X$ is a leaving group, and Red is an effective reducing agent [81].

Elemental metals, their inorganic salts, and inorganic complexes are examples of metal precursors that are used for metallic nanoparticle synthesis. The most common metal nanoparticles used for environmental applications and their inorganic precursors are listed in Table 2. Eq. (2) shows the chemical equation for the synthesis of zero-valent iron nanoparticles, using ferric chloride as the precursor, sodium borohydride as the reducing agent, and cetyltrimethylammonium bromide as the surfactant.

$$2\text{FeCl}_3 + 6\text{NaBH}_4 + 18\text{H}_2\text{O} \rightarrow 2\text{Fe}^{0} + 21\text{H}_2 + 6\text{H}_3\text{BO}_3 + 6\text{NaCl}$$

The synthesis method of metal nanoparticles can be also categorized by the media in which the nanoparticles are formed. According to this classification, there are two major methods for synthesis of metallic nanoparticles (especially for synthesis of zero-valent iron nanoparticles: solution synthesis or a water-in-oil emulsion synthesis [19, 82, 83]. Solution synthesis involves the synthesis of metal nanoparticles by chemical reduction of the metal salt in solution [84]. Generally, stirring the solution after addition of the reducing agent is needed to make sure that the reducing agent is distributed uniformly throughout the solution. Furthermore, to prevent possible oxidation of the synthesized nanoparticles, excess amount of reducing agent is usually added into the reaction solution. Although this method is straightforward, the limitation is that control of particle size and size distribution remains a challenge.

The water-in-oil emulsion method provides nanoparticles with improved size-control [83]. In this method, an aqueous solution of metal ions is added into an oil phase, and a water-soluble co-solvent is added into the formed emulsion. The reducing agent is usually added into the system as the last step in the reaction. Metal nanoparticles synthesized by this method are more uniform in size and also have fewer tendencies to aggregate.

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Metal precursors</th>
<th>Synthetic procedure used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Iron(II) sulfate</td>
<td>Solution synthesis</td>
</tr>
<tr>
<td></td>
<td>Iron(III) chloride</td>
<td>Water-in-oil emulsion</td>
</tr>
<tr>
<td>Iron-copper</td>
<td>Iron(II) sulfate</td>
<td>Co-reduction</td>
</tr>
<tr>
<td></td>
<td>Copper(II) nitrate</td>
<td></td>
</tr>
<tr>
<td>Iron-nickel</td>
<td>Iron(II) sulfate</td>
<td>Co-reduction</td>
</tr>
<tr>
<td></td>
<td>Nickel(II) chloride</td>
<td></td>
</tr>
<tr>
<td>Iron-palladium</td>
<td>Iron(II) sulfate</td>
<td>Successive reduction</td>
</tr>
<tr>
<td></td>
<td>Palladium(II) chloride</td>
<td></td>
</tr>
<tr>
<td>Iron-silver</td>
<td>Iron(II) sulfate</td>
<td>Successive reduction</td>
</tr>
<tr>
<td></td>
<td>Silver(I) nitrate</td>
<td></td>
</tr>
<tr>
<td>Gold-platinum</td>
<td>Gold(III) chloride</td>
<td>Co-deposition</td>
</tr>
<tr>
<td></td>
<td>Palladium(II) chloride</td>
<td></td>
</tr>
<tr>
<td>Gold-silver</td>
<td>Gold(III) chloride</td>
<td>Electrochemical reduction</td>
</tr>
<tr>
<td></td>
<td>Silver(I) nitrate</td>
<td></td>
</tr>
<tr>
<td>Palladium-tin</td>
<td>Palladium(II) acetate</td>
<td>Co-deposition</td>
</tr>
<tr>
<td></td>
<td>Tin(IV) chloride</td>
<td></td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>Titanium(IV) isopropoxide</td>
<td>Sol-gel method</td>
</tr>
</tbody>
</table>
2.2. Synthesis of bimetallic nanoparticles

Metallic or bimetallic nanoparticles can be synthesized by an in situ method. In this case, metal precursors deposit on the surface of the stabilizer. The stabilizer is then soaked in a solution of reducing agent, resulting in reduction of the precursor and formation of nanoparticles on the polymer [85–87].

Bimetallic alloy nanoparticles (i.e., metallic entities comprising atoms of two different metallic elements) offer improved catalytic properties relative to their single-metal counterparts [88, 89]. Studies have shown that the alloy structure of bimetallic nanoparticles affects the catalytic properties [90–92]. The crystal structure of bimetallic alloy nanoparticles may vary from the bulk alloy, depending on the synthetic procedures and distribution of each metal [93]. Bimetallic nanoparticle alloys are usually synthesized by one of three methods, depending on the desired composition of the nanoparticles: co-reduction, successive reduction, or thermal decomposition.

2.2.1. Co-reduction Two corresponding metal ions are simultaneously reduced by refluxing in alcohol or other suitable solvent in the presence of a stabilizing ligand. Most bimetallic nanoparticles are susceptible to oxidation, and therefore Schlenk line techniques are usually used during the synthesis procedure, and once prepared, if needed, the nanoparticles are stored under nitrogen to avoid oxidation by air.

