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Green Synthesis and Characterization of nano Zero Valent Iron Using Banana Peel Extract

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Abstract
Banana (*Musa paradisiaca var. sapientum* (L) Kunt.) peels were discarded as inevitable wastes in compsumtion which wasted our resources and no have environment added value. In this paper, we report a novel use of the water peel extract of Banana to produce nano Zero Valent Iron by reduction of $FeSO_4.7H_2O$. The phytochemicals present in the peel extract served as effective reducing and capping agent. The nZVI were characterized by UV-Visible spectroscopy, Fourier Transform Infra Red (FTIR), Scanning Electron Microscopy (SEM) and X-Ray Energy Dispersive Spectrofotometer (EDS) methods. In the UV–Vis spectrum, the absorption spectra of colloidal nZVI showed a surface plasmon resonance (SPR) peak at a wavelength of 215 nm. Fourier transform infra-red spectroscopy measurements showed the nZVI having a coating of phenolic compounds indicating a possible role of biomolecules responsible for capping and efficient stabilization of the the green synthesized zero-valent iron nanoparticles. SEM and EDS methods confirmed the successful synthesis of the spherical nZVI with diameters of 10–70 nm.
Keywords: Green synthesis, banana peel extract, nano Zero Valent Iron, characterization

1. Introduction

In the recent years, nano Zero Valent Iron (nZVI) have attracted a great deal of attention due to their efficiency in removal of different types of contaminants from aqueous solutions (Fazlzadeh et al., 2017). The nZVI can be preparation through physical (Kharissova et al., 2015), laser ablation (Wang et al., 2012), electric arc discharge (Hosseynizadeh Khezri et al, 2012), microbial and chemical methods. These methods require expensive instruments, high-energy (Kalyan Kamal et al., 2014), release of inimical chemicals (Ravindran et al, 2013), culture of cell (Baker et al., 2013) and wasteful purifications (Awwad et al, 2013). The traditional synthesis of nZVI used a variety of organic solvents and reducing agents like sodium borohydride ($NaBH_4$) (Pattanayak & Nayak, 2013), hydrazine, sodiumdodecyl sulphate (Kiruba et al, 2013). These reducing agents pose great risks to the environment; it also creates harmful by products to human health such $NaBH_4$ which also generates unsafe by product/hydrogen gas (Sampath et al., 2014).

As an innovation, new processes have been devised in the green synthesis of nZVI using extracts of natural product in the last few years. The green synthesis nZVI using extract plant 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 (Wei et al., 2016). Many reports are available on green synthesis of nZVI by plant extract like *green tea* leaf extract (Shahwan et al., 2011), *Tree leaf* extracts (Machado et al., 2013), extract of *Terminalia chebula* fruit (Awwad et al., 2013), *Oolong* and *black tea* leaf extract (Wei et al., 2016), *sorghum bran* extract (Njagi et al., 2011), *eucalyptus* leaf extract and *Tridax procumbens* (Wang et al., 2014).

The natural antioxidants from the peels of a variety of fruits have gained attention. The fruit peels were also the material resources could be used for the green synthesis in addition to the leaves of plants. Banana peel as a good source of antioxidants, an underutilized source of phenolic compounds (Kokila, et al., 2015). These peel wastes were discarded which no have environment added value. Therefore, it is necessary to the resource utilization of banana peels. In this work, a simple green method was developed to synthesize nZVI using banana peel extracts as reductants and stabilizing reagents. This work reached the resource utilization of banana peels, avoided pollution problems and resource wastes, and improved the synthesis process of nZVI.

2. Materials and Methods

2.1 Materials

Banana (*Musa paradisiaca var. sapientum* (L) Kunt.) peel, ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) from iron scrap (Sunardi, 2009), and deionized water was used as solvent throughout the experiment.

