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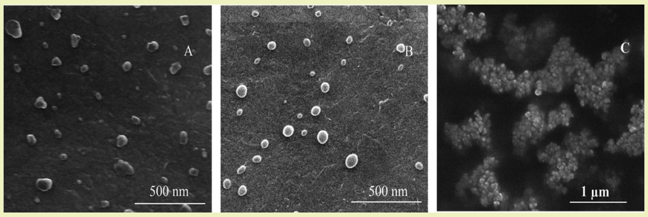
Characterization of Iron−Polyphenol Nanoparticles Synthesized by Three Plant Extracts and Their Fenton Oxidation of Azo Dye

Zhiqiang Wang,*[†,‡] Cheng Fang,[†,‡] and Mallavarapu Megharaj[†,‡]

[†]Centre for Environmental Risk Assessment and Remediation, University of South Australia, Mawson Lakes SA 5095, Australia
[‡]Cooperative Research Centre for Contamination Assessment and Remediation of Environments, Mawson Lakes SA 5095, Australia

ABSTRACT: In this paper, iron−polyphenol nanoparticles (Fe−P NPs) were synthesized using the extracts obtained from Australian native plant leaves, these being *Eucalyptus tereticornis, Melaleuca nesophila*, and *Rosemarinus officinalis*. The Fe−P NPs synthesized from the extracts were characterized using scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The results show that the reaction between iron ions and polyphenols can form complex nanoparticles with sizes ranging from 50 to 80 nm, the surface of which presents organic characters. The synthesized nanoparticles were then utilized as a Fenton-like catalyst for decolorization of acid black 194 in solution. The batch experiments showed that 100% of acid black was decolorized, and over 87% total organic carbon (TOC) was removed. In addition, removal of acid black 194 fitted well to the pseudo-first-order model. Compared with the conventional Fenton reaction, the Fenton-like reaction with Fe−P NPs takes place more sustained and carefully within 200 min. Furthermore, it does not need to adjust pH for the reaction.



KEYWORDS: *Green synthesis, Iron complex nanoparticles, Plant extracts, Acid black 194, Fenton-like catalyst*

INTRODUCTION

In recent years, iron-based nanoparticles have attracted much interest in contaminated land and groundwater remediation due to their large surface-to-volume ratio.[1] Extensive studies have demonstrated that nano-zero-valent iron (nZVI) particles are effective in degrading many common environmental contaminants such as chlorinated organic compounds, including perchloroethene (PCE), trichloroethene (TCE), carbon tetrachloride (CT), nitrate, TNT, royal demolition explosive, and pesticides (lindane), as well as heavy metals such as Pb(II) and Cr(VI) in groundwater.[2] Field tests have shown much promise concerning in situ remediation,[3] where the nZVI particles can remain in suspension for extended periods of time to establish an in situ treatment zone. Furthermore, it is demonstrated that both As(III) and As(V) exhibit strong adsorption onto iron oxide nanocrystalline surfaces.[4] Various chemical and physical methods have been developed for the synthesis of iron-based nanoparticles and the modification of their surface properties.[2] The physical and chemical methods employ toxic chemicals as reducing agents, organic solvents, or nonbiodegradable stabilizing agents and are therefore potentially dangerous to the environment and biological systems. In addition, most of these methods require complex controls or nonstandard conditions making them quite expensive.

In our previous study,[5] novel green iron−polyphenol complex nanoparticles have been synthesized by eucalyptus leaves. Through X−ray absorption spectroscopy (XAS) analysis, it was found that the Fe−P NPs are amorphous materials with a ferric ion located in nanoparticles chelated by plant polyphenols. The Fe−P NPs structure has been proposed as shown in Figure 1. In order to understand the properties of this type of material in more detail, three extracts from Australian native plants, *Eucalyptus tereticornis* (A), *Melaleuca nesophila* (B), and *Rosemarinus officinalis* (C), were used to synthesis iron nanoparticles in this study. The Fe−P NPs were characterized using SEM, EDX, XRD, and FTIR for understanding the difference in the morphology, as well as the reactivity of synthesized iron-based nanoparticles using various plant extracts. To determine whether they can be used for the oxidation of organic contaminants, azo dye acid black 194 was

