Green Remediation of Hexavalent Chromium Using Naturally Derived Flavonoids and Engineered Nanoparticles

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29.1 Introduction

Contaminated ground- and surface water supplies such as the municipalities, wells, lakes, and rivers exhibit various levels of contamination that can pose numerous health risks. The release of contaminants into the environment can occur during production, use, and disposal of chemicals, thereby leading to potential contamination of water supplies. Among the numerous sources of pollution is...
treated wastewater, which is reinjected into groundwater aquifers for indirect reuse. In order to reach drinking water quality standards, surface water typically requires both filtration and disinfection because of its exposure to the environment and the higher potential for contamination. Industry and municipalities use about 10% of the globally accessible runoff and generate a stream of wastewater that flows or seeps into rivers, lakes, groundwater, or the coastal seas [1]. These wastewaters contain numerous chemical compounds in varying concentrations. About 300 million tons of synthetic compounds used in industrial and consumer products partially find their way into natural waters. Additional pollution comes from diffuse sources such as agriculture, where 140 million tons of fertilizers and several million tons of pesticides are applied each year [2]. The input of 0.4 million tons of oil and gasoline components through accidental spills represents yet another important source of water pollution. Other notable sources of contamination include the intrusion of salty water into groundwater due to over-exploitation of aquifers, the human-driven mobilization of naturally occurring geogenic toxic chemicals, including heavy metals and metalloids, and the biological production of toxins and malodorous compounds.

Groundwater is normally considered to be the purest source of water because it is naturally filtered as it passes through the layers of rock and sediments in an aquifer. However, the geology of the rocks in the aquifer may have a major impact on the quality of the groundwater and quite often, the technology required to remove these contaminants can be more complicated and expensive than surface water treatments. As a result of extensive regulations, guidelines, and water quality testing, drinking water supplies in the United States are among the cleanest and safest in the world, yet despite efforts to standardize the cleanliness and quality of drinking water nationwide, the quality of water served by individual systems varies over time due to changes in the water source from which it is drawn and the treatment it undergoes. To date, an effective and sustainable global strategy against this insidious and mostly unseen contamination of aquatic environments barely exists. Source controls and technical systems, such as wastewater treatment plants, only function as partial barriers, but major challenges remain. The source, behavior, and treatment of the relatively small number of pollutants [3], such as acids, salts, nutrients, and natural organic matter, occurring at μg/L to mg/L concentrations are relatively well understood. However, high nutrient loads can lead to increased primary production, oxygen depletion, and toxic algal blooms. In such cases, the challenges are to predict ecosystem responses, to optimize treatment technologies, and to develop integrated policies at the scale of river basins [4].

The effects of the thousands of synthetic and natural trace contaminants on the aquatic environment are difficult to assess at low to very low concentrations (pg/L to ng/L) [5]. These chemicals are ubiquitous in natural waters, not only in industrialized areas but in more remote environments as well. Some chemicals such as heavy metals are not degraded at all, while others such as persistent organic compounds (e.g., DDT, lindane, or polychlorinated biphenyls) are
degraded only very slowly. These can therefore be transported via water or air to locations hundreds or even thousands of miles away from their source [6,7]. Some compounds that are less persistent and not prone to long-range transport may still be of concern if they are continuously emitted or form problematic (bio) transformation products [8]. Examples of this category include hormones and drugs, or persistent degradation products of surfactants such as nonylphenol. Therefore, assessing the impact of micropollutants in aquatic systems is a formidable task requiring improved analytical and modeling tools to probe the distribution, bioavailability, and biological effects of single compounds and/or chemical mixtures. Thus methods to classify existing and new chemicals on the basis of their potentials on human health and the environment must be continually refined. Moreover, mitigation technologies to reduce the impact of micropollutants as well as strategies to minimize their introduction into the environment require further development.

