

# SYNTHESIS AND CHARACTERIZATION OF IRON NANOPARTICLES AND ITS ASH RICE HUSK SUPPORTED NANOCOMPOSITE

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## Abstract

Iron nanoparticles together with the ash rice husk supported iron nanocomposites (nZVI and ARH-nZVI) have been prepared by bottom-up method via chemical reduction using sodium borohydride. These zerovalent iron nanoparticles were characterized using Ultraviolet-Visible (UV-VIS) Spectroscopy and Fourier Transform Infrared Spectroscopy (FT-IR). Both nZVI and ARH-nZVI were characterized by Scanning and Transmission Electron Microscopy (SEM and TEM), Energy Dispersive X-ray (EDX) and their points of zero charge were also determined. The spectra from UV-VIS depicted the absorption bands of zerovalent Iron around 320nm. The SEM and TEM showed the morphology, size and shapes of the nanoparticles and nanocomposites which are mostly spherical clusters of chain-like structures, coarse surfaces of about 10 – 15nm indicating a high surface area suitable for adsorption studies. The EDX spectra gave the characteristics peaks of the nanoparticles and nanocomposites, the information on the surface atomic distribution and the chemical elemental composition couple with the percentage composition of the nZVI and ARH-nZVI. The point of zero charge for nZVI and ARH-nZVI as determined by salt addition method were 6.80 and 7.80 respectively. This research unraveled that these novel nanoparticles and nanocomposites are promising and potential adsorbents for adsorption of toxicants.

*Keywords: EDX, FT-IR, nZVI, ARH-nZVI, SEM, TEM and UV-Visible.*

## Introduction

Nanotechnology is the science of structuring matters into a large surface area which holistically possesses unique characteristics. National Nanotechnology initiative established a generalized description that it is about manipulation of matter with at least one dimensional size from 1 – 100nm (Barbara and Nora, 2005). There are several definitions of nanoparticle but the main bottom line is that matters with very small sizes are created. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials, and energy production (Saini, 2013; Cristina, *et al.* 2007).

Modern synthetic chemistry has reached the point where it is possible to prepare small molecules to almost any structure. These methods are used today to manufacture a wide variety of useful chemicals

such as pharmaceuticals or commercial polymers. There are a number of applications of Nanotechnology. As reported by Carney (2010), the general applications of nanoparticles are: It improves membranes both for water purification (e.g., nanofiltration, reverse osmosis) and for CO<sub>2</sub> capture; nanotechnology-based coatings have been and are being developed to help insulate and reduce heat loss to increase overall operating efficiency; to limit and prevent corrosion in utility boilers; to improve corrosion, erosion and wear resistance in boiler tubes and to improve fuel efficiency. Also, effective lubricants that can withstand severe chemical and physical conditions have been developed with nanotechnology; nanotechnology has been used to produce unique, ultrafine microstructures that result in properties that are superior to those achievable by standard welding metallurgy; it is used in synthesis of nano-based enzymes to improve fuel efficiency and catalysts to improve the efficiency of sulphur removal in wet flue gas desulfurization (FGD) scrubbers; it is being used in the development of large-scale batteries and capacitors to increase available power and decrease recharge time and it is also used in synthesizing nanosensors and nanofluid such as Silicon-carbide/water fluid.

As a result on industrialization, there is a constant release of contaminants into the environments which necessitated research in the development of efficient and cost effective adsorbents. In recent times, low cost adsorbent such as rice husk (Dada et al.2013) and other inorganic adsorbent such as Manganeses hexacyanoferate(II)/(III) (Adekola *et al.* 2007) among others have been used. However, the current trend of research is the application of nanotechnology for heavy metal remediation via the use of nanoparticles and nanocomposites. This is the reason why research in the preparation and characterization of zerovalent Iron and Manganeses together with their ash rice husk supported composites has been the main focus of this paper. A number of researchers have reported the preparation and utilizations of iron nanoparticles (López-Téllez, *et al.* 2011; Hardiljeet, *et al.*2010). However, the ash rice husk supported iron nanoparticles still remains a novel potential adsorbents. Manganese nanoparticles via borohydride reduction and its ash rice husk supported has not been reported by any researcher; hence these become a novel and potential adsorbent and their characterizations become imperative as subject of consideration in this paper.