2.2 Synthesis of nZVI

Banana peel extract (BPE) was used as a reducing agent for the synthesis of nZVI. The fresh banana peels were washed repeatedly with distilled water to remove dust and dirt in it. Approximately 25 g of peel was taken in a glass of 250 ml containing 75 ml of double-distilled water and then boiled peel at 80° C for 10 minutes and filtered through Whatman No 1 filter paper. The resulting filtrate is stored at 4° C and is used as a reducing and stabilizing agents (Sunardi et al., 2017). The green synthesis method is the same as our previously study. In the work, the nZVI synthesis of both the precursor and the reducing agent is mixed into clean sterilized flask in a 1:1 proportion. For the reduction of Fe ions, 5 ml filtered BPE mixed with 5 ml of freshly prepared 0.005 M aqueous solution of $FeSO_4$ with constant stirring at room temperature. In particular time changes the color changes from brown to black shows the synthesis of nanoparticles.

2.3 Characterization

The formation of nanoparticles can be observed by UV-Visible spectroscopy (Shimadzu UV-1650pc Spectrophotometer). Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700, USA), The size, morphology and distribution of the nZVI were characterized by Scanning Electron Microscopy (SEM, JEM-2100HR, Japan), Energy-Dispersive X-ray Spectroscopy (EDS, Oxford X-Max 50, German).

3. Result and Discussion

The formation of nZVI of the filtrate was investigated by the observation of the change in the color of the solution. When BPE and aqueous ferrous sulfate solutions were mixed, color of the solution immediately turns black from brown and intense fine black precipitates appeared in tubes. It is indication of nZVI formation as previously reported (Wei et al., 2016; Mystrioti et al., 2016; Ravikumar et al., 2016). Figure 1 shows the photograph of the color change of the formation of nZVI by green synthesis of BPE. Banana peels are mainly composed of polyphenol (Sathya, 2014), pectin, cellulose and hemicelluloses and the functional groups related with these polymers as well as the proteinaceous matter may be involved in reducing the Fe^{2+} ions to Fe^0 (Kokila et al., 2015). Biological components, particulary polyphenols are known to interact with metal salts through these functional groups and iniate their reduction to nanoparticles (Nadagouda et al., 2010).

The formation of nZVI with polyphenols took place through the following steps: (1) complexation with Fe salts, (2) simultaneous reduction of Fe ions, (3) capping oxidized polyphenols (Nadagouda et al., 2010). Polyphenols can directly complex and then reduce iron (Fe^{2+}) to zero valent (Fe^0) particles. The reduction and oxidation processes in the reaction depend on the reduction potentials (E^0) of reagents. The reduction potensial of polyphenol is 0,57 V which sufficient to reduce Fe^{2+} ions to Fe^0 (reduction potential -0,44 V) (X. Wang et al., 2017). The general reaction mechanism of synthesis of Fe^{2+} with polyphenols and other polyol compounds can be written as:

$$nFe^{2+} + 2Ar\text{-}(OH)_n \rightarrow nFe^0 + 2nAr{=}O + 2nH^+$$

where, Ar is the phenyl group and n is the number of hydroxyl groups oxidized by Fe^{2+} (Mystrioti et al., 2016).

The reduction of Fe^{2+} ions by BPE in solutions was confirmed using UV-Vis spectra. UV-Vis analysis was carried out to confirm the formation of nZVI. The color changes from brown to black due to the excitation of surface plasmon resonance (SPR), which is the collective oscillation of the conduction electrons when excited with visible light. Metal nanoparticles should have a SPR absorption (Jain et al., 2009). Figure 1 shows to synthesis nZVI by indication of suitable SPR at 215 nm. These results was found very similar to the obtained as reported previously (Kiruba Daniel et al., 2013; Harshiny et al., 2015).