In the past 10 years, emerging technologies such as phytoremediation, bioremediation, and permeable reactive barriers have become popular new tools. These novel treatments have begun to compete with more established technologies such as solidification/stabilization, soil vapor extraction, and thermal desorption for soil, and pump and treat systems for groundwater remediation [9]. At the very forefront of these emerging technologies lies the development of nanotechnology. Currently a wide variety of potential remedial tools employing nanotechnology are being examined at the bench scale for use in wastewater and soil remediation. One emerging nanotechnology, nanosized zerovalent iron (ZVI) and its derivatives, has reached the commercial market for field-scale remediation and studies. One of the emerging compounds of concern is chromium. Chromium usually occurs in its compounds in the form of chromium (VI) or chromium (III), which are the most stable and common oxidation states of chromium. Compounds of chromium (VI) and chromium (III) have different solubilities and toxicities [10]. Chromium (III) is essential to animals and human beings. It is recommended that a daily uptake of 50–100 µg is helpful for human beings, without toxic effects observed even at a higher dosage [11]. In contrast, chromium (VI) has been proven to be highly toxic, and some chromates are considered as carcinogens [12]. Unfortunately, a large amount of chromium (VI)-containing wastes arise every day from tanning, electroplating, wood preservation, dying, and production of chromium chemicals. Therefore, many countries have adopted severe restrictions on disposals of those industrial wastes. Quite a few methods for the removal of chromium (VI) have been studied, such as biosorption, ion exchange, solvent extraction, nanofiltration, micelle-enhanced ultrafiltration, adsorption with inorganic sorbent materials, reduction, and precipitation [13].

We have developed new treatment approaches based on catalytic reduction of Cr(VI) to the benign form \{(Cr(III))\} using palladium nanoparticles (PdNPs). This chapter examines the most current information regarding metal contamination and the in situ remediation of chromium. This work focuses on the use of PdNPs for the catalytic conversion of Cr(VI) to Cr(III) using formic acid (FA) and sulfur.
Subsequent practical application in aqueous samples indicates a complete elimination of Cr(VI). Finally, this chapter also discusses the use of naturally occurring flavonoids as reducing agents for Cr(VI).

### 29.2 Nanotechnologies for site remediation and wastewater treatment

The development and implementation of water treatment technologies have been mostly driven by three primary factors: the discovery of new rare contaminants, the promulgation of new water quality standards, and cost [14]. For the first 75 years of this century, chemical clarification, granular media filtration, and chlorination were virtually the only treatment, processes used in municipal water treatment [15]. However, the past 20 years have seen a dramatic change in the water industry’s approach to water treatment, in which water utilities have started to seriously consider alternative treatment technologies to the traditional filtration/chlorination treatment approach. Regardless of the water treatment technology employed to clean drinking water, most water systems add chlorine or other disinfectants to ensure water remains clean within the water distribution system. Disinfection of drinking water supplies was an important advance in public health and a major accomplishment of the twentieth century. The Safe Drinking Water Act (SDWA) directs the US EPA to establish national standards for contaminants in public drinking water supplies. Enforceable standards are to be set at concentrations at which no adverse health effects in humans are expected to occur and for which there are adequate margins of safety achievable with the use of the best technology available.

Nanotechnology, the science and art of manipulating matter at the atomic and molecular level, has the potential to substantially enhance environmental quality and sustainability through pollution prevention, treatment, and remediation. The nanotechnology industry is increasingly promoting nano as a “green” technology that will improve the environmental performance of existing industries, reduce consumption of resources and energy, and allow achievement of environmentally benign economic expansion. Cost-effective remediation techniques pose a major challenge for the EPA in the development of adequate hazard removal techniques that protect the public and safeguard the environment. The EPA supports research into new remediation approaches that are more productive and cost-effective in removing contamination than currently available techniques [16].

Metallic substances of significant concern in remediation of soils, sediment, and groundwater are arsenic, chromium, mercury, lead, and cadmium. Nanotechnology offers the possibility of more effective remediation due to the higher surface-to-volume ratios of nanomaterials, and the possibility of novel collection and separation protocols due to the unique physical properties of nanomaterials is feasible. Specific control and design of materials at the molecular level
may impart increased affinity, capacity, and selectivity for pollutants, thereby reducing releases of such hazardous materials to the air and water, providing safe drinking water, and minimizing quantities and exposure to hazardous materials.