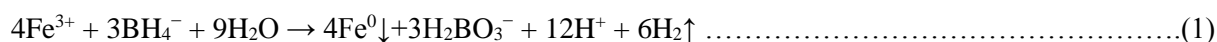
## **Materials and Method**

### **Preparation of Ash Rice Husk (ARH)**

The base material used here is the locally available and cost effective ash rice husk prepared from rice husk collected from cereal mills in Ilorin. Rice husk was screened, washed and dried in the oven at about 80 - 90°C for 2 days. About 140g of the dried sample of rice husks was calcined at 550°C for 3hours in the muffle furnace resulting into about 16.35g of rice husk ash (RHA) following the procedure reported in the literature (Atta *et al.*, 2012). Ash rice husk (RHA) was cool and stored in the desiccator for

further characterizations and uses. Ash content was determined by weighing about 5g of each of the rice husk in a crucible and heated in a muffle furnace at 550°C. The ash was transferred into a desiccator to cool.

In a typical procedure for nZVI synthesis, 6.22g of FeCl<sub>3</sub> was dissolved in a mixture of 1000ml of absolute ethanol and deionized deoxygenated water (sparged with nitrogen gas) in ratio 1:4 respectively to form 0.023M solution. This mixture was denoted as solution A. 4.70g of NaBH<sub>4</sub> was dissolved in 1000 ml of deionized deoxygenated water (sparged with nitrogen gas) to form 0.125M solution, denoted as solution B. For better formation of nano-scale zerovalent Iron (nZVI), more of NaBH<sub>4</sub> solution is needed than Fe<sup>3+</sup> solution. Then solution B was added drop by drop to solution A in a glove box under anaerobic condition. Ferric ion was reduced to zerovalent iron under according to the reaction:



As soon as the borohydride solution was added to Ferric Chloride solution, black particles of (nZVI) appeared and the mixture was further stirred for 3h. Iron powder was separated from the solution using vacuum filtration apparatus and a cellulose nitrate membrane filter (Millipore filter) of 0.45µm. Fe<sup>0</sup> (nZVI) was further washed with absolute ethanol three times and dried in a Genlab oven at 50°C overnight.

The preparation of Ash rice husk supported iron nano-composites (ARH-nZVI) was carried out following steps similar to some reported in the literature (Xi *et al.*, 2011; Shahwan *et al.*, 2010; Uzum *et al.*, 2009): 6g of ARH was added to 1000ml of 0.023M Ferric earlier prepared and this was stirred for 3h forming solution C. The solution B prepared above was added drop wisely to solution C. Black colour of nZVI was dispersed in ARH forming ARH-nZVI. The mixture was further stirred for 2 hours to prevent agglomeration after which it was washed with absolute ethanol. ARH-nZVI was separated from the solution using vacuum filtration apparatus and a cellulose nitrate membrane filter (Millipore filter paper made in Germany) of 0.45µm and dried in a Genlab oven at 50°C overnight.

### **Characterization of nZVI and ARH-nZVI**

#### **UV-VIS Spectra analysis**

A Beckmann Coulter DU 730 Life Science UV-VIS spectrophotometer in the Department of Chemistry, University of Ilorin, was used to determined absorption band for nZVI. The reduction of metallic Fe<sup>3+</sup> by borohydride was monitored by measuring the UV-Vis. A small aliquot was drawn from the reaction mixture and a spectrum was taken from a wavelength scan from 200nm to 600nm. Figure 1 shows the UV-VIS spectrum for nZVI

#### **FTIR Analysis**

The IR spectra provided information about the local molecular environment of the mixture on the surface of nZVI. Fig. 2 and 3 show the FTIR spectra of nZVI and ARH for comparative purpose respectively.

