

New Method of Synthesis of Stable Zero Valent Iron Nanoparticles (Nzvi) by Chelating Agent Diethylene Triamine Penta Acetic Acid (DTPA) and Removal of Radioactive Uranium From Ground Water by using Iron Nanoparticle

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Abstract

Nowdays, iron nanoparticles due to their unique characteristics are used in all of sciences and technology. These nano particles due to their electrical, magnetic, optical and catalytic properties and having high area and activity that is prompted by their small size and most importantly many scientists from the entire world are interested in their low cost production. In this project we used method of reduction in the liquid phase for synthesis of iron nano particles. Unlike synthesis so far has been done and they used different kinds of surfactants and capping or they used starch for stabilization, we used chelating agent diethylene triamine penta acetic acid (DTPA) for increasing the stability of iron nano particles for the first time in the world. Ammonium iron(II) sulfate were used for make iron nano particle and Sodium borohydride was used for reduction. This method not only was simple and cheap but also didn't need special instruments. Also determining of structure, size, particles distribution and surface morphology of this nano particles we used the analysis of FT-IR, XRD and SEM that all of them showed the synthesis of zero valent iron nanoparticles, metallic iron, has been done correctly. The average of synthesis of zero valent iron nano particles is 18 nm and crystal structure of nano particles was designed by using vertical nano lab software. Finally, we studied operation Removal of Radioactive Uranium From groundwater by using iron nanoparticle.

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1. Introduction

Nowadays, iron nanoparticles due to their unique characteristics are used in all of sciences and technology these nano particles due to their electrical, magnetic, optical and catalytic properties and having high area and activity that is prompted by their small size and most importantly, many scientists from all of the world are interested in their low cost production. The rapid development of nano technology has been caused research in using and different application such as: enviromental catalytic, nuclear, military, medicinal, agricultural and fuel industries application. Because of the importance of nanoparticles the slogan of 2011 has been named " nano iron future technology ".

Nowadays, different ways are used to eliminate contaminants of water. The most common of them is chemical and physical treatments that include: Ion exchange, Membrane filter, chemical sequestration and Microbial conversion. All of them have high capital and operating costs and also make a lot of sludges. During recent years, metal with zero using (such as: Fe0, Zn0, Al0) valent was an useful factor for improving of contaminant water and was studied. Among these metals, zero valent Iron because of their cheapness, non-toxic, quicke reaction, high efficiency at reducing of contaminants such as Ar, Cr , Pb, Cd, Cu, Hg ,U... From Ground water uses more than other metals[1].

2. Chelating agent and Application to Stable Nano zero valent iron(NZVI)

Usage of nZVI in air i.e. in the presence of oxygen is a challenging task. When this material comes in contact to air, immediately oxide formation takes place. Moreover, ignition property of nZVI makes the material difficult to handle. In order to stabilize nZVI many researchers have employed the nZVI synthesis with a wide variety of stabilizing agents, surfactants and capping agents.

For example, He et al. [3] reported that by using food-grade water soluble starch both the disposability and the reactivity of Fe nanoparticles were improved. But the starch stabilized Fe became less stable, as evidence by the appearance of floc precipitates after 2 days, thereby limiting long-term storage and commercial application of these Fe nanoparticles. Also, Niu et al. [2]. Used starch during the synthesis of nZVI as dispersing cum stabilizing agent and according to He et al. [4] A stock solution of Fe(II) was added to the CMC solution to prepare desired concentration of Fe and CMC. The mixture was purged with N₂ for 15min to complete the formation of the Fe-CMC complex. The Fe(II) ions were then reduced to Fe(0) using sodium borohydride to the mixture. But we used chelating agent Diethylene Triamine Penta Acetic acid (DTPA) for increasing the stability of iron nano particles for the first time in the world. Chelation is the formation or presence of two or more separate coordinate bonds between a polydentate (multiple bonded) ligand and a single central atom. Usually these ligands are organic compounds, and are called chelants, chelators, chelating agents, or sequestering agents. The ligand forms a chelate complex with the substrate. Chelate complexes are contrasted with coordination complexes composed of monodentate ligands, which form only one bond with the central atom. Chelants, according to ASTM-A-380, are "chemicals that form soluble, complex molecules with certain metal ions, inactivating the ions so that they cannot normally react with other elements or ions to produce precipitates or scale ".

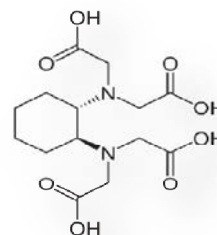


Fig. 1. Instruction of Diethylene Triamine Penta Acetic acid (DTPA) Chelating Agent.