As shown in Eq. (3), addition of sodium borohydride to a solution of ferrous sulfate (FeSO$_4$) and nickel(II) chloride (NiCl$_2$) with a 4:1 Fe/Ni ratio resulted in the co-reduction of the metal ions leading to the formation of Fe/Ni bimetallic nanoparticles [94].

$$2\text{Fe}^{2+}(\text{Ni}^{2+}) + \text{BH}_4^- + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^0(\text{Ni}^0) + 2\text{H}_2 + \text{BO}_2^- + 4\text{H}^+ \quad (3)$$

2.2.2. Successive reduction Successive reduction of metal ions is a suitable procedure for bimetallic alloy nanoparticles where the metal ions have a large difference in reduction potential. In this case, the metal ion with the more negative reduction potential is reduced first, followed by the second metal, which will be reduced either chemically or by reflux in an alcohol solution.

Successive reduction was used to synthesize iron/palladium (Fe/Pd) nanoparticles because of their position in the chemical series [95, 96]. In this case, iron nanoparticles were first synthesized by solution synthesis using sodium borohydride as the reducing agent. This was followed by addition of the palladium salt to the solution containing the iron nanoparticles. Eq. (4) shows formation of Fe/Pd nanoparticles by the successive reduction method [95–98].

$$\text{Fe}^{2+}\text{Pd}^{2+} \rightarrow \text{Fe}^{2+} + \text{Pd}^0 \quad (4)$$

2.2.3. Thermal decomposition Increased temperature can have significant effects on nucleation and growth during nanoparticle formation. Thermal decomposition usually takes place by heating the corresponding metal precursors with varied ratios, usually acetates, in the presence of the stabilizing ligands.

3. Characterization

The size, shape, and morphology of nanoscale materials has a major influence on their chemical and physical properties and their reactivity. Thus, characterization of nanoparticles is important toward understanding their reactivity with various substrates including environmental pollutants. Typically, the characterization of metallic and bimetallic nanoparticles involve microscopic, X-ray, and spectroscopic techniques including transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), Brunauer-Emmett-Teller method (BET), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), and extended X-ray absorption fine structure (EXAFS). These are the most relevant and common characterization techniques used and will be briefly discussed in this article.

3.1. Transmission electron microscopy

Thirty-four years after the discovery of the electron by J.J. Thompson in 1897, Max Knoll and Ernst Ruska in Germany found a way to propel them through a sample to create an image in a way remarkably similar to optical microscopy to create the first TEM. This method uses an electron beam emitted by a tungsten filament at a high voltage of 100 keV as the source of radiation. An image is formed by the interaction of the electrons transmitted through the specimen. As TEM allows the direct visualization of particles (Figure 3), it provides important information about particle formation, shape, and size distribution. TEM specimens are placed on the sample holder, which typically consists of a carbon-coated copper grid. The sample for analysis is prepared by either dropping a few microliters of the nanoparticle solution onto the grid or quickly contacting the carbon-coated side of the sample holder with the analyte solution. The sample is allowed to dry prior to being placed in the instrument for analysis. High resolution transmission electron microscopy (HRTEM) allows the analysis of nanoparticles with resolution up to 0.8 Å. This is made possible by using a high-voltage power (200–300 keV) supply for the electron beam. HRTEM allows the determination of the crystal structure at the subnanometer scale. Although TEM and HRTEM are very useful methods, they have limitations. The high-voltage electron beam that is used in these methods can potentially damage the sample, especially in the case of biological materials.

3.2. Scanning electron microscopy

SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimen. The
operational principles of SEM are similar to those of TEM. In SEM, high-voltage (a few electron volts to 100 keV) electron beam excites the samples. The electron beam is scanned across the sample in a raster scan using scan coils. The process includes generation of low-energy secondary electrons that are emitted from the surface to form an image. The main difference between the images produced by TEM and SEM is that SEM provides images of external morphology, whereas TEM provides images of the internal structure. Figure 4 is a representative SEM image of Fe/Ni bimetallic nanoparticles used for organohalide degradation.

3.3. Atomic force microscopy

AFM is a surface probe technique that has been efficient in characterizing nanoscale materials [99]. This method is able to resolve details of particle surfaces with atomic level resolution. The AFM operates by allowing an extremely fine sharp tip to either come in contact or very close to the sample in the x-y raster pattern. This tip moves up and down along the z-axis. The AFM opened the door to imaging materials, such as polymers and biological samples that do not conduct a current. Providing three-dimensional surface profile is an advantage of AFM over the electron microscope methods (TEM and SEM). In addition, AFM can work in ambient air pressure and there is no need to a vacuum environment.

3.4. Brunauer-Emmette-Teller method

In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller developed a substantially useful surface area analysis technique, which was later named BET (taken from the first letter of each of the authors’ last name) [100]. BET allows the determination of the effective surface area of a material...
by applying the BET theory to the amount of nitrogen gas, which adsorbs isothermally on the surface of that material at 77 K. The theory of BET surface area analysis, in fact, is an extension of another theory developed by Irving Langmuir [101]. The difference between Langmuir’s work and BET is that, in BET, the adsorption of gas molecules on the surface of a material is taken into consideration. Thus, the BET theory suggests a multilayer mechanism for the adsorbed nitrogen.

This theory can be expressed as shown in Eq. (5):

$$\frac{P}{V(P_0-P)} = \frac{1}{V_m C} + \frac{(C-1) P}{V_m C P_0}$$

where $P$ and $P_0$ are the equilibrium pressure and the saturation pressure of the adsorbates, respectively, $V$ is the volume of the gas that can be adsorbed on the unit mass of material at pressure $P$, $V_m$ is the monolayer adsorbed gas quantity, and $C$ is a constant that can be calculated using the heats of adsorption in each layer.