### 29.2.1 Bimetallic nanoparticles remediation approach

Bimetallic particles are those particles on which a thin layer of catalytic metal (e.g., Pd, Pt, which are not active in themselves) is doped onto the surface of the active (reducing) metal, Fe or Zn, as shown in Figure 29.1. Physically mixing the two metals does not increase the rate of reaction; the palladium must be doped onto the surface [9]. Doping palladium on the surface sets up a galvanic couple, which increases the rate of corrosion of the iron and hence increases the rate of oxidation and reduction. Palladium and nickel have also been found to significantly enhance the dechlorination of polychloroethylene (PCE) in a zerovalent silicon/water system [8]. Another advantage of these bimetallic particles is that they can add stability, as ZVI particles lose reactivity within a few days while Fe/Pd particles remain active for at least 2 weeks. This is regardless of the fact that the galvanic couple increases the iron corrosion rate during oxidation and reduction reactions. Doping the zinc surface with palladium can also prevent passivation occurring [9].

Bimetallic catalysts [17] are especially interesting for several reasons: combining two metals may provide control over the catalytic activity, selectivity, and
stability, and some combinations may exhibit synergistic effects [18]. Moreover, by controlling the type of cluster synthesized, one can improve the “catalyst atom economy” [19]. The control of homogeneity, dispersion, and alloying extent has a profound influence on the surface properties which affect the catalytic activity and stability of the bimetallic NPs. The alloying extent in bimetallic NPs causes changes in atomic distribution in bimetallic NPs which has a strong influence on physicochemical properties of NPs [20]. Theory of nanoparticle catalysis, electrocatalysis, and modeling of these reactions involving simulations of the reaction kinetics on nm-supported catalyst particles based on electronic structure and chemisorption properties of supported metal clusters have been studied [19]. Particle size, support, and effects of electrochemical and chemical promotion on metal films and nanoparticles have been exploited for the design of novel nanostructured material based on transition metal compounds for electrocatalysis.

Palladium-mediated redox reactions are not new and pure Pd clusters have been shown to give lower catalytic activities (44%) compared to the alloy Ni—Pd (63%), showing Pd cluster to be less active than the Ni—Pd core—shell clusters. As all these catalysts contain the same amount of palladium, this indicates that the core—shell structure results in more Pd atoms on the surface. The total coordination number around Ni atoms in bimetallic clusters is usually higher than that around Pd [20], suggesting that the Pd atoms are located preferentially on the surface. The tendency of Pd to go to the surface may explain the difference in activity between the Pd clusters and the alloy Ni—Pd clusters noting that no reaction takes place when the Ni clusters or Ni(II) alone are used. Therefore, it is likely that only Pd is responsible for the catalysis in the case of the alloy and the core—shell clusters. The most important finding is that by combining palladium with another non-reactive metal (in this case Ni), we can increase the activity per Pd atom (segregated Pd clusters < alloy Ni—Pd clusters < core—shell Ni—Pd clusters).

Environmental applications of zerovalent metals (ZVMs) also overlap with the burgeoning field of nanotechnology. However, use of zerovalent single metals to reduce chlorinated organics has some drawbacks [21]. For example, even when nanoscaled ZVI particles are used, the metal mass normalized observed rate constant for dechlorination of TCE is still very low, in the order of $10^{-2}$ L/g h [21]. More important is that a hydroxide or oxide layer will form on the particle surface during the reaction or upon contact of the nanoparticles with air, significantly reducing their reactivity and decreasing the effective use of the metal particles. Efforts to improve the ZVM technique have led to the use of Ni/Fe and Pd/Fe particles to dechlorinate chlorinated organics [19]. Reports show that physical addition of Pd$^0$ or Ni$^0$ micron-sized powder could reactivate Fe$^0$ particles that have lost their surface activity [19]. It has been reported that the reduction of chlorinated organics by bimetallic particles happens via hydrodechlorination instead of electron transfer, in which Fe or Zn acts as the reducing agent, and Ni or Pd acts as a catalyst.
Figure 29.2 shows the applicability of this approach in FA reduction of hexavalent chromium. The latter are good hydrogenation catalysts and have a high ability to dissociate $H_2$ \cite{21}. The introduction of a second metal not only increases the reactivity and reduces the accumulation of toxic by-products, but has been reported to make the particles more stable in air by inhibiting the oxidation in some cases \cite{21}.

