

Green Synthetic Nano Iron of *Suaeda salsa* and Removal of Hexavalent Chromium from Water

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Abstract. In this paper, nano-irons were successfully synthesized by *Suaeda salsa* extraction (SSE) and properties of the nano-iron particles were studied. Results of scanning electron microscopy (SEM) showed that the average of particle size of nano-iron particles were about 23~53 nm. In addition, the selected area electron diffraction (SAED) and X-ray diffraction (XRD) indicated that most of the synthesized nanoparticles were amorphous, but only a few were crystalline. Moreover, energy dispersive spectrometer (EDS) and fourier transform infrared spectroscopy (FTIR) reflected that the nano-iron particles were coated with organic substances containing O-H, C=C, C-N and other functional groups, which were as reducing agents and stabilizers during the synthesis of nano-iron particles. At 25 °C, when the dosage of nano-irons was 1.0 g/L and the initial concentration of Cr(VI) was 5 mg/L, the removal rate of Cr(VI) could reach 100% in 5 minutes.

1. Introduction

Nano-iron particles have attracted more and more attention due to their high specific surface area and reactivity, which have been successfully used for the removal of the pollutants in soil^[1], ground water^[2,3] and industrial productions^[4], such as the reduction of dechlorination^[5-7] for halides, the removal of heavy metals and non-metals^[8-10] in ground water, and the degradation of organic matter in wastewater^[11]. In addition, nano-iron particles also can be used as fillers in permeable reaction walls to remove inorganic salts in ground water, such as nitrate^[12]. So nano-iron remediation technology is considered as a flexible, high potential technology^[13] in the field of water pollution control.

Traditional physical and chemical techniques have been successfully used for the synthesis of nanoparticles^[14,15], but these technologies are expensive and involve the use of hazardous chemicals. Green synthetic nano-iron particles are more environmentally friendly, safer and can replace the chemical and physical synthesis methods^[16-18]. Plants are the most suitable for large-scale synthesis of nano-iron because they are cheap and easy to get. The leaves, roots, seeds and stems of plants all can be used for the synthesis of nano-iron particles^[19]. The materials currently extracted from nature plants have been used for the preparation of nano-iron particles, such as *green tea*^[20], *sorghum bran*^[21], *wine residue*^[22], *myrobalan fruit*^[23], *aloe leaf*^[24], *bone flesh*^[25]. The plant polyphenols as reducing agents and masking agents are considered to be one of key factors in the synthesis of nanoparticles^[26].

Chromium and its compounds are widely found in the natural environment. Cr(VI) in water is mainly from industrial wastewater such as electroplating, smelting, tanning, printing and dyeing. It is



mainly with hexavalent and trivalent valence. The toxicity of Cr(VI) is 100 times that of Cr(III), which is more easily absorbed by the human body which inducing rhinitis, tuberculosis, cancer and other diseases. At present, some studies have shown that nano-irons can be used for the removal of Cr(VI) from water^[27,28].

The green synthesis method of nano-iron is not only simple, no secondary pollution, but also the synthetic materials used in this method are natural plants with rich source and cheap price. Therefore, it is extremely important to search for a rich source of green plants for the synthesis of nano irons. *Suaeda salsa* (SS) is a highly productive, salt-tolerant plant that is easily accessible from all over the northern coastal areas. *Suaeda salsa* contains a large number of amino acids, flavonoids, fatty acids, vitamins and anthocyanins, in which anthocyanins and flavonoids have high antioxidant properties^[29]. In this paper, the extraction of *Suaeda salsa* was been used in an attempt whether nanoscale iron could be synthesized and nano-iron particles synthesized from *Suaeda salsa* (SS-FeNPs) were studied by SEM, EDS, XRD, TEM and FT-IR. Moreover, reactivity of the SS-FeNPs was investigated by the removal rate of Cr(VI).

2. Experimental section

2.1. Equipments

The main equipments: TD5M low speed large capacity centrifuge (Shanghai Lu Xiangyi Centrifuge Instrument Co. Ltd.). DZF type vacuum drying oven (Beijing City Yong Guangming Medical Instrument Co. Ltd.). Atomic absorption spectrophotometer (Thermo Electron Corporation, M6). UV-VIS spectrophotometer (America's Unique 2800 UV/VIS). Scanning electron microscope (SEM): Hitachi SU8020 ultra high resolution scanning electron microscope. X ray diffraction (XRD): D8 Advance Bruker Germany X ray diffractometer, scanning range of 8θ to 10θ , the scanning rate is 2θ / min. Fourier transform infrared spectroscopy (FTIR): spectral instruments Tensor 27 infrared spectrometer, scanning range of $4000\sim 400\text{ cm}^{-1}$.