3. Experimental

3.1. Materials

Ammonium iron(II) sulfate(NH_4)₂Fe(SO₄)₂·6H₂O, Ethanol(C₂H₅OH), purchased from Merck Company, Diethylene Triamine Penta Acetic acid (DTPA) (C₁₄H₂₃N₃O₁₀), Sodiumborohydride (NaBH₄) purchased from Sigma Alderich Company and water Dionized, Nitrogen Gas. All materials used without further purification.

3.2. New Synthesis Method of Zero Valent Iron NanoParticle By Diethylene Triamine Penta Acetic acid(DTPA) Chelating Agent

In this method we study in synthesis of stable zero valen Iron nanoparticles by Diethylene Triamine Penta Acetic acid (DTPA) Chelating Agent In this method, at first we dissolve 0.1 Molar Ammonium iron(II) sulfate (2.941gr) with 75ml water Dionized.

Also we dissolve 0.01 Molar Diethylene Triamine Penta Acetic acid (DTPA) (0.200gr) with 50ml water Dionized, then were mixed in a Two necked round bottomed flask by using propeller mixing. After that we dissolve 0.5 Molar Sodium borohydride (0.9457g) with 50ml water water Dionized. Next, added dropwise into the mixture solution (15 min). Slowly the solution turned to black colour. The black coloured particles were washed trice with absolute ethanol and finally filtered, dried, and pulverized under inert gas nitrogen. Finally, for determining of structure, size, particle distribution and surface morphology of these nano particle, we used the analysis of FT-IR, XRD and SEM that all of them showed the synthesis of zero valent iron nanoparticles, metallic iron, has been done correctly. Powder XRD analysis was done using Bruker D8 Advance Diffractometer (Bruker AXS, Germany) with Cu K α radiation ($\lambda = 1.54\text{\AA}$). XRD pattern of stabilized nZVI samples was recorded over a 2θ range of 10-90°.

FT-IR (Avatar-330, Thermo Nicolet, USA) and SEM (Cambridge,S-360) The sample surface images were taken at different magnifications.