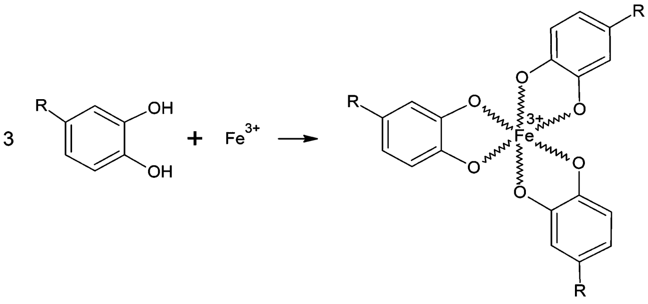


Figure 1. Proposed chemical structure of Fe−P NPs. R groups are typically H, OH, galloyl esters, or carbohydrate groups, depending on the compound.[5]

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selected as a model compound. It is one of the most popular in leather, polyamide, silk and wool blended fabric dyeing, direct printing in wool, silk fabric fiber, and nylon nonwoven microfabric dyeing.[6]

■ EXPERIMENTAL SECTION

Biosynthesis of Fe−P NPs. The synthesis method is the same as our previous study.[5] The plant leaves extract was prepared by heating 100 g of plants leaves added to 500 mLof Milli-Q water (trademark for ultrapure water) at 80 °C for 1 h. After settling for 1 h, the extract was vacuum-filtered. A solution of 0.10 M $FeCl_3$ was prepared by adding 16.23 g of $FeCl_3$ in 1.0 L of Milli-Q water, and subsequently, 0.1 M $FeCl_3$ solution was added to the leaves extracts in a 2:1 ratio. The formation of Fe−P NPs was marked by the appearance of iron black precipitate, and the Fe−P NPs were separated by centrifuging at 7000 rpm. The powders of Fe−P NPs were frozen at −20 °C and then were dried in a freeze-dryer at −45 °C with the pressure at 10 Pa for 24 h.

Characterizations and Measurements. Morphological characteristics were analyzed using scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) using FEI Instruments Quanta-450-FEG. Localized Fe−P NPs elemental information from the chosen region was obtained via EDS in conjunction with SEM.

XRD patterns of Fe−P NPs samples synthesized from various plant extracts were obtained using a Philips PANalytical-Empyrean instrument. The source consisted of Cu Kα radiation (λ = 1.54 Å). Each sample was scanned within the 2θ range of 10−70 °.

The Agilent 660-IR was used to examine the functions groups on the surface of Fe−P NPs. Samples for FTIR measurement were prepared by mixing a 1% (w/w) specimen with 100 mg of KBr powder and pressed into a sheer slice. An average of 32 scans was collected for each measurement with a resolution of 2 cm^{-1}.

A Shimadzu TOC-LCSH total organic carbon (TOC) analyzer was used to measure TOC during the degradation reaction.

Fenton-Like Oxidation of Acid Black 194. All the chemicals used in this study were analytical reagent grade and used without further purification. A solution containing100 mg L^{-1} acid black 194 (Sigma-Aldrich) was prepared by dissolving 100 mg of acid black 194 in 1 L of Milli-Q water. A 10.0% H_2O_2 solution (v/v) was prepared from a stock 30.0% H_2O_2 solution (Sigma-Aldrich) by dilution with Milli-Q water.

All the degradation experiments were carried out using various Fe−P NPs synthesized by eucalyptus (A), melaleuca (B), and rosemary (C) with 110 μL added to 50 mL of acid black 194 solution at an initial concentration of 100 mg L^{-1} and 10 mL of 10% H_2O_2, respectively. This was done to compare their oxidation of acid black 194. Mixed solutions were left at their initial pH level and stirred at 200 rpm at room temperature to the desired time intervals. The concentration of acid black solution was measured using a Jasco V530 spectrophotometer at λ_{max} = 578 nm. The blank experiments were carried out with a H_2O_2 solution that did not contain Fe−P NPs to assess the oxidation capability of H_2O_2 in dye degradation. Then the removal rate of TOC was determined by Shimadzu TOC-LCSH.