### **SEM – EDX Analysis.**

A TESCAN Vega TS 5136LM scanning electron microscope (SEM) with integrated energy dispersive x-ray analyser (EDX) typically at 20 kV at a working distance of 20 mm was used for the morphological studies. Samples were prepared for scanning electron microscopy (SEM) by coating them in gold using a Balzers' Sputtering device. However, for the EDX, samples were not coated, TESCAN Vega TS 5136LM was also used for EDX analysis. SEM micrographs of different magnifications were viewed. This was done at Rhodes University, South Africa. Fig. 4 and 5 show the SEM micrographs for nZVI and ARH-nZVI while the EDX spectra for nZVI and ARH-nZVI are shown on Figure 6 and 7 respectively.

### **TEM Analysis**

A Zeiss Libra 120 transmission electron microscope at 80KV was used to examine the microstructures of nZVI and ARH-nZVI. For TEM studies, samples were dispersed in absolute ethanol, dropped on the copper grid and allowed to dry properly before carrying out the analysis. TEM micrographs are shown on figures 8 and 9 for nZVI and ARH-nZVI respectively.

### **Point of Zero Charge**

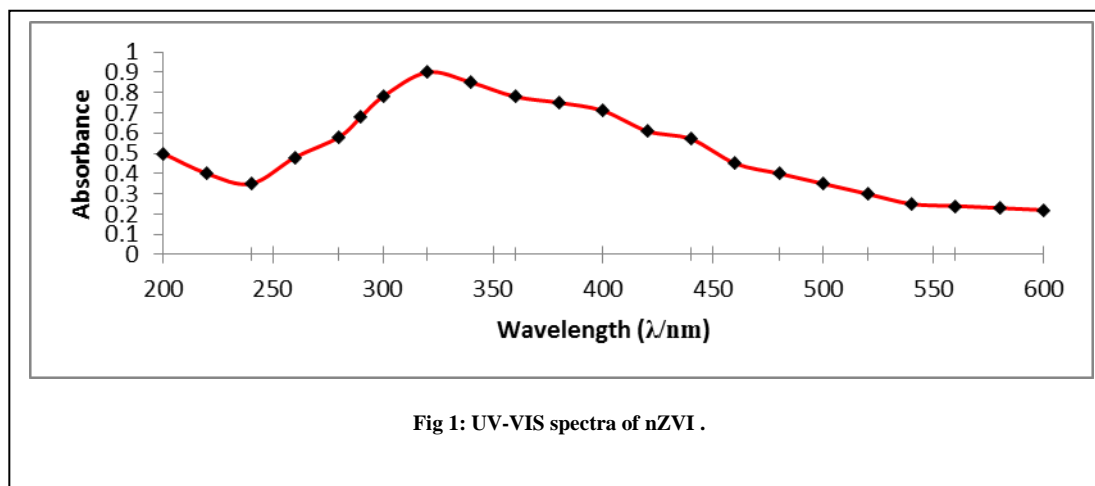
Point of zero charge (PZC) is defined as the pH at which a solid surface submerged in an electrolyte, exhibits zero net charge. It is the pH at which that surface has a net neutral charge.  $H^+$  ions reside on surface rather than enter low-pH ( $H^+$ -rich) solution, resulting in positively charged ( $H^+$ -rich) surface.  $H^+$  ions enter high-pH solution, resulting in negatively charged ( $H^+$ -poor) surface (Jaafar *et al.*, 2013)

The point of zero charge of the each of the nZVI and ARH-nZVI were determined by the solid addition method. In a typical procedure following the step proposed by Srivastava *et al.*, 2005, to a series of 100 cm<sup>3</sup> plastic bottles, 50 cm<sup>3</sup> of 0.1M NaNO<sub>3</sub> solution of known strength was transferred. 100mg of nZVI was added to 50 cm<sup>3</sup> of 0.1M NaNO<sub>3</sub> with varying pH from 2 to 12 and capped immediately. The suspensions were then agitated on the orbital shaker and allowed to equilibrate for 48 h with intermittent shaking. The pH values of the supernatant liquid were noted. The difference between the initial and final pH ( $pH_f$ ) values ( $pH = pH_i - pH_f$ ) was plot-ted against the  $pH_i$ . The point of intersection of the resulting curve at which  $pH_i$  gave the point of zero charge. The procedure was repeated for ARH-nZVI. The figures below represent the PZC for nZVI and ARH-nZVI.