In this technique, the nitrogen multilayer adsorption is measured as a function of relative pressure to determine the overall specific surface area for the nanoparticles. Specific surface area and surface porosity of nanoparticles are important parameters of nanoparticles especially when the particles are used as catalysts.

### 3.5. X-ray photoelectron spectroscopy

XPS is a widely used technique for both quantitative and qualitative characterization of materials, especially of nanostructures, polymers, and biomedical structures. Although the photoelectric effect was discovered at the beginning of the 20th century, the XPS method was developed in the 1960s by the Swedish physicist Kai Siegbahn, who later was awarded the Nobel Prize in physics for his discoveries. The method is useful for obtaining chemical state information, composition of a material and quantity of each component, layer thickness information, and empirical formulas. In a typical XPS measurement, the number of electrons detected is plotted as a function of the binding energy of the electrons. Each peak acquired is a characteristic of a specific element [102]. Figure 5 provides characteristic data for a Fe/Ni bimetallic nanoparticles sample.

### 3.6. X-ray diffraction

XRD is an important technique used for characterization of crystalline structures. The technique provides information on the thickness of thin films and multilayer materials, crystalline phases and orientation, atomic arrangement, and other important properties of the crystalline structure. When the X-ray beam interacts with a crystalline structure, it produces a pattern characteristic of the substance being analyzed [103]. In this method, X-ray radiation from a source passes through the material. The beam is scattered after passing through the sample resulting in the formation of diffraction peaks. The diffraction pattern is based on the chemical composition of the sample. Using the Scherrer’s equation, the particle size can be calculated:

$$t = \frac{0.89 \lambda}{\beta \cos \theta}$$

where $t$ is the thickness, $\lambda$ is the wavelength of the X-ray beam, $\theta$ is the angle corresponding to the peak, and $\beta$ is the full-width at half maximum, also called the integral breadth.
The peak position, peak width, and the peak intensity can be used to determine the chemical composition and the particles size. Figure 6 shows a representative XRD pattern for Fe/Pd bimetallic nanoparticles.

### 3.7. Energy dispersive X-ray spectroscopy

EDX is an analytical technique used for the determination of the chemical composition of the sample. EDX is an X-ray fluorescence method, in which a very high energy beam, typically in the range of 10–20 keV collides with the sample, excites the specimen, and causes it to emit X-ray radiation. EDX can be coupled with electron microscopy to provide a powerful analytical tool for the characterization of nanomaterials in which one can determine the chemical composition...
in a specific nanoparticle. Thus, EDX provides quantitative data on the composition of each element in a sample.

3.8. Extended X-ray absorption fine structure

EXAFS is an X-ray absorption spectroscopy technique that uses synchrotron radiation as the X-ray source. The EXAFS method is based on the scattering of the photoelectron from the neighbor atoms. This scattered photoelectron can return to the absorbing atom and thus change the absorption coefficient $\mu(E)$ to cause EXAFS. The technique is especially useful for the characterization of bimetallic nanoparticles because it provides detailed structural information about the near-neighbor metals surrounding the X-ray absorbing metal, including the number, chemical identity, electron density as well as inter-atomic distances [104].

4. Applications of nanoparticles in the remediation of organohalides

4.1. Organohalide remediation using metallic nanoparticles

4.1.1. Iron nanoparticles

In the early 1990s, zero-valent iron emerged as a viable method for the remediation of organohalide pollutants. In most cases, the technique was effective, although some concerns arose due to the inefficiency of zero-valent iron to reduce organohalides such as chlorinated ethylenes into benign products. Thus, alternative routes to improve the performance of zero-valent iron were sought. Among these was the use of nanoscale zero-valent iron particles that were expected to have improved reactivity due to the high surface to volume ratio. The introduction section of this article provides background information on the reaction mechanism of zero-valent iron with organohalides.

Zero-valent iron nanoparticles have also been used for treatment of lindane and atrazine, two well-known pesticides, by Joo and Zhao [105]. Shih et al. [106] studied the degradation mechanism of zero-valent iron nanoparticles toward the dehalogenation of hexachlorobenzene (HCB). Their study focused on the pH dependence, effect of mass concentration of zero-valent iron nanoparticles, and temperature on the dehalogenation process. The results indicate that the dechlorination efficiency increases with increased mass concentration of nanoparticles from 2.0 to 20.0 g/l. However, around 60% of HCB were remediated using ZVI NPs after 96 h at 45°C while in the same time period, only 40% of HCB were degraded at 5°C and 25°C. Analysis of the degradation reaction products showed that HCB was dechlorinated. Figure 7 shows the changes in concentration of each component with the time [106]. By-product analysis indicated that degradation starts with the loss of one chlorine atom and formation of pentachlorobenzene (PCB). The following steps involved loss of more chlorines and formation of tetrachlorobenzenes, trichlorobenzenes (TCBs), and finally 1,2-dichlorobenzene as the end product.

4.1.2. Platinum nanoparticles

Although zero-valent iron is the most common metallic nanoparticle that has been reported for the remediation of organohalides, there are also other metals that are effective. Liu et al. [107] reported hydrodechlorination of monochlorobenzene in the presence of colloidal Pt nanoparticles stabilized on polyvinylpyrrolidone (PVP). Unlike the hydrodechlorination of chlorobenzene using other metallic nanoparticles, which result in formation of other environmental pollutants such as benzene, aniline (AN), and naphthalene, a complete degradation of chlorobenzene to produce aliphatic products was reported. Benzene was an intermediate, and its concentration increased during the first 4 h of the reaction but later reduced as it underwent degradation by the Pt catalyst to form cyclohexane. High catalytic efficiency of the Pt catalyst working under a hydrogen atmosphere allowed the complete degradation of chlorobenzene.