### 29.2.2 Remediation of chromium using nanotechnology

Chromium (VI) is one of the major industrial contaminants in groundwater and a known human carcinogen. Hexavalent chromium (Cr(VI)) is believed to be the third most common pollutant at hazardous waste sites as well as the second most common inorganic contaminant after lead \cite{4}. The chromate can readily cross cell membranes and be converted into reactive Cr(IV) and Cr(V) as well as stable Cr(III)–DNA adducts, causing mutation and cancer \cite{5}. Thus, site remediation is often needed to reduce the risks it poses to humans and the ecosystem. Consequently, the reduction of Cr(VI) to Cr(III) in both aqueous and natural soil media is a prerequisite step in the eradication of environmental hazards associated with high levels of Cr(VI).

We report the feasibility of using Pd nanoparticles as innovative catalysts in the conversion of reducible contaminants from toxic to benign forms. Cr(VI) is a known carcinogen while the trivalent chromium salts are believed to be non-toxic. The ability of Pd nanoparticles to catalyze the rapid reduction of Cr(VI) to Cr(III) using reactive sulfur intermediates produced \textit{in situ} has been demonstrated \cite{22}. We used a microchamber set at 130°C as shown in Figure 29.3A and the
FIGURE 29.3
(A) Schematics of a nanoreactor designed for Cr(VI) remediation into Cr(III) using composite in the presence of Pd nanoparticles; (B) design and application of a nanoreactor designed for remediation of Cr(VI) into Cr(III) using FA in the presence of Pd nanoparticles.
reduction mixture consisted of PdNPs and sulfur (PdNPs/S), which generated highly reducing sulfur intermediates that effected the reduction of Cr(VI) to Cr(III). UV/visible spectroscopy and cyclic voltammetry were employed to monitor the reduction process. The results showed that 99.8% of 400 mM Cr(VI) was reduced to Cr(III) by PdNPs/S in 1 h compared to 2.1% by a control experiment consisting of sulfur only. The rate of Cr(VI) reduction was found to be dependent on temperature and pH and was greatly enhanced by the addition of PdNPs. Subsequent application of this approach in the reduction of Cr(VI) in soil and aqueous media was conducted. In contrast to the control experiments with and without PdNPs or sulfur, >92% conversion rate was obtained in the presence of PdNPs/S within 1 h. This represents over a 500-fold improvement in conversion rate compared to current microbial approaches. XPS analysis provided the confirmation regarding the oxidation states of Cr(VI).

### 29.2.3 Determination of Cr(VI) concentration

In order to determine the extent of the catalytic reduction of Cr(VI) due to PdNPs at a fixed temperature, three different experimental setups were used. These include (i) a buffered Cr(VI) solution involving neither the FA nor the PdNPs as controls; (ii) a buffered reaction mixture consisting of Cr(VI) and FA; and (iii) a buffered reaction mixture containing Cr(VI), FA, and PdNPs. For each experiment, the reaction mixture contained 5.0 mL of a 10.0 mM Cr(VI), 220 µL FA, 1.68 mL of 0.5 M buffer (acetate buffer pH 2.0), and 100 µL of colloidal PdNPs. The temperature of the 7.0 mL cocktail reaction mixture was raised to 45°C and the temperature maintained for a period of 5 min or more. Samples were periodically withdrawn from the reaction vessel and transferred immediately into an ice bath at 4°C to minimize any further reactions during the 3 min time lapse. Samples were then passed through a 0.2 µm membrane filter before carrying out spectrophotometric analysis on the filtrate. The residual Cr(VI) concentrations were determined after appropriate dilution of the resulting mixtures. The rate of change in Cr(VI) was determined as the difference in the initial and final Cr(VI) concentrations over time expressed as a percentage. To ascertain negligible Cr(VI) reduction at 4°C, tests were performed on possible Cr(VI) reduction at that same temperature for a period of 30 min.

