



# Green synthesis of Fe nanoparticles using *Citrus maxima* peels aqueous extracts



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## ABSTRACT

Fruit peels were discarded as inevitable wastes in the production of fruit juice which wasted our resources and caused pollution problems. In this paper, iron nanoparticles were synthesized using *Citrus maxima* peel extracts to reduce Fe(III) in aqueous solution. The nanoparticles were characterized by TEM, EDS, XPS, FTIR, DLS and Zeta potential methods. Based on the characterization results, irregular iron nanoparticles with diameters of 10–100 nm were synthesized successfully. Moreover, the nanoparticles were mainly composed of Fe<sup>0</sup> nanoparticles which were coated with various biomolecules from the extracts as capping or stabilizing agents.

## 1. Introduction

In recent years, the green synthetic iron nanoparticles (Fe NPs) materials used in environmental remediation have attracted more attention. Iron nanoparticles can be prepared through traditional synthetic methods. However, these traditional synthesis methods employed toxic, corrosive and flammable chemical substances, and required specific equipment and higher costs [1,2]. To solve these problems that are present in traditional synthesis methods, the biosynthesis of nanoparticles using natural products extracts has emerged as a cost-effective, simple and environmentally friendly alternative method. And it neither utilizes hazardous materials for the reductants or capping agents, nor generates any hazardous wastes.

Some studies on the preparation of Ag, Au and FeO nanoparticles using extracts of various plants such as eucalyptus [3], Manimuni [4], hibiscus [5], black tea (*Camellia sinensis*) [6], *Hordeum vulgare* and *Rumex acetosa* [7] were reported. Plant extracts contained abundant chemical constituents, such as phenols, reducing sugars, ascorbic acids and others, which were responsible for the bioreduction of metal ions and the stabilization of the nanoparticles. The fruit peels were also useable material resources for green synthesis except for plant leaves. Besides, *Citrus maxima* peels accounted for a higher share of the capsule: about 33–40% (based on actual measurement results) and contained various photochemicals like pectin, essential oil, flavonoids, polysaccharide compounds and so on [8–10]. These peel wastes were discarded which caused pollution problems and resource wastes. Therefore, it is necessary to the resource utilization of *Citrus maxima*

peels. In this work, a simple green method was developed to synthesize Fe nanoparticles using *Citrus maxima* peels extracts as reductants and stabilizing reagents. According to the FTIR and XPS analysis, the compositions of Fe nanoparticles were proposed. This work reached the resource utilization of *Citrus maxima* peels, avoided pollution problems and resource wastes, and improved the synthesis process of Fe nanoparticles.

## 2. Experimental

### 2.1. Synthesis of Fe nanoparticles

The fresh *Citrus maxima* peels were washed several times and then milled. The peels (12 g) were boiled with 100 mL ultrapure water at 353 K for 80 min. The extracts were centrifuged and passed through 0.45 µm filter membranes, then stored in a refrigerator at 277 K. Fe nanoparticles were synthesized by adding the extracts to 0.10 mol/L FeCl<sub>3</sub> solution in a 3:1 volume ratio at room temperature. The immediate color changing from yellow to black indicated the formation of Fe nanoparticles. The obtained Fe NPs were expressed as Cm-Fe-NPs. Fe<sup>3+</sup> solution and extracts were mixed in different volume ratios to synthesize nanoparticles, and then these synthesized nanoparticles were used to treat Cr(VI) solution.