4.1.3. Palladium nanoparticles

Hildebrand et al. [108] reported the dechlorination of chlorobenzene using palladium nanocatalysts. The novelty of Hildebrand et al.’s work was that the palladium nanoparticles were bound to the surface of nanoscale magnetite, which was used as a ferromagnetic carrier. The overall catalysts could easily be recovered from the wastewater treatment site using a magnetic field.

4.2. Remediation of organohalides using bimetallic nanoparticles

Bimetallic nanoparticles display unique size- and shape-dependent chemical and physical properties relative to their single metal counterparts [109–112]. The reactivity of bimetallic nanoparticles has been exploited for the remediation of organohalide pollutants. In addition to improved reactivity, bimetallic nanoparticles also display enhanced stability toward oxidation [95]. For example, the use of zero-valent iron nanoparticles for remediation of
organohalides has been very common; however, one of the major limitations that results in decreased reactivity is the formation of an oxide layer on the surface of zero-valent iron nanoparticles. This layer acts as barrier and blocks the surface active sites of nanoparticles [113]. Introducing a second metal to zero-valent iron, for example, nickel, platinum, palladium, or zinc to forming bimetallic nanoparticles, enhances the dehalogenation rates relative to using iron nanoparticles alone [18, 19, 46, 114]. Figure 8 shows the efficiency of synthesized Fe/Pd nanoparticles in degradation reaction of lindane after exposure of nanoparticles to air and water.

Most reports that utilize bimetallic nanoparticles have made use of supportive membranes to reduce the tendency of the nanoparticles toward aggregation. The supportive membranes also aid in the recyclability of the bimetallic nanoparticles from water. To make the nanoparticles compatible with the supportive membranes, specific stabilizers should be used, for example, carboxymethyl cellulose (CMC) [95, 115], PVP, PEG 2000, and octa(diaceticaminophenyl)silsesquioxane [112].

4.2.1. Fe/Pd bimetallic nanoparticles

Fe/Pd particles have been effective toward the degradation of organohalides. The combination of Fe and Pd metals is advantageous because palladium serves as a metal on which hydrogen gas is adsorbed. Hydrogen gas results from the corrosion reaction of iron. H₂ is then transformed to form H⁺ or H⁻ and aids in the dehalogenation reaction to combine with the halogen atom or to replace the halogen atom, respectively [116].

Scheme 1 shows a schematic reaction between Fe/Pd nanoparticles and a polychlorinated biphenyl (PCB) as a schematic remediation reaction for organohalides [116]. Here, the Fe component of the nanoparticle acts as the electron source, while the Pd component of the nanoparticles plays the role of the catalyst. In this case, a three step reaction occurs. As shown in Eqs. (7)–(12), the reaction begins with the generation of hydrogen gas, followed by Fe corrosion. In the second step, the generated hydrogen gas combines with Pd and is embedded into the Pd crystal lattice [117]; the last step is the dehalogenation reaction [Eq. (12)].

\[
\begin{align*}
\text{Fe} + 2\text{H}^+ & \rightarrow \text{Fe}^{2+} + \text{H}_2 \quad \text{(in acidic solutions)} \quad (7) \\
\text{Fe} + 2\text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \quad \text{(in basic solutions)} \quad (8) \\
\text{Fe} + \text{RCl} + \text{H}^+ & \rightarrow \text{RH} + \text{Fe}^{2+} + \text{Cl} \quad (9) \\
\text{Pd} + \text{H}_2 & \rightarrow \text{Pd.H}_2 \quad (10) \\
\text{Pd} + \text{RCl} & \rightarrow \text{Pd...Cl...R} \quad (11) \\
\text{Pd.H}_2 + \text{Pd...Cl...R} & \rightarrow \text{RH} + \text{H}^+ + \text{Cl}^- + 2\text{Pd} \quad (12)
\end{align*}
\]

Chlorinated methanes, polychlorocyclohexanes, PCBs, chlorinated aromatics [118, 119], and chloroacetic acids [120] are examples of different organohalides that have been efficiently remediated using Fe/Pd NPs [94].

Paknikar et al. reported the degradation of γ-hexachlorocyclohexane (lindane) using Fe/Pd bimetallic nanoparticles [113]. Lindane is an organohalide used in agriculture as a pesticide and also as a pharmaceutical in the treatment of lice and scabies. Lindane is highly stable and is a persistent organic pollutant. Although it has not been proven that lindane is a carcinogen, it is known that lindane is a neurotoxin as well as an endocrine disrupter in humans [121]. Fe/Pd nanoparticles have been shown to be strong catalysts for the degradation of lindane. Figure 9 shows the change in concentration of lindane as it is degraded and the change in concentration of cyclohexane as it is formed vs. exposure time. Lindane concentration decreases with time due to degradation, whereas the cyclohexane concentration increases. Paknikar et al. reported Fe/Pd bimetallic nanoparticles as the first system for lindane degradation with a long life span, in which the dechlorination...
process does not yield toxic intermediates such as 1,2,4-TCB under ambient reaction condition.