Sadik and coworkers [23] further designed a nanoreactor shown in Figure 29.3B. The reactor employed colloidal Pd nanoparticles catalyst for the reduction of Cr(VI) to Cr(III) using FA as the reducing agent. The reaction kinetics of Cr(VI) reduction and the effects of other parameters such as the temperature, the FA concentration, the pH, Pd loading, and elemental hydrogen were studied. Based on the experimental results, this approach has shown that colloidal PdNPs enhanced the reduction rate Cr(VI) to Cr(III). The reduction of Cr(VI) to Cr(III) was dependent on temperature, pH, the amount of PdNPs, and FA concentration with optimum reduction at 45°C and over 99% reduction at low pH values.
29.2.4 **Removal of Cr(VI) from complex aqueous media**

We have tested the use of PdNPs/S mixture in the removal of Cr(VI) to Cr(III) in a complex aqueous media containing 400, 500, 800, and 1000 µM of Cr(VI). To achieve this, we mimicked the mineral composition of the natural environment by using m9k buffer. Figure 29.4 shows the results obtained. PdNPs/S reduced 400 µM of Cr(VI) at a rate of 99.8(±0.2)% per hour compared with 2.1(±0.9)% per hour and 65.22(±3.3)% per hour by respective controls of sulfur only and PdNPs only. It is believed the drop in the residual amount of Cr(VI) in the presence of PdNPs only was consistent with the adsorption of Cr₂O₃ onto Pd surfaces and the probable retention of Cr(VI) by sample matrices during the filtration process [24–28]. In the process, drops in residual amounts of Cr(VI) that depended on the initial Cr(VI) concentration were obtained (Figure 29.4). This represents over 500-fold improvement in conversion rate compared to current microbial approaches [25–29]. Table 29.1 gives the comparison of the nanoremediation approaches for Cr using microbial, Bio-Pd, FeNPs, and PdNP methods. Using Pd/NPs, 99.8% removal of Cr(VI) in 336 µM concentration was achieved within 5 min as opposed to ~90% removal from 100 µM using Bio-Pd method [30].

29.3 **Naturally occurring flavonoids as reducing agents for hexavalent chromium**

Currently the demand for a safe and cleaner environment is the concern of scientists. Consequently the reduction of heavy metals from the ecosystem is one of the
most important research activities being pursued by most research groups, in order to find better ways to remove heavy metals from the environment. However, the use of green approach, particularly naturally occurring flavonoids, to reduce the levels of heavy metals is still rare. The overall goal of this section was to reduce toxic hexavalent chromium to its trivalent state using naturally occurring flavonoid, namely quercetin (QCR) and two of its derivatives (quercetin pentaphosphate (QPP) and quercetin sulfonic acid (QSA)). The specific objectives were to eliminate the use of organic solvents and to minimize the overall reaction time using PdNPs. These objectives were successfully achieved as highlighted below and a comparative study with previous studies from our laboratory was therefore carried out.

Flavonoids are a subclass of the polyphenols, which are characterized as containing two or more aromatic rings, each bearing at least one aromatic hydroxyl and connected with a carbon bridge [31,32]. For flavonoids, this bridge consists of three carbons that combine with an oxygen and two carbons of one of the aromatic rings (A ring) to form a third 6-member ring (C ring) (Figure 29.5). The flavonoids are further divided into subclasses based on the connection of the B ring to the C ring, as well as the oxidation state and functional groups of the C ring. Individual flavonoids are identified and characterized by hydroxylation and conjugation patterns of the B ring, as well as the conjugation patterns of hydroxyls on the A and C rings.
A number of these polyphenols have shown interesting biological activities [33] and lately, modification for applications in environmental remediation [34]. However, this class of compounds utility has been hampered by solubility difficulties.