2.2. Green synthesis of nano irons

Extracts preparation: first, the samples were washed, dried and crushed, and dissolved in deionized water with a certain amount of the beaker, then placed in the water bath at 80°C for 1 h (the selection of temperature and time based on previous studies on tea polyphenols), then the *Suaeda salsa* extraction is obtained.

Synthesis of nano irons: the extracts were mixed with 0.10 M FeCl_3 with the ratio of 32:4 and 16:2 at the room temperature, respectively. You would find that the solution color quickly changed from orange to brownish black. It showed that nano irons were synthesized. The nano-iron particles prepared by the two solutions were denoted as SS₁-Fe NPs and SS₂-Fe NPs, respectively.

2.3. Removal experiments of Cr(VI)

The prepared SS₁-Fe NPs and SS₂-Fe NPs were added to 100 mL of Cr(VI) solution with the initial concentration of 5 mg/L, and the removal experiments were carried out in an oscillator with a rotation speed of 250 r/min at 25°C . Experiments were sampled at 1, 2, 5, 8 and 10 minutes. Then the water samples were quickly filtered with the $0.22\ \mu\text{m}$ filters. The amount of Cr(VI) in the filtrate was measured at the wavelength of 540 nm by the method of diphenylcarbyl two-well spectrophotometer, and the reactivity of nanometer irons was evaluated by the removal rate of Cr(VI).

The removal rate was calculated according to the following eq.(1).

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

In eq.(1), R is the removal rate of Cr(VI), %. C_0 is the initial concentration of Cr(VI) in the solution, mg/L. C_t is the concentration of Cr(VI) in the solution at t minutes, mg/L.

3. Results and discussions

3.1. Characteristics of green synthetic nano-irons

3.1.1. SEM and EDS. Figure 1(a) and 1(c) showed the SEM images of dried solids from SSE and SS-Fe NPs respectively. From figure 1(a), the SS-Fe NPs were spherical and ellipsoidal, while the surface of dried solids from SSE had no similar particulate matter in figure 1(a). The results showed that the nano-iron particles were synthesized after the reaction between the *Suaeda salsa* extract and the iron salt, and the particle size distribution was about 23~53nm.

Figure 1(b) and (d) indicated that the EDS of the dried solids from SSE and the SS-Fe NPs respectively. From figure 1(b), the dried solid from SSE didn't contain iron. The elements of the extract mainly contained C, O and other elements, of which the mass fraction of C in SSE accounted for 26.61%, and the mass fraction of O in SSE accounted for 37.61%. It can be seen from figure 1(d) that the mass fraction of Fe in SS-Fe NPs was 20.24%, while that of pure extraction of *Suaeda salsa* was iron-free. The results further explained that the nano-iron particles were synthesized from the extract of the *Suaeda salsa* and the iron salt.