Bachas et al. [116] studied the dehalogenation process of 3,3′,4,4′-tetrachlorobiphenyl (PCB77), a polychlorinated biphenyl, using Fe/Pd nanoparticles. PCBs consist of a biphenyl structure with 1–10 chlorine atoms. Thus, there are 209 possible structures for PCBs, and 130 of them are commercially available. PCBs are chemically inert, nonvolatile chemicals with a large dielectric constant. They are highly soluble in hydrocarbons and do not undergo oxidation, reduction, addition, elimination, or electrophilic substitution reactions except under extreme conditions [122]. Their use has been regulated since 1979 [123–125].

Before 1979, PCBs were broadly used in various applications, for example, as coolants, as insulating fluids in capacitors, hydraulic fluids, vacuum pump fluids, pesticide extenders, plasticizers, lubricant oils, and adhesives. This wide application of PCBs, along with their high toxicity and persistence in the environment, makes them toxic environmental pollutants and increased efforts to develop efficient remediation processes for PCBs are required.

Bachas et al. [126] studied the degradation of PCB77, using both Pd nanoparticles and Fe/Pd bimetallic nanoparticles. Although an external hydrogen supply was needed when Pd nanoparticles were used, there was no need for an external hydrogen supply when Fe/Pd nanoparticles were used. This is due to the ability of the Fe component of the Fe/Pd nanoparticles to generate hydrogen in situ. Figure 10 shows the concentration profile of PCB77 and dechlorination intermediates and products in the presence of Fe/Pd nanoparticles. The decrease in the concentration of PCB77 occurs due to its degradation, whereas the increase in the concentration of biphenyl is as a result of its formation as the main product of the remediation process. As shown in Scheme 2, other PCBs were formed as intermediates of the degradation process.

The kinetics of the dechlorination reaction in the presence of Fe/Pd bimetallic nanoparticles were found to follow pseudo-first-order kinetics [127, 128]. Thus, Eq. (13) can be used to describe the kinetics of dechlorination of PCB77 utilizing Fe/Pd nanoparticles:

\[
\frac{dC}{dt} = k_{obs} C = k_{SA} \rho \alpha a C
\]

where \( C \) is the concentration of PCB77, \( \alpha \) is the surface area of the nanoparticles, \( \rho \) is the loading of the nanoparticles, \( k_{obs} \) is the observed rate constant, and \( k_{SA} \) is the surface area normalized rate constant.

\( k_{obs} \) and \( k_{SA} \) were determined using Eq. (12) for the reaction with Pd nanoparticles and Fe/Pd nanoparticles. The results showed that there was a sevenfold improved efficiency for the Fe/Pd nanoparticles during the dechlorination process of PCB77 [116].

\( p \)-Nitrochlorobenzene (\( p \)-NCB) is an organohalide that has been extensively used in the manufacture of explosives, pesticides, and dyes [129]. The toxicity of \( p \)-NCB has resulted in the development of several methods for its degradation including bioremediation [130], Fenton oxidation [131], O3/UV degradation [132], and photocatalytic oxidation [133]. Although zero-valent Fe nanoparticles were found to be more effective toward the remediation of \( p \)-NCBs [36, 134] relative to the aforementioned methods, the tendency of Fe nanoparticles to aggregate during the degradation process is a major limiting factor [135]. Thus, bimetallic nanoparticles have attracted much attention for this purpose. Dong et al. [95] investigated the degradation of \( p \)-NCB utilizing Fe/Pd nanoparticles stabilized by sodium CMC and compared the results with nonstabilized and stabilized Fe nanoparticles. Their studies showed that a 0.2-g/l dose of bimetallic nanoparticles could degrade 100% of \( p \)-NCB in 40 min, whereas there was insignificant degradation when unpalladized Fe nanoparticles were used.
Figure 11 compares the concentration profiles of \( p \)-NCB degraded using stabilized bimetallic Fe/Pd nanoparticles and non-stabilized Fe nanoparticles [95]. The small amount of \( p \)-chlooroaniline (\( p \)-CAN), AN, and inorganic chloride (Cl) produced is an indication that these are intermediates formed during the remediation process.

Dong et al. also investigated the kinetics of the degradation process of \( p \)-NCBs [95]. They extracted the reaction rate equations for all organic compounds involved in the process and integrated them to obtain the concentration dependence for each of the components.

\[
C_{p-NCB} = e^{-k_1 t}
\]

(14)

\[
C_{p-CAN} = \frac{k_1}{(k_2 - k_1)(e^{-k_2 t} - e^{-k_1 t})}
\]

(15)

\[
C_{AN} = 1 - C_{p-NCB} - C_{p-CAN}
\]

(16)

Using the above equations, they were able to calculate the concentration of each organic component in the reaction at time \( t \), having \( k_1 \) and \( k_2 \) as the corresponding reaction rates for disappearance of \( p \)-NCB and \( p \)-CAN, respectively.

4.2.2. Iron/nickel bimetallic nanoparticles As discussed earlier, zero-valent Fe is an effective electron mediator, and thus, its combination with other noble metals, for example, Ni or Pd, to form bimetallic nanoparticles is a promising approach for the degradation of organohalides. In the case of bimetallic nanoparticles involving Fe, the Fe atoms serve as the electron mediators while the second metal acts as the catalyst for the hydrodehalogenation process [136].
Fe/Ni bimetallic nanoparticles are attractive catalysts for organohalide degradation due to the corrosion stability of Ni, its low cost, and availability [94]. Ni is also effective when combined with Fe because it can reactivate the surface. For example, Cheng and Wu [25] showed that physical addition of microscale Ni particles resulted in the reactivation of zero-valent Fe particles that had lost their surface activity.