Removal experiments were carried out using 2 mL Cm-Fe-NPs to remove 3 mL 100 mg/L Cr(VI) solution in the 10 mL plastic centrifuge tubes. Then the tubes were agitated at 250 r/min and 298 K. The quantification of Cr(VI) was performed using the diphenylcarbazide

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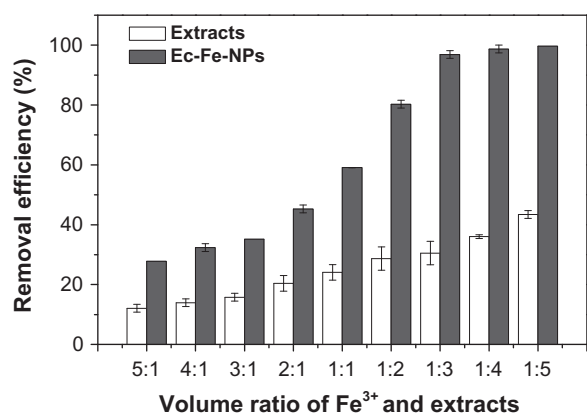


Fig. 1. The reactivity of Fe NPs with Cr(VI) at various ratios of Fe<sup>3+</sup> and extracts.

method.

## 2.2. Characterization of Fe NPs

The size, morphology and distribution of the Ec-Fe-NPs were characterized by transmission electron microscopy (TEM, JEM-2100HR, Japan), energy-dispersive X-ray spectroscopy (EDS, Oxford X-Max 50, German), X-ray photoelectron spectrum (XPS, ESCALAB 250, German), fourier transform infrared spectroscopy (FTIR, Nicolet 6700, USA), dynamic light scattering and zetasizer potential (DLS, Malvern, UK).

## 3. Results and discussion

The volume ratio of Fe<sup>3+</sup> solution and extracts was studied which played a role in influencing the synthetic efficiency. As a control, only extracts were used to remove Cr(VI). When the extract ratio increased, the removal efficiency of Cm-Fe-NPs and extracts also increased. When the volume ratio of Fe<sup>3+</sup> and extracts was 1:3, the removal efficiency of Cm-Fe-NPs and extracts were 96.87% and 30.53% respectively (Fig. 1). The Cm-Fe-NPs could remove Cr(VI) effectively. Therefore, the synthesized optimal condition was at the volume ratio of 1:3.

The average diameter of Cm-Fe-NPs was 93.8 nm (Fig. S1a in Supporting information) by dynamic light scattering methods. The zeta potential of the Cm-Fe-NPs was found to be +19.4 mV (Fig. S1b in Supporting information), which indicated that the Cm-Fe-NPs were moderately stable [11]. As shown in the TEM images, the sizes of the synthesized particles ranged from 10 to 100 nm whose shapes were irregular (Fig. 2a,b). These nanoparticles were capped by biomolecules present in the peel extracts which may improve their dispersion and stability [12]. EDS patterns were illustrated in Fig. 2(c), which contained the intense peaks of Fe, N, C and O elements. The presence of the Fe element (11.08%) presumably inferred that Fe nanoparticles have been synthesized. The presence of N, C and O elements confirmed that some biomolecules covered on the Fe NPs' surface corresponding to the TEM images.

FTIR spectroscopy was used to determine the vibration characteristics of chemical functional groups. In the FTIR spectrum of Cm-Fe-NPs (Fig. 3a), the band at 3292.84 cm<sup>-1</sup> was probably assigned to O-H stretching vibration which may be phenolic hydroxyl present in polyphenolic compounds [13]. The band at 2927.78 cm<sup>-1</sup> was assigned to C-H stretching vibration present in fatty acids [14]. The stretching vibration of C=O at 1638.55 cm<sup>-1</sup> in aldehydes and ketones indicated the presence of phenolic acid and terpenoid. The bands at 1350.99 cm<sup>-1</sup> (bending vibration of C-H), 1026.60 cm<sup>-1</sup> (C-N stretching vibration) indicated the presence of phenols and aliphatic amines [13]. These functional groups suggested that the phenols, polysaccharide, aliphatic amines and organic acids existed in the extracts. The FTIR spectroscopy of Cm-Fe-NPs did not change much compared with