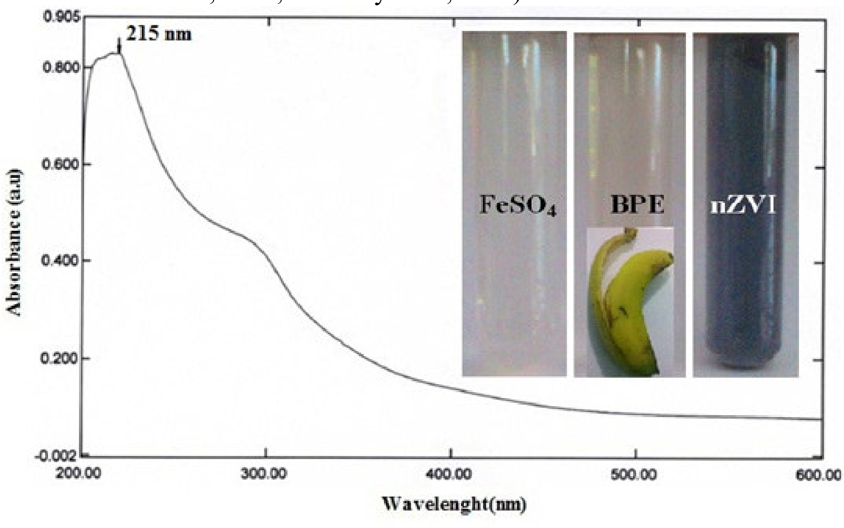

Figure 1. UV-Vis spectra of nZVI and vials containing of ferrous sulfate, BPE and nZVI.

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FTIR analysis was performed to determine the functional groups on banana peel extract and predict their role in the synthesis of nZVI. The band intensities in different regions of the spectrum for the BPE and nZVI were analyzed and are shown in Figure 2. The broad and intense absorption peaks at around 3,471 cm^{-1} in corresponden to the O-H stretching vibrations of phenols and carboxylic acids (Njagi et al., 2011; Kokila et al., 2015). The shift from 3,471 to 3,388 cm^{-1} may indicate the involvement of O-H functional groups in the synthesis of nZVI. The stretching vibration of C=O at 1,638 cm^{-1} in aldehydes and ketones indicated the presence of phenolic acid (Shahwan et al., 2011) and terpenoid (Wei et al., 2016) or C=N bending in the amide group (Kokila et al., 2015). A shift in this peak shift from (1,638 to 1628 cm^{-1}) indicates the possible involvement of carboxyl or amino groups may of the BPE extract in nanoparticles synthesis (Kokila et al., 2015). A peak at 1,466 cm^{-1} corresponded to the in-plane bending vibration of –OH in phenol (Shahwan et al., 2011; Harshiny et al., 2015). The shift in the peak of 1,466 to 1,393 cm^{-1} indicating the involvement of the phenol group of BPE in the synthesis of nZVI. The peaks at 697 cm^{-1} in accordance with the C-H stretching of aromatic compounds.