Cwiertny et al. [137] showed that for Fe/Ni particles to display enhanced activity, the Ni and Fe atoms need to be in electronic contact with each other within the bimetallic particle. Another important factor is that having a layer of Ni nanoparticles on the iron surfaces (in a core-shell arrangement) is advantageous. In this case, the thickness of the Ni layer must be optimized so that it is not too thin to allow surface oxidation of the Fe and not too thick to prevent substrate activity with Fe [138].

The dehalogenation mechanism carried out by Fe/Ni nanoparticles follows a similar pathway to that of Fe/Pd nanoparticles [139–143]. Lim et al. [143] showed that a 2.5-g/l concentration of Fe/Ni bimetallic nanoparticles can completely reduce carbon tetrachloride three times faster than the same concentration of Fe nanoparticles alone (Figure 12) [143]. Xu et al. [139] demonstrated the remediation of p-NCB using Fe/Ni bimetallic nanoparticles. The dehalogenation efficiency was found to depend on the Ni loading of the Fe/Ni bimetallic nanoparticles. Bimetallic nanoparticles containing 2.0% Ni resulted in 100% dechlorination efficiency of p-NCB, whereas 0.5% of Ni loading resulted in only 51% dechlorination efficiency (Figure 13). The effect of bimetallic nanoparticle concentration, pH, and temperature on the dechlorination process of p-NCB was also studied. The results suggested that increasing the reaction temperature enhanced the dechlorination efficiency. However, increase in pH decreased the efficiency. The products of dechlorination p-NCBs were p-CAN, AN, and inorganic chloride.

Fe/Ni bimetallic nanoparticles were also found to be effective in the remediation of p-chlorophenol (p-CP). Zhang et al. [140] demonstrated the complete degradation of p-CP within 60 min of exposure to a relatively low concentration (0.4 g/l) of Fe/Ni bimetallic NPs with 5 wt% of Ni loading. The initial concentration of p-CP was reported to undergo complete degradations to inorganic chloride and phenol under ambient temperature and pressure in the presence of Fe/Ni bimetallic nanoparticles. Temperature and pH dependence of the reaction were found to have a similar effect as was seen in the case of p-NCB dechlorination. In addition, it was shown that increasing the mass concentration of bimetallic nanoparticles enhanced the dechlorination efficiency.

Fe/Ni bimetallic nanoparticles have also been effective toward the remediation of other organohalides including pentachlorophenol [141], monochlorobenzene [142], brominated diphenyl ethers [102], TCE [11], carbon tetrachloride [143], chloroform [143], and brominated methanes [94].

![Figure 11](image_url) Concentration profiles of p-NCB degraded using stabilized bimetallic (A) Fe/Pd nanoparticles and (B) nonstabilized Fe nanoparticles. (Taken with permission from Dong et al. [95]. Copyright © Elsevier.)
was reduced after 48 h of treatment. Concentration profiles of different chlorobenzene derivatives showed the formation of PCB, tetrachlorobenzene, TCB, and dichlorobenzene with no selectivity toward a stepwise dechlorination process.

4.2.4. Other bimetallic nanoparticles

Although iron-based bimetallic nanoparticles have been most commonly used for improving the dehalogenation process of organohalides relative to zero-valent iron technology, there have been recent developments in using non-iron-based bimetallic nanoparticles as well. Lo et al. [98] synthesized palladium/tin (Pd/Sn) bimetallic nanoparticles stabilized on a resin and demonstrated their effectiveness toward the degradation of TCE in aqueous media. Their investigation was motivated by work reported by Boronina and Klabunde [145], who showed that tin metal is an electron donor that is effective toward the dehalogenation of organohalides. An added advantage to using tin is its stability in groundwater relative to zero-valent iron. Within a short time, much of the TCE had been dechlorinated, indicating the effectiveness of the Pd/Sn bimetallic nanoparticles.

Metal composed of Ag or Au are typically not considered to be catalytic; however, on the nanoscale, these metals have unique properties that are not often in their bulk counterparts. For example, Zhou et al. [97] prepared Ag/Au bimetallic nanoparticles using an underpotential deposition-redox placement technique and used the bimetallic nanoparticles as the cathode for electrochemical reduction of benzyl chloride. Platinum/palladium (Pt/Pd) bimetallic nanoparticles [146], iron/silver (Fe/Ag) bimetallic nanoparticles [147], and gold/platinum (Au/Pt) bimetallic nanoparticles [148] are increasingly being...
investigated for dehalogenation, and it is expected that, with optimization of reaction conditions, such nanoparticles can prove to be effective and more stable that iron-based bimetallic nanoparticles systems.

4.3. Degradation of organohalides via MET catalysts

In 2001, Roberts et al. [149] demonstrated through theoretical calculations that the degradation of chlorinated ethylenes would undergo favorable thermodynamic pathways if two-electron transfer reductants were used relative to one-electron transfer reductants. The calculations showed that two-electron reduction potentials for degradation of chlorinated ethylenes were more positive compared with one-electron reduction potentials. Despite this prediction, very few reports [150, 151] have appeared in the literature that show the reduction of chlorinated ethylenes via a two-electron pathway. Identifying two-electron or MET catalysts and understanding their reactivity could potentially yield viable methods for the remediation of organic pollutants at mild conditions.