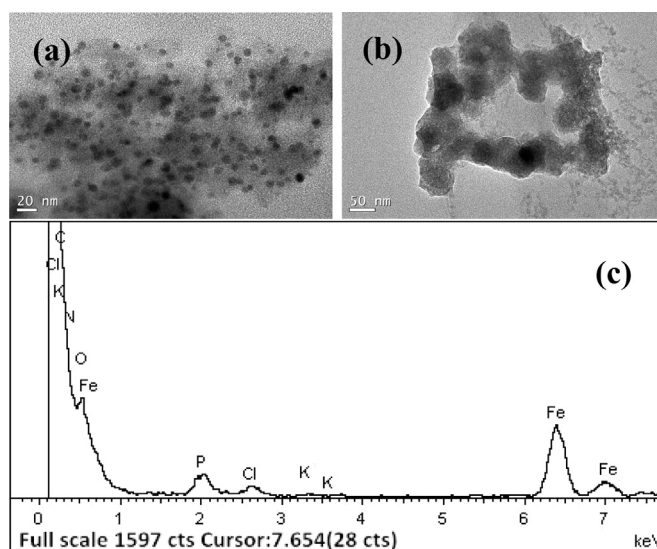
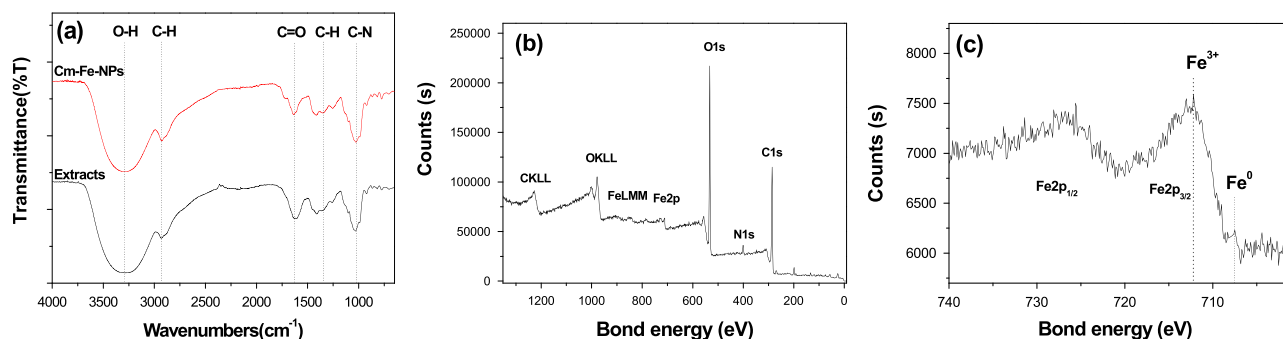


Fig. 2. (a, b) TEM images and (c) EDS spectrum of the prepared Cm-Fe-NPs.

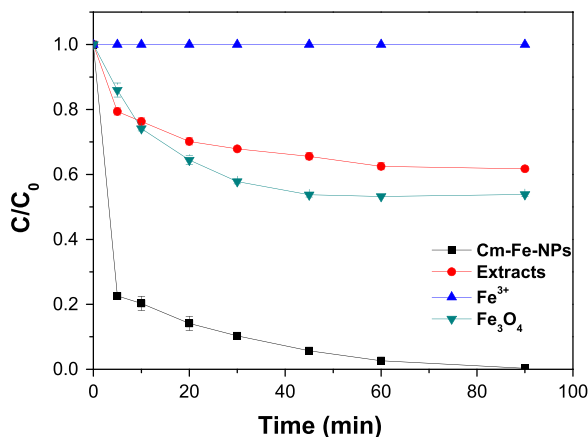
the extracts. The shifting of the bands at 3278.05 cm<sup>-1</sup>, 2930.59 cm<sup>-1</sup>, 1608.55 cm<sup>-1</sup> and 1029.80 cm<sup>-1</sup>, which might be the vibration peaks of O-H, C-H, C=O and C-N, probably implied that the phenols, organic acids and aliphatic amines were stabilizing agents in the synthesis.