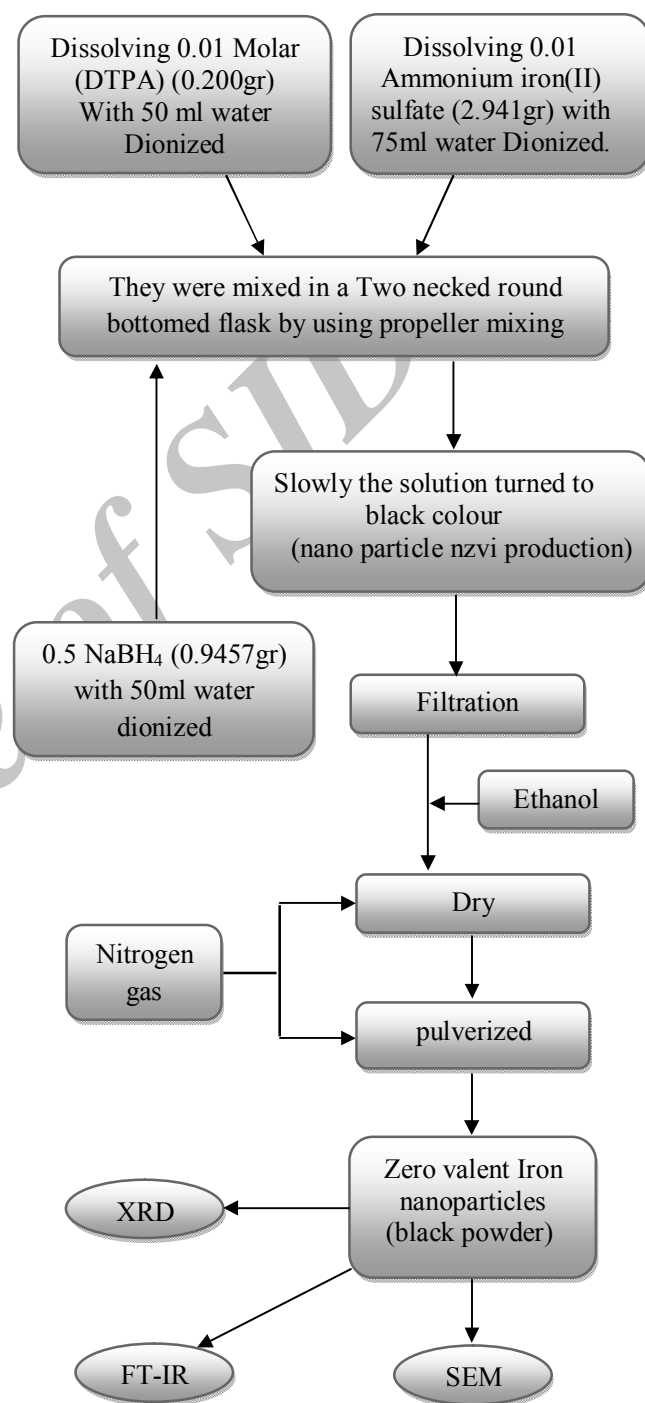


Fig. 2. Producing chart of zero valen Iron nano particles By Diethylene Triamine Penta Acetic acid (DTPA) Chelating Agent.

3. 3. Results and Discussion

Table.1 shown the result of analysis nano zero valent iron Synthesis by X'Pert HighScore software.

Table 1. Result of Analysis (nzvi) by X'Pert HighScore Software.

Matched Peak by	00-003-1050
Tip width [$^{\circ}$ 2Th.]	0.4800
FWHM [$^{\circ}$ 2Th.]	0.4723
Height [cts]	1.26
Pos. [$^{\circ}$ 2Th.]	43.5603
d-spacing	2.07773
Crystal system	cubic
Volume of cell	23.22
Form	spherical

Fig. 3 Shown the X-ray diffraction pattern of iron nanoparticles Synthesis. The average (nzvi) synthesis is 18 nm. The peak appearing at 2θ value of $\sim 44.7^{\circ}$ which matches the value for Fe0 reported in JCPDS (00-003-1050), indicated mainly the formation of nano iron in zero valent state.

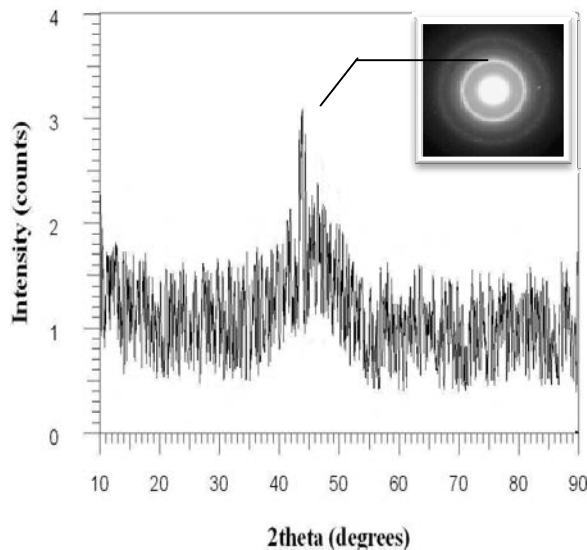


Fig. 3. XRD Pattern of Iron nanoparticles Synthesis.

Fig. 4 Shown the crystal structure cubic nano zero valent iron (nzvi) synthesis by vertical nano lab software.

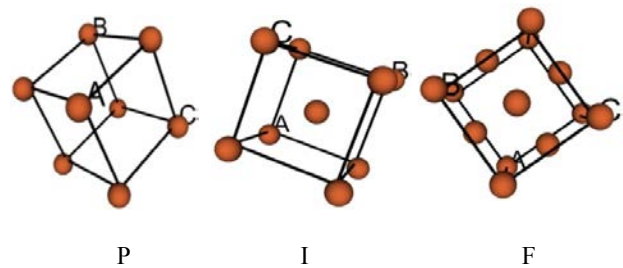


Fig. 4. Crystal Structure Cubic (model P,I,F) Nano zero valent iron (nzvi) Synthesis by Vertical nano lab Software.

Surface morphologies of nZVI were carried out by SEM analysis and it was shown in Fig.5 nZVI particles were uniform in size and spherical in shape and the average size of nano zero valent iron particles is 18 nm.