Our group [152] has shown that chlorinated ethylenes can be reduced via MET catalysts. The reduction rate constants of the chlorinated ethylenes cis-1,2-dichloroethylene (cis-DCE), TCE, and tetrachloroethylene (PCE), reduced by FMNH₂ under anoxic conditions, were investigated. The MET catalyst consisted of flavin mononucleotide (FMN) anchored to nanocrystalline TiO₂. FMN is a riboflavin and is a redox-active chromophore found in many enzymes and photoreceptors [153, 154]. FMN can be reduced to form FMNH⁺ or the well-known two-electron, two-proton FMNH₂, as shown in Scheme 3 [153]. The redox active behavior of FMN led us to investigate its reactivity with chlorinated ethylenes and to further identify whether it could be used to deliver multiple electrons.

In aqueous solution, FMN was not fully reduced to FMNH₂ but instead yielded the semiquinone radical FMNH⁺. The reactivity of FMNH⁺ toward the chlorinated ethylenes cis-DCE, TCE, and PCE was investigated. The results showed that FMNH⁺ was not oxidized to FMN even after several days of stirring. This observation indicated that FMNH⁺ was not strong enough to reduce any of the chlorinated ethylenes investigated. As FMNH⁺ was found to be unreactive toward chlorinated ethylenes, we investigated the reactivity of FMNH₂ with cis-DCE, TCE and PCE. We found that if FMN is photoreduced in MeOH, as opposed to water, it undergoes a two-electron, two-proton reduction to form FMNH₂ and MeOH is oxidized to formaldehyde. FMNH₂ thus carries two electrons [155]. The reactivity of FMNH₂ with the chlorinated ethylenes cis-DCE, TCE, and PCE was investigated and was found to be effective. Although the observed efficient reactivity of FMNH₂ in MeOH solvent with chlorinated ethylenes was encouraging, the inability to generate FMNH₂ in aqueous solution provided a limitation toward using the two-electron transfer system of FMNH₂. To overcome this limitation, TiO₂ was used as an electron donor to reduce FMN to FMNH₂ in an aqueous solution. In this case, FMN molecules were anchored to the surface of crystalline TiO₂ nanoparticles (Figure 15). TiO₂ band gap excitation produced an electron-hole pair. Band gap irradiation of FMN/TiO₂ system in aqueous solution yielded FMNH₂/TiO₂. In this case, the conduction band electrons (e⁻ CB) contribute to the reduction of FMN to FMNH₂, but due to the high rate of TiO₂ electron-hole recombination in aqueous solution, electrons did not accumulate in the TiO₂ conduction band.

Addition of the chlorinated ethylenes cis-DCE, TCE, and PCE with FMNH₂/TiO₂ in aqueous solution in the dark resulted in degradation (Figure 16). Reduction rate constants are shown in Table 3. Furthermore, reduction rate constants of the chlorinated ethylenes with FMNH₂ in methanol solvent were compared with the values obtained with FMNH₂ anchored to TiO₂ in aqueous solution using the relationship lnA=ln(A₀)-kt. Second-order rate constants were abstracted for plots of kobs vs. [chlorinated ethylenes] for cis-DCE, TCE,

![Scheme 3](image-url) Structures of various redox states of FMN, FMNH⁺, and FMNH₂. (Taken with permission from Ciptadjaya et al. [152]. Copyright © American Chemical Society.)
and PCE. The results were compared with the reduction rate constants obtained from FMNH₂ in methanol solution (in the absence of TiO₂) (Table 3). Data showed that the reduction rate constants obtained when FMNH₂ anchored to TiO₂ was used as the catalysts were an order of magnitude higher than when FMNH₂ was used in solution. This increased reactivity was attributed to shifts in the FMN/FMNH₂ formal reduction potentials (E₀') when FMN was anchored onto the TiO₂ surface relative to FMN in fluid solution. Thus, FMN bound to TiO₂ was always a stronger reductant than FMN in fluid solution.

Enhanced reactivity of FMNH₂ was investigated by combining its reactivity with that of the TiO₂ conduction band electrons [TiO₂(e⁻ CB)]. The multiple electrons from FMNH₂ as well as the TiO₂(e⁻ CB) were modulated to react with chlorinated ethylenes. In MeOH solution, TiO₂ band gap excitation resulted in the reduction of FMN to FMNH₂ while electrons were trapped in the TiO₂ conduction band. Addition of excess cis-DCE, TCE, or PCE to FMNH₂/TiO₂ e⁻ CB resulted in the loss of trapped electrons accompanied by the oxidation of FMNH₂ to FMN (Figure 17). Reduction rate constants abstracted using the relationship lnA=ln(A₀)-kt showed that the presence of TiO₂ conduction band electrons increased the rate constants by two orders of magnitude relative to FMNH₂ in solution and by one order of magnitude relative to FMNH₂ anchored to TiO₂ (in the absence of conduction band electrons). The enhanced reactivity of FMNH₂ in the presence TiO₂(e⁻ CB) was attributed to influence of the TiO₂(e⁻ CB) on the FMNH₂⁻, which enhances reactivity toward chlorinated ethylenes.