There were lines of carbon, oxygen, iron and nitrogen in the XPS spectrum. In the XPS spectrum of iron 2p-electrons (Fig. 3c), signals at 725.5 eV and 712.2 eV corresponded to the binding energy electron components of Fe2p<sub>1/2</sub> and Fe2p<sub>3/2</sub>. However, there was not a distinct satellite peak. The Fe(2p<sub>3/2</sub>) peaks centered at 712.2 eV belonged to Fe (III). It was, thus, inferred in the presence of iron oxides with iron atoms in combined (III) oxidation states. Moreover, the XPS spectrum was similar with reports of Yamashita T previously published. So it can confirm the presence of iron oxide Fe<sub>3</sub>O<sub>4</sub> with iron atoms in combined (II and III) oxidation states [15,16]. The mild peak at around 707 eV was assigned to Fe<sup>0</sup> [17]. Because the Fe nanoparticles were exposed to air in the sample preparation, dry and test processes, the surface of Fe<sup>0</sup> nanoparticles were oxidized. Therefore, the nanoparticles synthesized in extracts of *Citrus maxima* peels mainly contained nano-Fe<sub>3</sub>O<sub>4</sub> and Fe<sup>0</sup>.

The removal efficiency variations of Cr(VI) by extracts, Fe<sup>3+</sup> solution, nano-Fe<sub>3</sub>O<sub>4</sub> and Cm-Fe-NPs were shown in Fig. 4. Cr(VI) could not be removed by Fe<sup>3+</sup> solution. At 90 min, the removal reaction reached equilibrium, and the removal efficiencies using *Citrus maxima* peel extracts and Fe<sub>3</sub>O<sub>4</sub> were 38.26% and 46.16%, respectively, which were much lower than that of the Cm-Fe-NPs (99.29%). On the basis of the removal efficiency of the four materials, it could demonstrated that the Cm-Fe-NPs had greater reactivity than others in the removal of Cr(VI). So the extracts may reduce part of Cr(VI) by their antioxidant content. The removal rate changed slower with times, which demonstrated the removal mechanisms for Cr(VI) were reduction and adsorption. In the XPS spectrogram of Cm-Fe-NPs after reactions, for Cr 2p-electrons, the peak at 577 eV corresponded to Cr(III). Moreover, Fe<sup>3+</sup> and ≡OH was detected in the reaction products (Fig. S2 in Supporting information). Therefore, reduction have dominated the removal process. In the XPS spectrum of Fe<sub>3</sub>O<sub>4</sub> after removing Cr(VI), Fig. S3 (in Supporting information) presents the Cr(2p<sub>3/2</sub>) and Cr(2p<sub>1/2</sub>) peaks centered at 576.9 eV and 586.5 eV, which completely contributed to Cr(III) and Cr(VI), respectively. But the reducing ability of nano-Fe<sub>3</sub>O<sub>4</sub> was limited, so the adsorption have dominated the removal process. According to the results the dynamic experiments and XPS characterization, in the Cm-Fe-NPs materials, Fe<sup>0</sup> mainly played an major role in the removing of Cr(VI).



**Fig. 3.** (a) FTIR spectrum of *Citrus maxima* peels extracts and green synthesized Cm-Fe-NPs, (b) Overview XPS spectrum of Cm-Fe-NPs and (c) XPS spectrum of iron 2p-electrons of Cm-Fe-NPs.



**Fig. 4.** Removal efficiency of the different repair materials for Cr(VI): Fe<sup>3+</sup>, Extracts, Fe<sub>3</sub>O<sub>4</sub> and Cm-Fe-NPs.

#### 4. Conclusions

In this study, Cm-Fe-NPs were prepared using *Citrus maxima* peel extracts successfully and the green synthetic Fe NPs were characterized. Based on the characterization results, the Ec-Fe-NPs were surrounded by biomolecules with diameters in a range of 10–100 nm. The green synthesis methods of Fe NPs using *Citrus maxima* peel extract were feasible which recycled the peel wastes sufficiently and created economic benefits.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.matlet.2016.09.029.

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