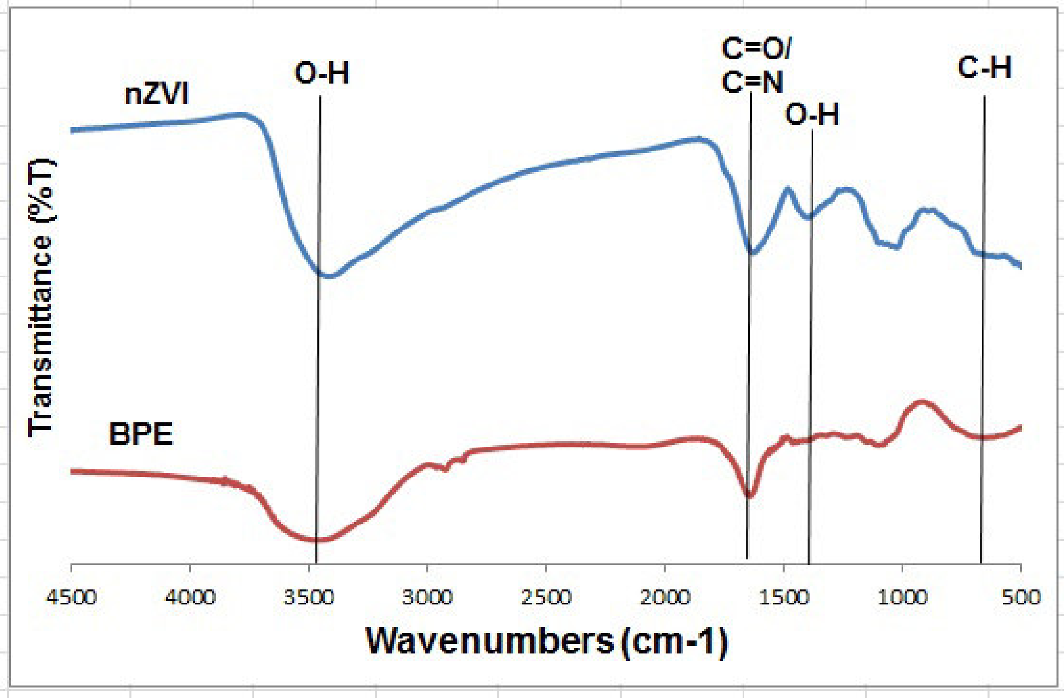

Figure 2. FTIR spectra of BPE and nZVI

SEM images in addition to an EDS spectrum of nZVI are shown in Fig. 3a,b. As shown in the SEM images, the sizes of the synthesized particles ranged from 10 to 70 nm whose shapes were irregular. These nanoparticles were capped by biomolecules present in the peel extracts which may improve their dispersion and stability. EDS patterns were illustrated in Fig. 3(b), which contained the intense peaks of Fe, C and O elements. The presence of the Fe element (19.64%) presumably inferred that nZVI have been synthesized. The presence of N, C and O elements confirmed that some biomolecules covered on the nZVI surface corresponding to the SEM images.

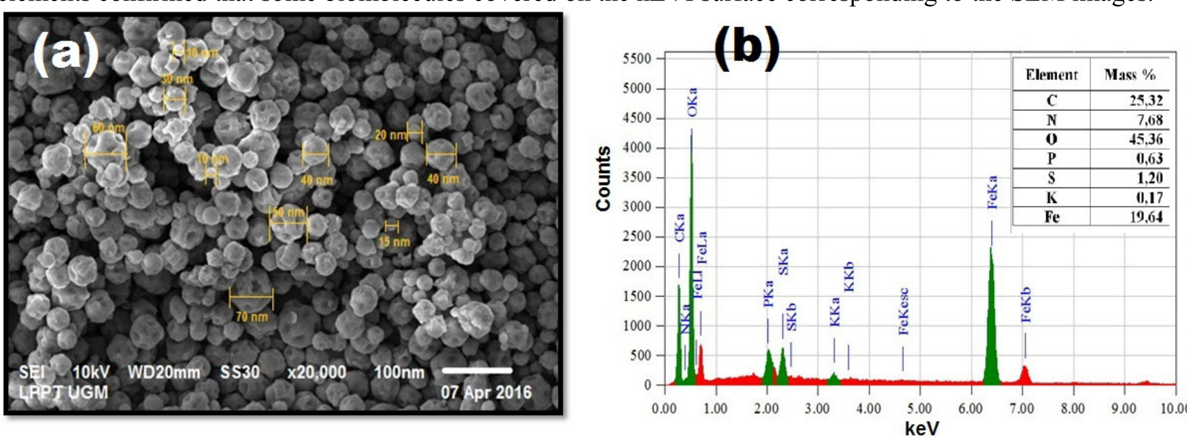

Figure 3. (a) TEM images and (b) EDS spectrum of the nZVI

5. Conclusion

In this study, nZVI were prepared using banana peel extracts successfully and the green synthetic nZVI were characterized. Based on the characterization results, the nZVI were surrounded by biomolecules with diameters in a range of 10–70 nm. The green synthesis methods of nZVI using banana peel extract were feasible which recycled the peel wastes sufficiently and created economic benefits.

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