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Synthesis and Spectral Characterization of Iron Based Micro and Nanoparticles

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Abstract: Nanotechnology is gaining tremendous impulsion in the present century due to its capability of modulating metals into their nanosize. They exhibit a high surface/volume ratio leading to different properties far different from those of the bulk materials. The development of uniform nanoparticles has been intensively pursued because of their technological and fundamental scienti?c importance. The use of iron-based technologies is a rapidly developing field, with a range of techniques proposed which make use of iron as a reductant, or as a sorbent, which have been tested at various scales of application. In this study the iron based materials were synthesized by precipitation method and characterized with SEM equipped with EDS, UV-VIS, FT-IR, Raman, particle size determination and Zeta potential.

Key words: Iron · Nanoparticles · Zero valent · SEM · UV-VIS · FT-IR · Raman spectroscopy

INTRODUCTION

Nanotechnology is a new scientific field being developed since 1980s. Nanotechnology is the manipulation of individual atoms and molecules to create materials and devices with vastly different properties. The physical and chemical properties of metal nanoparticles are mainly determined by its size, shape, composition, crystallinity and structure [1,2]. Control over these parameters is crucial for a successful utilization of the size-dependent properties that are unique to nanoparticles like assembly of monolayer-protected nanoparticles into crystalline arrays of one-, two- or three-dimensions. Nanoparticles are a special group of materials with unique features and extensive applications in diverse fields [3]. Studying these particular features has always been of great interest to many scientists. In fact, nanoparticles display completely unique properties in comparison with their large-size counterparts [4]. For environmental applications, nanotechnology offers the potential of novel functional materials, processes and devices with unique activity toward recalcitrant contaminants, enhanced mobility in environmental media and desired application flexibility [5,6]. Environmental nanotechnology is considered to play a key role in the shaping of current environmental engineering and science.

In the environment, iron plays an important role in contaminant mobility, sorption and breakdown due to its role as an electron donor (i.e. during the oxidation of Fe^{2+} to Fe^{3+}) and, in its various mineral forms, as a precipitant/sorbent substrate. The variable oxidation state of iron, its ability to co-ordinate to oxygen, nitrogen and sulphur atoms and to bind additional small molecules, mean that iron is one of the most important trace elements in biological systems and plays an important role in many reactions in the human body. Over the last few years, various synthetic methods have been developed to produce iron nanoparticles [7,8] modify the nanoparticle surface properties [9,10] and enhance the efficiency for field delivery and reactions [11,12].

In this study we have synthesized and characterized the iron based nano and micro particles. The characterization of these materials has been done by SEM equipped with EDX, UV-VIS, XRD, FT-IR, Raman, particle size determination and Zeta potential.

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MATERIALS AND METHODS

Synthesis of Zero Valent Iron Nano Materials: Production of ZVI involved a reduction method using two main chemicals which were $FeSO_4.7H_2O$ and $NaBH_4$ [13]. The $NaBH_4$ functions as a reducing agent in order to reduce the iron sulphate ($FeSO_4.7H_2O$) in form of solution to produce zero valent iron. The method comprised of four stages which were mixing, separating, washing and drying. These two chemicals were mixed by dropping 0.75 M of sodium borohydride ($NaBH_4$) solution into 100 ml of 0.1 M $FeSO_4$.7H2O continuously while stirring the reaction mixture well. Excess $NaBH_4$ was typically applied in order to accelerate the reaction and ensured uniform growth of iron particles. The resulted reaction occurs as follows:

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 + 2B(OH)_3 + 7H_2\uparrow \quad (1)$$

Immediately after the first drop of reducing agent into iron solution, black particle was appeared. Then, further mixing for 15 to 20 min produced the maximum yield of black iron particles. Black iron particles were then separated from the solution by vacuum filtration using Whatmann cellulose nitrate membrane filter (0.45 μm).

Synthesis of Fe_3O_4 Nano Particles: Nanoparticles of Fe_3O_4 were synthesized according to literature reported protocol [14,15] by hydrolysis of aqueous solution containing iron salts and a base at room temperature in ambient atmosphere. The $FeCl_3.6H_2O$ (1.35g) and $FeCl_2.4H_2O$ (0.6g) were dissolved in 50ml of distilled water at 30°C. To the above mixture, 50 ml of 0.5M NaOH was added rapidly while stirring vigorously under inert gas atmosphere (N_2). The Fe_3O_4 sediment was collected using a permanent magnet. The black powder was rinsed with double distilled water followed by washing with ethanol for several times to remove all impurities. A black precipitate was obtained under N_2 atmosphere and stored until use.