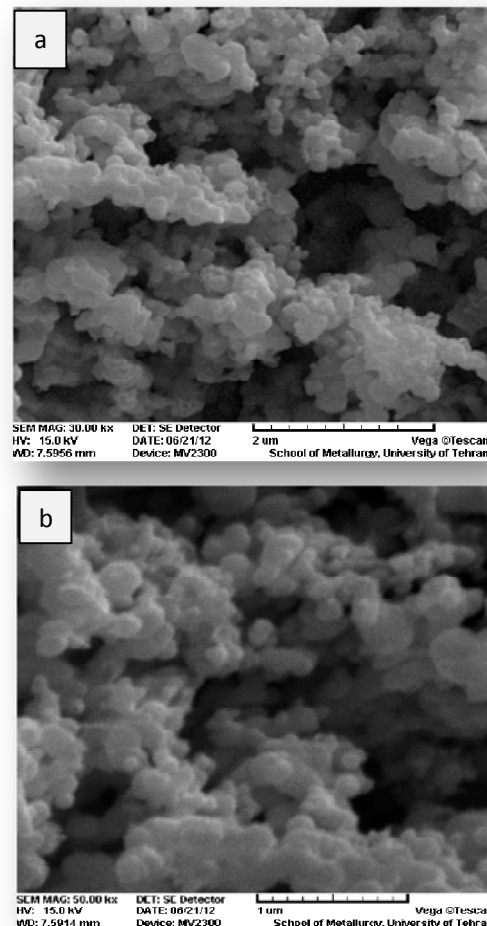


Fig. 5. SEM Images of Synthesized NZVI (a) ($\times 30000$) www.ID.ir

Fig.6 Shown FT-IR analysis result of nZVI sample. There was no existence of any functional group corresponding to any chelating agent used during the synthesis of nZVI except hydroxyl group at 3412 cm^{-1} which might appear due to partial oxidation of surface iron to lepidocrocite (FeOOH) and at 1320 cm^{-1} which are related to nitro agent groups.

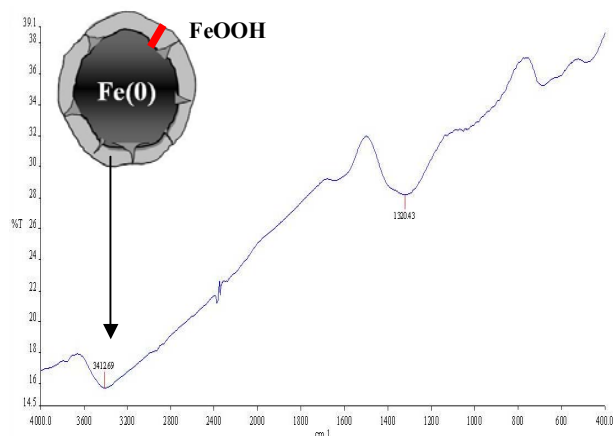


Fig. 6. FT-IR Spectrum of Synthesized NZVI.

4. Recognition About Radioactive Uranium

In recent times, water contamination from radiological materials has become a significant hazard to human health. Wastewaters containing uranium and other actinides generated in nuclear reactors in processes related to generating energy have been discharged for over 50 years. Many sites are contaminated with toxic uranium owing to solubilization of natural uranium, production of nuclear energy, and mining of uranium. Consequently, uranium is one of the most common radionuclides in soils, sediments, and groundwater. Acid in situ mining technology has been adopted as the main approach for exploiting uranium deposits as nuclear fuel. After the leaching process, the groundwater is generally characterized by very low pH and high levels of radioactive uranium. The radionuclide occurs as hexavalent uranyl (UO_2^{2+}) that is extremely

mobile, contaminating the groundwater resources. Generally, the long-lived radionuclides of the $^{238}\text{U}_{92}$ series are extremely hazardous owing to their chemical toxicity and high radioactivity [5].

Ingestion of uranium from contaminated water can cause adverse health effects including several forms of cancer, severe kidney or liver damage, birth defects, and even death. The World Health Organization has recognized U(VI) as a human carcinogen, and has recommended that its concentration in drinking water be below 15 micrograms per liter. Traditional ex situ remediation approaches based on pump-and-treat methods such as lime neutralization, anion exchange, activated aluminum and biosorption are extremely expensive and limited due to poor extraction efficiency, inhibitory competing ions, and massive waste production. Furthermore, bringing the radioactive contaminants to the surface level shall increase the health and safety risk factors for the cleanup workers and general public. Therefore, efficient and economical strategies are needed for treatment of uranium contamination in groundwater and prevent its further spread into deep subsurface [5].

5. Removal of Radioactive Uranium From Groundwater By Using Nano zero valent iron

In nature, uranium is present in two valence states, namely, hexavalent uranium, U(VI), and tetravalent uranium, U(IV). In groundwater at low pH values, the hexavalent form prevails, forming a highly soluble and mobile ionic compound, uranyl (UO_2^{2+}); however, at higher pH levels U(VI) can form carbonate and hydroxide compounds. Meanwhile, tetravalent uranium is very insoluble in water, as it forms uraninite, UO_2 . Reduction of uranium from U(VI) to the U(IV) form can prevent its migration through groundwater and effectively protect our drinking water sources.