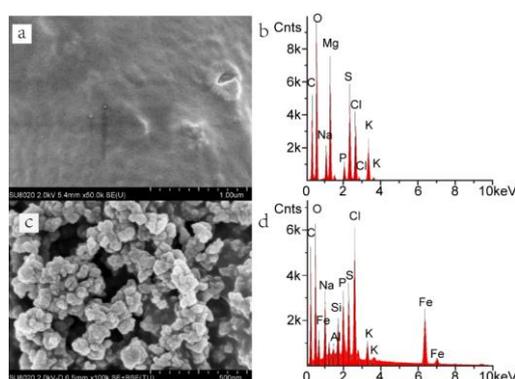


Figure 1. SEM images (a) (c) and EDS (b) (d) spectrum of SSE and SS-Fe NPs

3.1.2. SAED, XRD and TEM. Figure 2(a) showed that the X-ray diffraction (XRD) of SS-Fe NPs. In the vicinity of $2\theta=25^\circ$, there was a wide hump which may be the organic matter coated on the surface of the nanometer iron particles. This also showed that the organic matter in the extraction as reducing agents and stabilizers involved in the synthesis of nano-irons. There were no diffraction peaks corresponding to Fe_3O_4 , Fe_2O_3 , Fe_2O_3 and Fe^0 at 2θ of 34.2° , 32.8° , $20\text{-}30^\circ$ and 44.9° . The reason was that the surface of the synthesized nano-iron particles coated with a layer of thick organic matter, and XRD only could detect the characteristics of the particles surface. The figure 2(c) was the selected area electron diffraction (SAED) diagram of a small number of nano-iron particles, the bright circular area showed that the synthesized nanoparticles were crystalline, and in the detection process, we found that the SAED diagram of large part of the nano-iron particles showed a series of dispersed concentric rings, and indicated that the synthesized nano-iron particles were mostly amorphous. The reason for this phenomenon may be the fact that the synthesized nanometer iron particles had not yet accumulated before coated with a thick layer of organic matter on their surface, while the SAED can detect only the surface characteristics of the solid particles. Transmission electron micrograph of SS-Fe NPs also illustrated this point of figure 2(b). The dispersed flocs were organic substance covering the surface of the particles. The results thus indicated that organic matter on the surface of the particles was the reason for the absence of iron and oxide diffraction peaks in the X-ray diffraction pattern. Similar results were also obtained in Kumar^[23] and Makarov^[26], who pointed out that organic matter from green plants was encapsulated on the surface of nano iron particles, and hindered the crystallization process of nanoparticles.

3.1.3. FT-IR. In order to further determine the biological molecules contained in the extraction of *Suaeda salsa*, the FT-IR analysis of the extract was shown in figure 3. The peak absorption at 3124 cm^{-1} was the absorption peak of O-H, which was derived from polysaccharides in the extract of SSE. The absorption near 1627 cm^{-1} may be the stretching vibration absorption peak of C=C of the aromatic compound, which was derived from polyphenols in the extract of SSE. The stretching vibration absorption peak of aromatic amine in the vicinity of 1400 cm^{-1} . The flexural vibration of C-N in the corresponding amine of 1043 cm^{-1} . The weak absorption near 798 cm^{-1} was the bending vibration of C-H in the benzene ring. These functional groups indicated that the surface of the green synthetic nano iron was coated with organic matter.

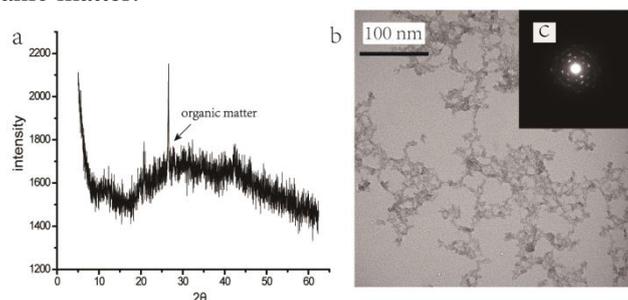


Figure 2. The XRD(a), TEM(b) and SAED(c) images of SS-Fe NPs

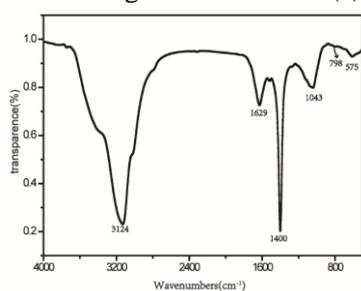


Figure 3. FT-IR spectrum of SSE

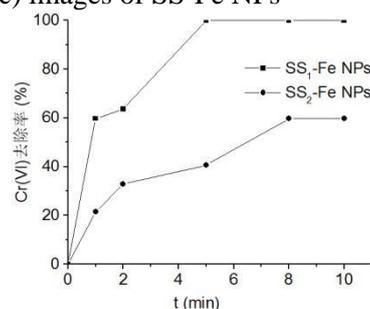


Figure 4. Removal of Cr(VI) with SS-Fe NPs

3.2. Removal efficiency of Cr(VI)

The reactivity of SS-Fe NPs was evaluated by the removal efficiency of hexavalent chromium. The results were shown in figure 4. The hexavalent chromium was removed by SS₂-Fe NPs. The removal rate of Cr(VI) increased rapidly with the progress of the reaction. The reaction reached the equilibrium after about 8 minutes, the removal rate of Cr(VI) was 59.72%. The reaction rate of removing hexavalent chromium with SS₁-Fe NPs was higher than that of the former under the same conditions. The reaction reached the equilibrium after only 5 minutes with the Cr(VI) removal rate of 100%. The above results showed that the SS-Fe NPs can effectively remove the hexavalent chromium from water.