■ RESULTS AND DISCUSSION

Characterization. The UV−vis spectra of Fe−P NPs colloid synthesized from plant extracts are shown in Figure 2. The continuous absorption in the visible range for these three Fe−P NPs solutions was observed where the spectra of A and B were obtained, but C proved to be different. The different absorption rates can be attributed to different components in the three plant leaves.[7] The peak at 300 nm in extract could constitute polyphenols.[8] Metal nanoparticles should have a surface plasmon resonance absorption in the UV−visible region.[9] In the spectra, no surface plasmon resonance absorption of iron metal nanoparticle has been observed; this indicated that formed iron nanoparticles have no metal properties on the particle surfaces due to polyphenols capping.

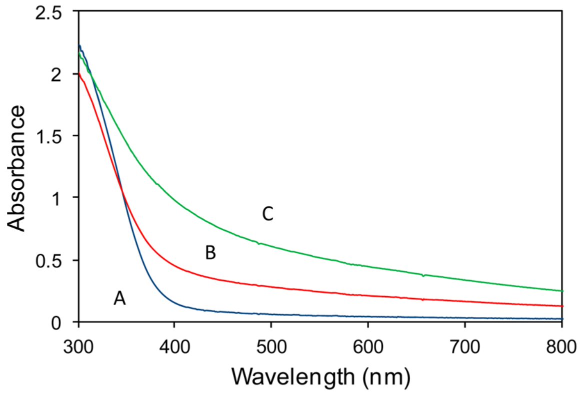

Figure 2. UV−vis spectra (absorbance vs wavelength) of Fe−P NPs colloid A, B, and C.

The plant extracts contain different kinds of polyphenols, and consequently, the resulting morphology and distribution of Fe−P NPs are also different. This was confirmed by the following SEM and EDS. SEM images of Fe−P NPs synthesized using plant extracts are shown in the abstract graphic. The SEM show that the Fe−P NPs A and B were well distributed and dispersed in colloid with spherical particles ranging from 40 to 60 nm. In contrast, Fe−P NPs C shows different structures, in which they were aggregated like grapes. This could be attributed to different components and concentrations of polyphenols in C plant extracts, which played key roles in dictating the final structures and size of the iron nanoparticles.[10] This is shown in Figure 2(C) where a different UV absorbance compared to Figure 2(A) and (B) is evident.

As shown in Figure 3, the elemental composition of Fe−P NPs synthesized using plant extracts was determined using EDS, where the EDS spectrum shows that Fe−P NPs are primarily composed of C, O, Cl, and Fe, where C and O are attributed to the polyphenols and other C-containing molecules in the plant extracts,[7,11] while Cl had originated from $FeCl_3$ precursor used in the synthesis of Fe−P NPs. The different C, O, Cl, and Fe contents in Fe−P NPs samples using the plant extracts were obtained, for example, 77.17% C, 21.63% O, 0.47% Cl, and 0.24% Fe using plant extract A; 36.19% C, 42.88% O, 9.62% Cl, and 8.58% Fe using plant extract B; and

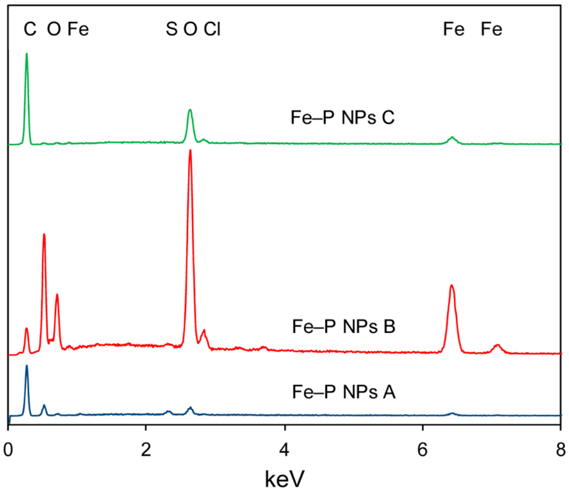

Figure 3. EDX spectrum of Fe−P NPs A, B, and C.