Iron monosulphide (FeS) (100 mesh, 99.9%) micro particles (MPs) was obtained from Aldrich.

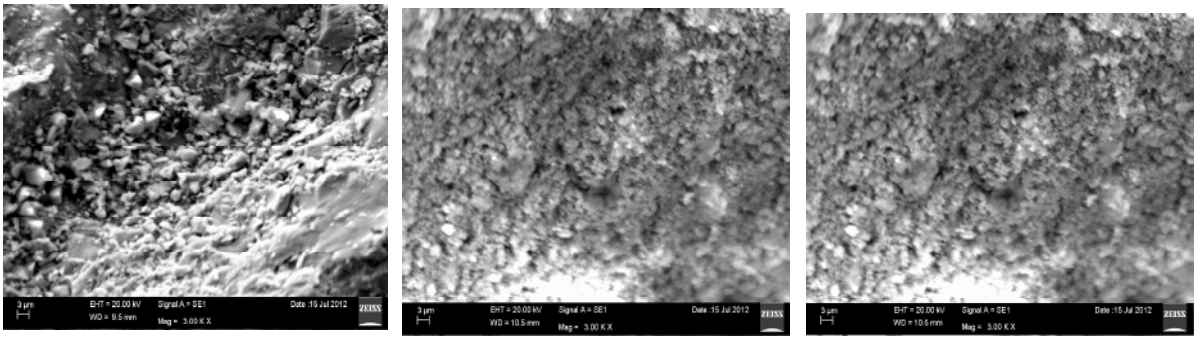
Characterization of Iron Based Materials

SEM and EDS : Morphological studies of the synthesized Fe (0), Fe(II) nanoparticles and Fe(II) microparticles were carried out by using scanning electron microscope (SEM) fitted with an Energy Dispersive Spectrophotometer (EDS) System (model CARL-ZEISS EVO MA 15). The sample was observed at 10,000X magnification with an accelerating voltage of 20 kV (Figs.1a, 1b and 1c). The energy dispersive X-ray analysis (EDX) reveals strong signal in the iron region and confirms the formation of iron nanoparticles. The other peak for Cl in Fe (II) is due to the precursors of Fe_3O_4 nano-particles (Figs. 2a, 2b and 2c).

FT-IR Spectroscopy: FTIR Spectra has been obtained for all the iron based materials with FTIR-Tensor 27 (Brutker). The strong bands for all the iron particles at 530.91 cm^{-1}, 536.36 cm^{-1}, 535.87 cm^{-1} correspond to iron, iron oxide nanoparticles and iron sulphide micro particles. The bands at the region 3200-3600 cm^{-1} are due to the -OH stretching (Figs. 3a, 3b and 3c).