Nano-scale zero-valent iron (nZVI) is of increasing interest for use in a variety of environmental remediation, water and waste water treatment applications.

The nZVI particles are highly mobile with high surface-to-volume ratio, and various types of nZVI have been widely studied as chemical reductants and adsorbents for environmental applications. This can be attributed to their low production costs and high efficiencies for the removal of a wide range of contaminants including heavy metals and chlorinated compounds. Their use for next-generation remediation technologies is directed at improving the efficacy, versatility and economics of treatment [5].

The fundamental concept is that nZVIs are a source of aqueous Fe(II), Fe(III), hydrogen, free radicals, and other species including precipitates of iron-hydroxy complexes that can significantly contribute to uranium removal. It must be noted that the bulk of the U(VI) is in contact with the reactive sites of the nZVI (nFe⁰) particles, so that reduction of U(VI) to U(IV) occurs as the UO₂²⁺ species is transformed to UO₂(s), and the nZVI (nFe⁰) is oxidized to the ferrous iron (Fe²⁺).

Another reaction occurs between the nZVI and the protons (H⁺) in solution to yield the ferrous ions (Fe²⁺), which in turn undergoes oxidation to the ferric form (Fe³⁺). Simultaneously, the U(VI) is reduced to U(IV) in the redox coupling reactions. The products UO₂(s) and Fe(OH)₃ (s) are synchronously coprecipitated and uranyl-ferric metal complexes are formed resulting in uranium immobilization. Fig. 7 Shown practical way Removal of Radioactive Uranium From groundwater by using iron nano Particle (NZVI) [5].

6. Conclusion

The present study has synthesized air stable nZVI by using Diethylene Triamine Penta Acetic acid (DTPA) chelating agents. The stability and characterization results clearly show that the present synthesis method would be useful to synthesize and could solve long pending stability issue of nZVI for its versatile applications in environmental remediation and water purification. Also the research that has been done showed that synthesized iron nanoparticles because of their high stability are the best selection for Removal of uranium from groundwater.

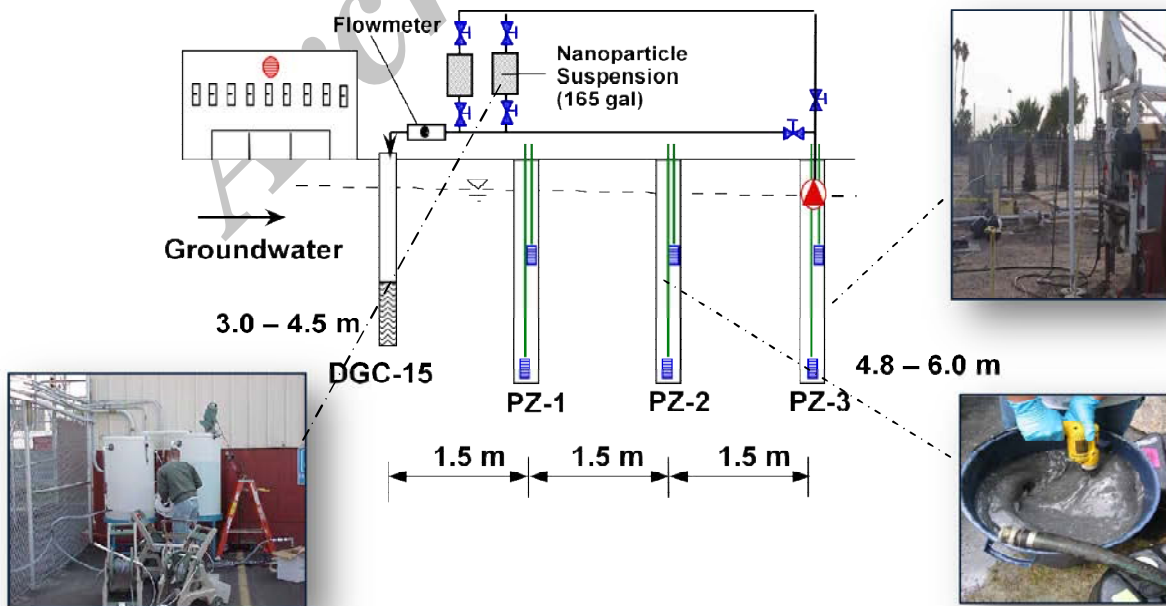


Fig. 7. Shown practical way Removal of Radioactive Uranium From groundwater by using iron nano Particle (NZVI) [6].

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