## **Results and Discussion**

### **UV-Vis Spectroscopy**

The nZVI was synthesized via chemical reduction method using borohydride in anaerobic environment. Absorption spectrum of these nanoparticles were recorded, as described in Figure 1 below.



In metal nanoparticles, the conduction band and valence band lies very close to each other in which electrons move freely. These free electrons give rise to a surface plasma resonance absorption band, occurring due to collective oscillation of electrons in resonance with light wave. The absorption spectrum showed a Surface Plasmon Resonance and peaks were observed between 280nm - 350nm for Fe-np and the wavelength with the maximum absorbance is around 340nm. This was in accordance with what was reported in the literature (Monalisa and Nayak, 2013).

**FTIR Analysis**

The peaks on Fig. 2 are 3345 cm<sup>-1</sup>, 3256 cm<sup>-1</sup>, 1632 cm<sup>-1</sup>, 1328 cm<sup>-1</sup>, 910 cm<sup>-1</sup>, and 686 cm<sup>-1</sup>. The broad and intense peak around 3345 cm<sup>-1</sup>, 3256 cm<sup>-1</sup> is due to the presence of O—H from alcohol used in washing nZVI to prevent rapid corrosion. 1632 cm<sup>-1</sup> may be attributed to H—O—H stretching of deionized deoxygenated water, 1328 cm<sup>-1</sup> corresponds to C—H bending, 910 cm<sup>-1</sup> is due to C—H bending out of plane and 686 cm<sup>-1</sup> is attributed to zerovalent iron, Fe<sup>0</sup> as reported in the literatures [Shahwan *et al.*, 2011; Chen *et al.*, 2010; Frost *et al.*, 2010].

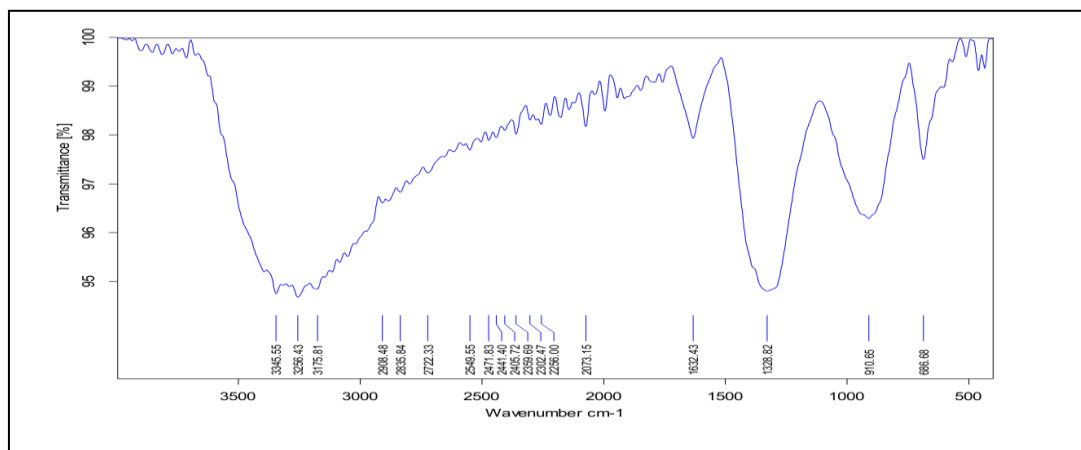
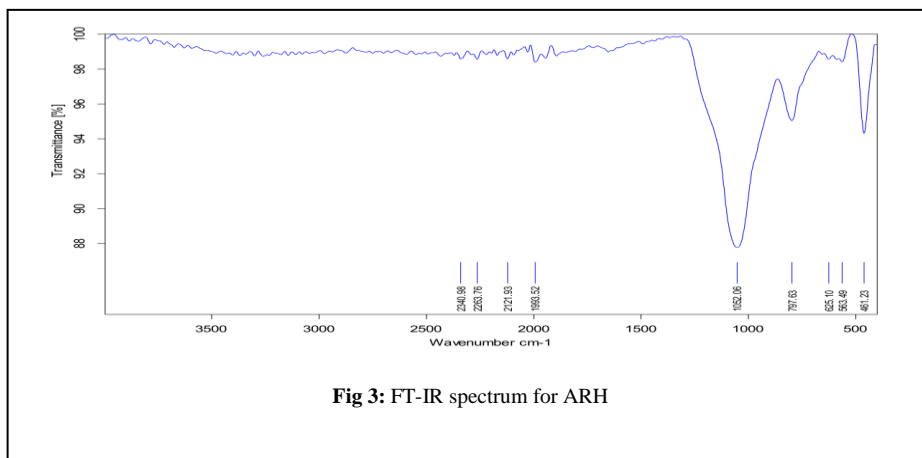