95.86% C, 2.2% O, 1.42% Cl, and 0.53% Fe using plant extract C. These values could be helpful in reflecting the elemental content on the surface and near surface regions of the NPs. This can explain why the surface of particles in the SEM images still looks cloudy even under adequate resolution conditions. These results can also explain why the iron nanoparticles have no metal properties on the particle surfaces. Additional elements like Na and Ca may correspond to impurities originating from the leaves.

The XRD patterns of Fe−P NPs samples synthesized by three plant extracts are shown in Figure 4. The patterns for the three Fe−P NPs samples lack distinct diffraction peaks, suggesting that the Fe−P NPs are amorphous. The broaden peaks at 20 and 28θ should be caused by organic matter.

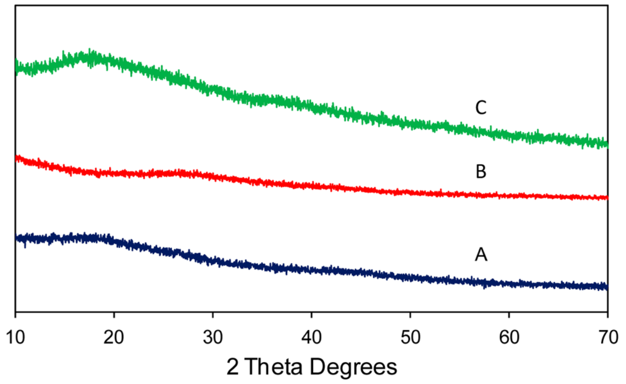

Figure 4. XRD spectra of Fe−P NPs A, B, and C.

Figure 5 shows the FTIR spectrum of the Fe−P NPs powder samples synthesized by three plant extracts, also revealing several peaks in the spectral range of 1000−3400 cm^{-1}. The peaks at 3344 cm^{-1} from Fe−P NPs (A), at 3369 cm^{-1} from Fe−P NPs (B), and at 3384 cm^{-1} from Fe−P NPs (C) are attributed to the O−H of H bond or carboxylic acid. The features around 2362 cm^{-1} obtained from plant extracts A and B presumably correspond to the O−H of carboxylic acids. The peak around 1609 cm^{-1} of these Fe−P NPs from the three extracts can relate to the C═C ring stretching in polyphenols. The peak at 1069 cm^{-1} Fe−P NPs synthesized by plant extract C is ascribed to the C═O of carboxylic acid, while the peaks around 1072 cm^{-1} from A and C could be attributed to the C−O of carboxylic acid. All of these indicated that the plant polyphenols should be the components in the powdered iron complexes nanoparticles, besides clinging on the surface of particles capping. This agrees with the proposed molecular structure.

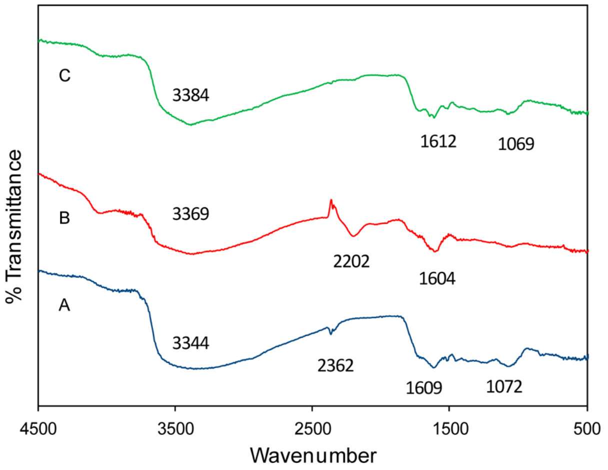

Figure 5. FTIR spectrum of Fe−P NPs of A, B, and C.