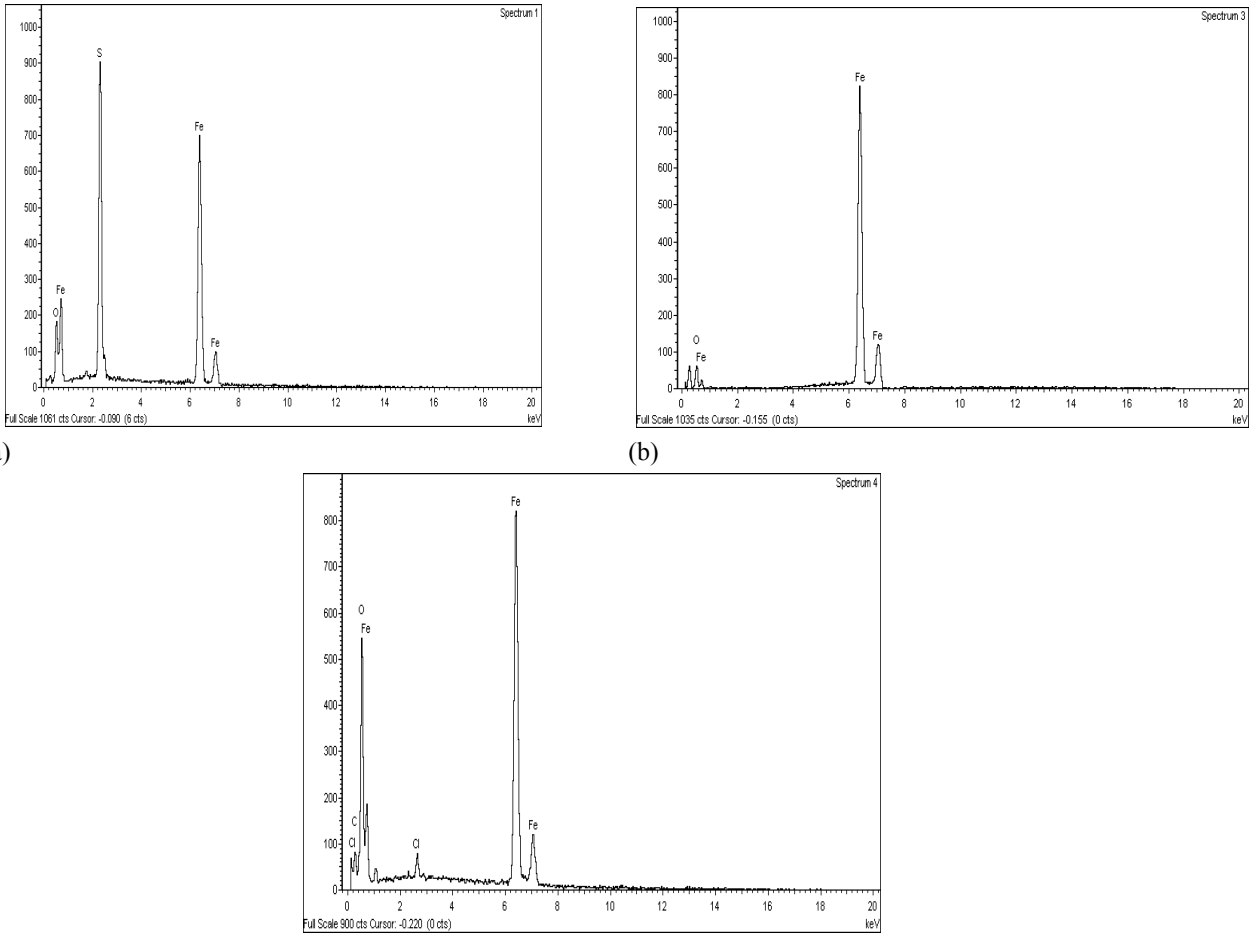
UV-VIS Spectroscopy: Probably one of the most universally utilized spectroscopy techniques, the absorption of electromagnetic radiation in the range from ultraviolet to visible is still a versatile research tool. Just as in the case of FT-IR, UV-VIS can be used to analyze certain compounds used in the functionalization of nanoparticles for dispersions and applications. Changes in the UV part of the spectrum can commonly be contributed to charge transfer (CT) bands between a surface metal cation and the functional ligand. From the spectra obtained by UV-VIS Spectrophotometer (Schimadzu) model No. UV 2450 it is known that a smooth and narrow absorption bands were obtained at 300 and 290 nm which is a characteristic of mono-dispersed iron nano-particles (Figs. 4a and 4b).

Particle Size Determination (DLS) and Zeta Potential: DLS is the measurement of fluctuations in scattered light intensity with time. These fluctuations in intensity arise due to the random Brownian motion of the nanoparticles. Therefore, the statistical behavior of these fluctuations in scattered intensity can be related to the diffusion of the particles. Since larger particles diffuse more slowly than smaller particles one can readily relate particle size to measured fluctuations in light scattering intensity. With modern instruments such as the SZ-100 the technique is rapid and reliable. The charge on the surface of particles is characterized by the SZ-100 by measuring the zeta potential of a suspension. The zeta potential of the sample is most often used as an indicator of dispersion stability. Large magnitude zeta potential values indicate that an electrostatically stabilized suspension will remain stable. Zeta potential was taken under the temperature of 25°C,



(a) (b) (c)

Fig. 1: a) SEM of FeS Mps 1b) SEM of nZVI 1c) SEM of Fe(II) NPs



(a) (b)

(c)

Fig. 2: a) EDS of FeS Mps 2b) nZVI 2c) Fe(II) NPs

the dispersion medium has the viscosity 0.893 mPa.s and the electrode voltage at 3.4V.The conductivity values of Fe (0), Fe (II) nanoparticles and Fe(II) (bulk) were obtained as 0.198, 0.231 and 0.231 mS/cm, respectively (Figs. 5a, 5b and 5c). The Zeta potential, electrophoretic mobility and particle size values of iron based materials were tabulated (Table1).