Fig 2: FT-IR spectrum of Zerovalent Iron Nanoparticles (nZVI)

The spectrum on Fig 3 below depicts the Ash Rice husk with three peaks 1052  $\text{cm}^{-1}$  corresponding to Si—O stretching, 797  $\text{cm}^{-1}$  due to Al—OH vibration band and 461  $\text{cm}^{-1}$  corresponds to Si—O bending (Srivastava *et al.*, 2005)



### SEM-EDX Analysis

The morphological features of nZVI and ARH-nZVI were revealed in the SEM micrographs in fig. 4 and 5. In figure 4, SEM image of ZVI showed a spherical surface of chain-like, aggregated molecules.

The chain-like aggregation is an indication of its magnetic property. This small NZVI particle provides a large surface area for the adsorption of toxicant useful in water remediation and this is in agreement with the report in reputable literatures (Chen *et al.*, 2011). SEM micrograph on figure 5 reveals the picture of a ash rice husk supported nanocomposite of iron. The surface shows an improvement on ordinary ash rice husk. There is an indication of the iron nano composite by a breakage of the aggregation, a sign of an hollow shape though not

deep showing that the two heterogeneous materials have a potential for adsorption. This ARH-nZVI is a novel adsorbent because virtually to the best of my knowledge, this composite has not been reported by any researcher.