Our group has been actively involved in the synthesis and characterization of flavonoid derivatives and reported the very first evidence of the removal of Cr (VI) from the environment using naturally derived flavonoids [35]. In this study, QCR and two successfully synthesized QCR derivatives named as QPP and QSA were used to reduce Cr(VI) from the environment. The derivatives were characterized using UV–vis spectroscopy, $^1$H NMR, $^{13}$C NMR, $^{31}$P NMR, and LC–MS techniques. The solubility study conducted on QPP found its solubility to be 840 mg/mL. Furthermore the solutions of QPP and QSA were found to be stable for more than 1 year at 0–4°C and the lifetime could be extended by storing at −20°C. The application of QCR and its derivatives (QPP and QSA) to remove Cr(VI) was very successful, with the results showing that QCR had a higher reduction efficiency of 99.8% (30 min), closely followed by QPP/PdNPs mixture at 96.5% (60 min), and then finally QSA/PdNPs mixtures at 91.7%. This highest reduction of QCR could be due to its higher hydrophobicity compared to QPP and QSA hence depicts stronger affinity for Cr(III).

The study revealed that PdNPs catalyst increased the reduction efficiency of chromium (VI) by ~36.5% while a change in operating temperature from 25°C to 45°C improved the efficiency by ~46.8%. The reduction results were validated in environmental (Binghamton University (BU)) and standard reference material (buffalo river sediments (BRS)) soil samples. The results indicated that the analysis could be completed within 1 h. However, the efficiency was found to be higher in BU soil than in BRS soil by 16.1%. It was found that QPP recorded the highest % atom economy of 94.6% and hence indicated higher enhanced performance compared to bioremediation approach which requires several months to achieve ~90% reduction efficiency [35]. The study clearly demonstrated that Quercetin, the water-soluble QPP and QSA, provides a green approach for the reduction of chromium (VI) from the environment.

We have shown that the presence of PdNPs in the reaction media showed remarkable enhancement in the conversion of Cr(VI) to Cr(III) in all the cases studied. FA/PdNPs composite registered the lowest reaction time of 5 min with an overall efficiency of 99.8%. Derivatization of QCR tremendously improved its solubility. It was also observed that reduction of Cr(VI) was pH dependent with higher reduction efficiencies observed at pH<3. QCR registered the highest % efficiency in both soil and water samples (95.6% BU soil) followed by QPP (90.5%) and finally QSA (89.1%). The overall reduction efficiency of QPP and QSA in the presence of PdNPs at 45°C in water samples over a period of 1 h was found to be 96.5% and 91.2%, respectively. Over 98% efficiency was achieved for QCR water samples. All the reactions followed a first-order kinetics with respect to Cr(VI).
29.4 Conclusions

We have reviewed the use of nanoparticles for the remediation of environmental contaminants such as chlorinated organic solvents, trichloroethylene, heavy metals, and others. Nanomaterials offer the possibility of more effective remediation due to their higher surface-to-volume ratios and the possibility of novel collection and separation protocols. This chapter has focused on in situ remediation of inorganic contaminants, specifically chromium. The removal of 99.8% Cr(VI) from complex aqueous media using Pd/NPs was achieved within minutes as opposed to ~90% removal using Bio-Pd method. This chapter also discusses the use of naturally occurring flavonoids as reducing agents for Cr(VI). However, it should be noted that despite the short reaction time reported for PAA and FA reductants (Table 29.2), the use of flavonoids presents greener chemistry involving naturally occurring flavonoids, and further supports the importance of consuming flavonoids such as QCR and its derivatives to successfully reduce Cr(VI) to benign Cr(III) in acidic medium of human digestive system and the environment. The temperature at which the reduction was achieved also compares well with most of the other methods in Table 29.2, apart from sulfur which required very high temperatures of about 130°C.

<table>
<thead>
<tr>
<th></th>
<th>[Cr(VI)] (mM)</th>
<th>Time (min)</th>
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<th>Overall Efficiency (%)</th>
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<tr>
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<td>5, Temp 45°C</td>
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<tr>
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