4. Conclusions

The nano-iron particles were successfully synthesized by the extraction of *Suaeda salsa*. The synthesized nano particles were spherical and the mean particle size of nano-iron particles was 23~53 nm. The results of crystal analysis showed that most of the synthesized nanoparticles were amorphous, and a few of them were crystalline. The surface of nano-irons was wrapped by organic matter with O-H, C=C, C-N and other functional groups, which were as reducing agents and stabilizers during the synthesis reaction. SS-Fe NPs could effectively remove the hexavalent chromium from water and have a great practical application in the field of water pollution control.

References

- [1] Machado S, Stawiński W and Slonina P 2013 *Sci. Total. Environ.* **461** 323-29.
- [2] Wang T, Gao Y and Jin X Y 2013 *J. Environ. Eng.* **09** 3476-82.
- [3] Qian Y J, Zhou X F and Zhang Y L 2012 *Sichuan. Environ.* **01** 128-33.

- [4] Abbassi R, Yadav A K and Kumar N 2013 *Ecol. Eng.* **61** 366-70.
- [5] Hou C, Ge X and Zhou Y 2010 *Chinese. Sci. Bull.* **55** 350-57.
- [6] Shih Y and Tai Y 2010 *Chemosphere.* **78** 1200-06.
- [7] Shih Y, Hsu C and Su Y 2011 *Sep. Purif. Technol.* **76** 268-74.
- [8] Celebi O, Uezuem C and Shahwan T 2007 *J. Hazard. Mater.* **148** 761-67.
- [9] Chang D, Chen T and Liu H 2014 *Chem. Eng. J.* **244** 264-272.
- [10] Zeng S L, Weng X L and Tong Y G 2015 *J. Environ. Sci-China.* **15** 002.
- [11] Taha M R and Ibrahim A H 2014 *J. Environ. Chem. Eng.* **2** 1-8.
- [12] Wang T, Lin J and Chen Z 2014 *J. Clean. Prod.* **83** 413-19.
- [13] Zhang W X 2003 *J. Nanopart. Res.* **5** 323-32.
- [14] Tan L, Liang B and Fang Z 2014 *J. Nanopart. Res.* **16** .
- [15] Gual A, Godard C and Castellón S 2012 *Catal. Today.* **183** 154-71.
- [16] Raveendran P, Fu J and Wallen S L 2003 *J. Am. Chem. Soc.* **125** 13940-41.
- [17] Sharma H S, Ali S F and Hussain S M 2009 *J. Nanosci. Nanotechno.* **9** 5055-72.
- [18] Narayanan S, Sathy B N and Mony U 2012 *ACS. Appl. Mater. Inter.* **4** 251-260.
- [19] Kharissova O V, Dias H V R and Kharisov B I 2013 *Trends. Biotechnol.* **31** 240-248.
- [20] Hoag G E, Collins J B and Holcomb J L 2009 *J. Mater. Chem.* **19** 8671.
- [21] Njagi E C, Huang H and Stafford L 2011 *Langmuir.* **27** 264-71.
- [22] Machado S, Pinto S L and Grosso J P 2013 *Sci. Total. Environ.* **445** 1-8.
- [23] Mohan Kumar K, Mandal B K and Siva Kumar K 2013 *S.A.P:M&B.S.* **102** 128-33.
- [24] Mohanraj S, Kodhaiyolii S and Rengasamy M 2014 *Appl Biochem Biotechnol.* **173** 318-31.
- [25] Kumar B, Smita K and Cumbal L 2014 *J Saudi. Chem. Soc.* **18** 364-69.
- [26] Makarov V V, Makarova S S and Love A J 2014 *Langmuir.* **30** 5982-88.
- [27] Yin X C, Liu W and Ni J R 2014 *Chem. Eng. J.* **248** 89-97.
- [28] Nie N, Ding Y Z and Li X Q 2013 *China. Environ. Sci.* **33** 443-47.
- [29] Hu B L and Wang Y 2001 *Chin. J. Mar. Drug.* **4** 29-31.