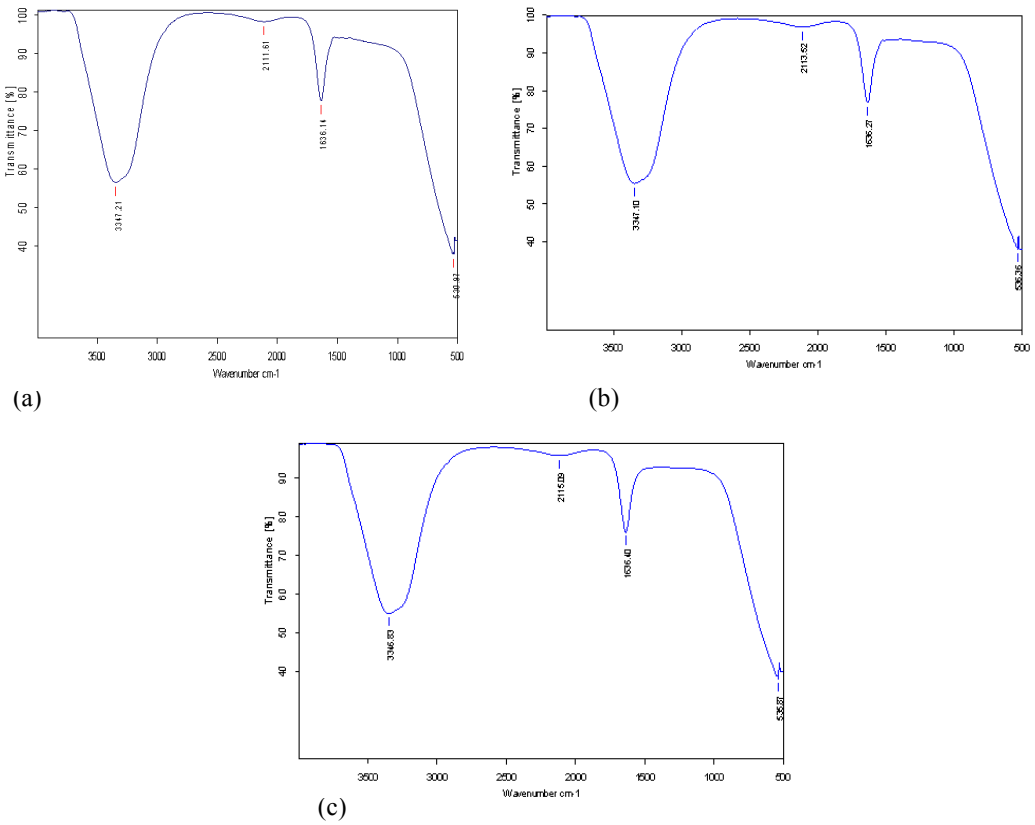


Fig. 3: a) FTIR of FeS Mps 3b) nZVI 3c) Fe(II) NPs

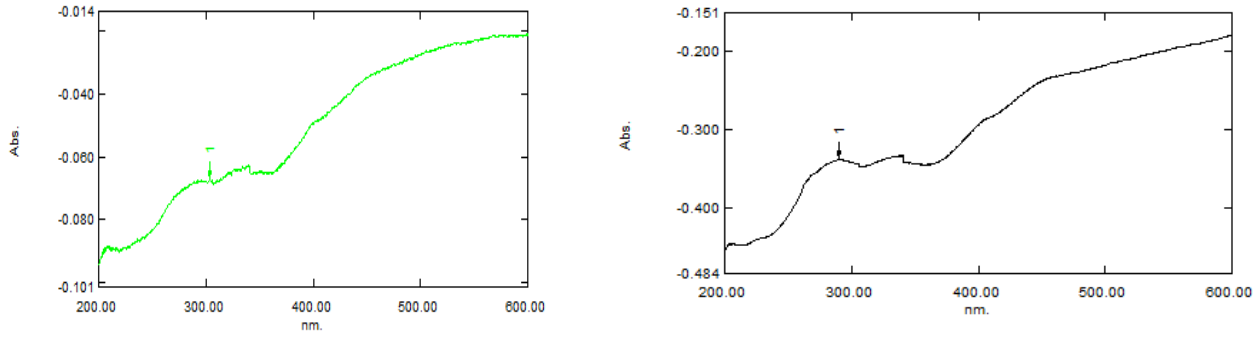
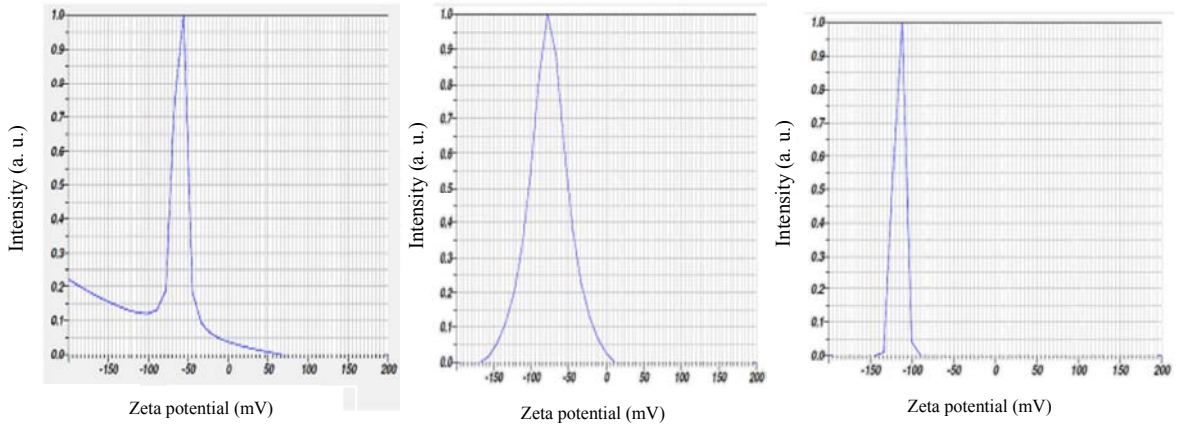