The degradation of chlorinated ethylenes by FMNH₂/TiO₂ (e⁻ CB) was monitored using GC/MS by analyzing the loss in cis-DCE, TCE, or PCE concentration. Figure 17B shows a plot of the decrease in corresponding chlorinated ethylene concentration (% m) over time. GC/MS analysis of the reaction solution showed consistent decrease in chlorinated ethylene concentration; however, there was no evidence for the formation of any products in the liquid phase. Halogenated intermediates, such as cis- or trans-DCE (which are typical products formed when zero-valent iron is used to reduce TCE or PCE), in this case were not detected during the course of TCE or PCE degradation. This prompted head-space analysis, which showed the presence of a mixture of gases including

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Pseudo-first-order rate constants (k, M⁻¹ s⁻¹) of cis-DCE, TCE, and PCE reduction by TiO₂(e⁻ CB), FMNH⁺, FMNH₂⁻, FMNH₂/TiO₂ in water, and FMNH₂/TiO₂(e⁻ CB) in methanol (data collected at room temperature at multiple error trials).</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂(e⁻ CB)</td>
<td>FMNH⁺</td>
</tr>
<tr>
<td>cis-DCE</td>
<td>No reaction</td>
</tr>
<tr>
<td>TCE</td>
<td>No reaction</td>
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<tr>
<td>PCE</td>
<td>No reaction</td>
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Figure 15 SEM image of nanocrystalline TiO₂ particles. Particle diameter is an average of 12 nm (scale bar=100 nm). (Taken with permission from Ciptadjaya et al. [152]. Copyright © American Chemical Society.)

Figure 16 UV-visible absorbance spectra of FMNH₂/TiO₂ in aqueous solution (left y-axis): (A) before irradiation, (B) after irradiation, and (C) after addition of TCE in the dark. Fluorescence spectra of FMNH₂/TiO₂ in aqueous solution and its reactivity toward TCE (right y-axis): (D) before irradiation, (E) after irradiation, and (F) after addition of TCE in the dark. (Taken with permission from Ciptadjaya et al. [152]. Copyright © American Chemical Society.)
compounds using reduction pathways. Significant efforts have been devoted toward establishing procedures to produce well-defined nanoscale particles. These particles have been demonstrated to have significant potential in various applications including biological, medical, optical, magnetic, catalytic, and environmental applications. Metallic and bimetallic nanoparticles have emerged as viable materials for degrading aliphatic and aromatic halogenated compounds, with bimetallic systems showing a clear advantage over their monometallic counterparts. The degradation pathway has primarily involved electron transfer pathways leading to dehalogenated by-products. Relative to most techniques, for example, photocatalytic pathways for dehalogenation, the use of metallic or bimetallic pathways is considered to be milder because the use of UV irradiation and formation of highly reactive radicals is avoided.

The functionalization of nanoscale materials with molecular catalysts also offers several advantages toward the dehalogenation of organohalides. The development of MET systems is a field that will lead to exciting opportunities beyond degrada- tion of pollutants but could render itself useful in other field such as water splitting and solar to chemical energy conver- sion. Establishing a firm understanding of the mechanisms of electron transfer in such new systems will certainly lead to advanced in nanoscale science and sustainability.

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References


5. Summary

This review has focused on the advanced made by nanoscale materials on the degradation of toxic halogenated organic ethylene. The lack of formation of cis-DCE or trans-DCE when TCE and PCE are reacted with FMNH₂ is in agreement with that of other catalysts that have been used for TCE and PCE dechlorination via a two-electron transfer reduction pathway. Furthermore, the results show that FMNH₂ is an effective catalyst for the degradation of chlorinated ethylenes, and its reactivity can be controlled by immobilizing it on semiconductor surfaces. Current studies in our group are focused on elucidating the products formed during each reaction, which will enable a clearer elucidation on the mechanism of two-electron reduction of chlorinated ethylenes by similar biologically relevant molecules.


Ali Bolandi received his BS degree in Applied Chemistry from Sharif University of Technology in Tehran-Iran. He joined Western Michigan University in 2010 as a PhD candidate. His current research interests focus on controlled synthesis of well-defined nanoscale materials and investigation of their role in multi-electron transfer reactions.

Setare Tahmasebi Nick was born in Tehran, Iran. She obtained her BS degree in Chemistry from Sharif University of Technology in 2007. She is currently a PhD student in Chemistry working under the supervision of Dr. Sherine Obare at Western Michigan University. Her research focuses on the design and synthesis of well-defined metallic nanoparticles, developing an understanding of the environmental safety, and biocompatibility with biological cells.

Dr. Sherine Obare is currently an Associate Professor of Inorganic Chemistry at Western Michigan University. She received her BS degree in Chemistry from West Virginia State University in 1998. She then obtained a PhD in Chemistry from the University of South Carolina in 2002 with Prof. Catherine J. Murphy. Thereafter, she joined Prof. Gerald J. Meyer’s research laboratory at the Johns Hopkins University as a Dreyfus Postdoctoral Fellow. In 2004, Dr. Obare joined Western Michigan University as an assistant professor and was promoted early to the rank of associate professor with tenure in 2009. Her research interests lie in the area of designing nanoscale materials with unique physical properties and exploiting these properties toward environmental remediation, improved health care, and alternative energy. Her work has been featured in over 100 publications in the form of journal articles, review articles, book chapters, and conference presentations. Dr. Obare’s work has received over 1000 citations.

Dr. Obare is the recipient of the 2009 George Washington Carver Teaching Excellence Award, the 2009 International Union of Pure and Applied Chemistry (IUPAC) Young Observer Award, the National Science Foundation CAREER award, and the 2010. Dr. Obare is an associate editor for the Journal of Nanomaterials. In 2010, she was awarded the NSF American Competitiveness and Innovation (ACI) Fellowship. She currently serves on the Executive Committee for the National Organization for the Professional Development of Black Chemists and Chemical Engineers (NOBCChE).