Fenton-Like Oxidation of Acid Black 194. To determine whether Fe−P NPs synthesized by the plant extracts in this study can be used as a heterogeneous Fenton-like catalyst for the degradation of azo dye, Fe−P NPs synthesized by the plant extracts have been evaluated, and acid black 194 was selected as a compound with 110 μL of Fe−P NPs added to 50 mL with an initial dye concentration of 50 mg L^{-1} and 10 mL H_2O_2. One hundred percent decolorization of acid black 194 was achieved after a Fenton reaction with the assistance of Fe−P NPs (A), Fe−P NPs (B), and Fe−P NPs (C) after reacting for 200 min, respectively. The removal process fitted well to the pseudo-first-order model (Figure 6). This indicates that azo dye such as acid black 194 can be oxidated by a Fenton reaction employing various synthesized Fe−P NPs using plant extracts. This is due to the fact that the oxidation is based on the action of the hydroxyl radical (OH•), which was generated in aqueous solution and resulted from a combination of Fe^{2+} and hydrogen peroxide, H_2O_2, as described below[12]

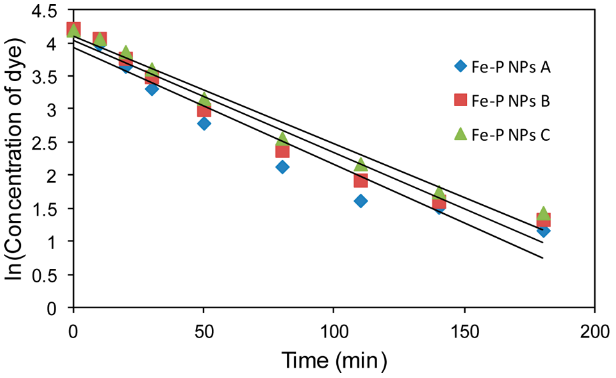

Figure 6. Degradation of dye with Fe−P NPs A, B, and C.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^- \quad (i)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH\bullet + H^+ \quad (ii)$$

In the case of azo dyes, the cleavage of the azo band (−N═N−) by OH• in the chromophore of the dye leads to decolorization of the dye solution.[8,13] High degradation efficiency was obtained using Fe−P NPs A. This can be attributed to good dispersibility of particles. Compared to Fe−P NPs A, less degradation of acid black 194 using both Fe−P NPs B and Fe−P NPs C was observed. This resulted from large-sized Fe−P NPs B and the aggregation of Fe−P NPs C according to the SEM images, leading to reduced activity of Fe−P NPs for Fenton oxidation. In regard to the minimization of acid black 194 using Fe−P NPs as a heterogeneous Fenton catalyst, it was found that over 87% of the TOC can be removed in four days. Compared with a conventional Fenton reaction, the Fenton-like reaction with Fe−P NPs takes place more sustained and carefully within 200 min. Furthermore, it does not need to adjust pH for the reaction, while optimum pH value should be around 3 in a conventional Fenton reaction.[12]

CONCLUSIONS

The synthesis and characterization of green Fe–P NPs using Australian native plant extracts from *Eucalyptus tereticornis*, *Melaleuca nesophila*, and *Rosemarinus officinalis* has been demonstrated. The reactions between an $FeCl_3$ solution and plant polyphenols can form chelated ferric-polyphenols nanoparticles, the surface of which shows organic characters. Different polyphenols in the three plants cause the differences in morphology of the Fe–P NPs. The synthesized Fe–P NPs as a heterogeneous Fenton catalyst to effectively degrade azo dye has been conducted, making them potentially useful for environmental remediation.

AUTHOR INFORMATION

Corresponding Author

*Fax: 61-08-83025037. E-mail: zhiqiang.wang@mymail.unisa.edu.au; dr.zqwang@gmail.com.

Notes

The authors declare no competing financial interest.

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