Fig. 4 UV-VIS spectra of 4a) FeS MPs 4b) nZVI &Fe(II) NPs

Table 1: Zeta potential, electrophoretic mobility and particle size determinations by SZ-100.

	Zeta potential (Mean) (mV)	Electrophoretic mobility (Mean) (cm^2/Vs)	Particle Size (nm)
Fe(0) (Nano)	-60.8	-0.000315	74.5
Fe(II) (Nano)	-77.0	-0.000398	60.6
Fe(II) (bulk)	-116.3	-0.000602	334

Raman Spectroscopy: Raman spectroscopy allows characterization of many types of samples without any specific preparation. The Raman spectra were obtained using a Lab RAM HR visible single spectrometer equipped by a microscope and a Peltier- cooled CCD detector. The 633 nm He-Ne laser line was used for excitation. Raman measurements were performed at room temperature and atmospheric pressure (Fig. 6). The characteristic peak positions of all the three iron based particles were determined in the Raman region of interest in this investigation: 100- 1200 cm^{-1}.



(a) (b) (c)

Fig. 5: Zeta potential values of 5a) nZVI 5b) Fe(II) Nps 5c) FeS MPs

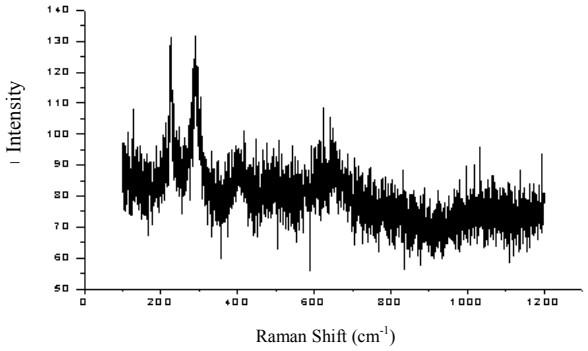


Fig. 6: Raman characterization of iron based nanoparticles

CONCLUSIONS

The present study demonstrated the synthesis and characterization of iron based nano materials (Fe(0), Fe(II) and microparticles (FeS). The formation of FeNPs was well studied. The Fe NPs and MPs characterization and morphology were studied with SEM, EDS and Particle size techniques. It is observed that the morphology of the nanoparticles varied with the ionic state of the particles. Analysis through UV-VIS, FT-IR and Raman spectroscopic techniques revealed the presence of iron and the associated molecules. Higher Zeta Potential values indicated the stabilization of the synthesized nanoparticles. The applications of these iron based materials for environmental remediation are in progress.

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Persian Abstract

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چکیده

نانوتکنولوژی بعلت قابلیت تعدیل فلزات در اندازه نانو توجه چشمگیری را معطوف خویش نموده است. این اندازه نانو نسبت سطح به حجم بالایی را فراهم می کند که منجر به خواص متفاوتی فراتر از توده مواد می شود. توسعه نانوذرات یکنواخت بعلت اهمیت علمی بنیادی و تخصصی به شدت در حال پیگیری می باشد. استفاده از فناوری مبتنی بر آهن زمینه ای است که با سرعت زیادی در حال توسعه می باشد که از آهن بعنوان کاهنده و یا جاذب استفاده می گردد و برای کاربردهای متنوعی آزمایش شده است. در این تحقیق مواد مبتنی بر آهن با استفاده از روش رسوب گذاری سنتز شد و خصوصیات آن با استفاده از SEM مجهز به EDS، UV-VIS، FT-IR، Raman، تعیین اندازه ذرات و پتانسیل زتا بررسی شد.