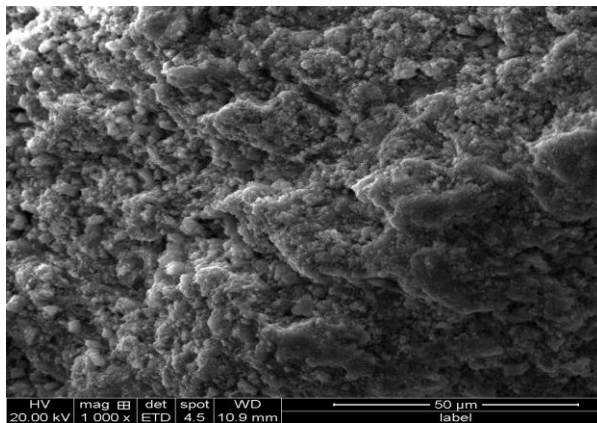


Fig 5: SEM for NZVI-ARH

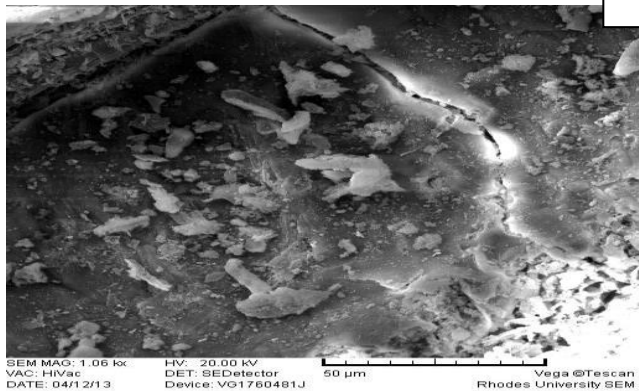


Fig 4: SEM for NZVI

**EDX Spectra.**

The EDX spectra from this analysis gave the characteristics peaks of the nZVI and ARH-nZVI, the information on the surface atomic distribution and the chemical elemental composition couple with the percentage composition of the prepared (Prema *et al.*, 2011).

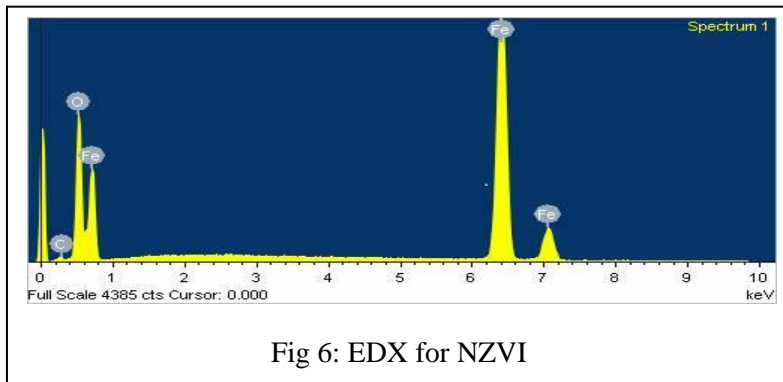


Fig 6: EDX for NZVI

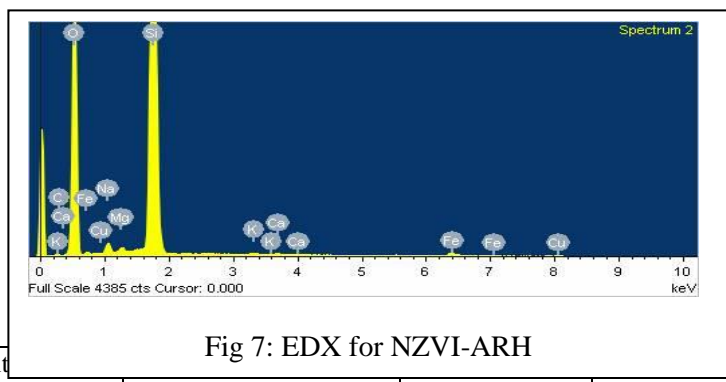


Fig 7: EDX for NZVI-ARH

		binding energy (keV)		
6	NZVI	Fe <sup>0</sup> (0.8, 6.4, 7.1)	C, O Au, Si, Cl, Na	Prema, <i>et al.</i> , 2011
7	NZVI-ARH	Si (1.8) & Fe <sup>0</sup> (0.8, 6.4, 7.1)	O, C, Ca, K, Cu, Na,	Frost, <i>et al.</i> ,

			Mg	2010; Zhu <i>et al.</i> ,2011
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Table 2: EDX Elemental percentage composition of NZVI

Element	Weight%	Atomic%
C K	1.72	4.75
O K	21.24	43.97
Fe K	86.47	51.28
Totals	109.43	100

Table 3: EDX Elemental percentage composition of NZVI-ARH

Element	Weight%	Atomic%
C K	3.00	4.26
O K	64.14	68.35
Na K	1.16	0.86
Mg K	0.36	0.25
Si K	42.33	25.70
K K	0.15	0.07
Ca K	0.17	0.07
Fe K	1.22	0.37
Cu K	0.26	0.07
Totals	112.80	100

Table 1 summaries the data on the EDX spectra 6 and 7, Nano-scaled zerovalent iron is found at the energy levels 0.8KeV, 6.4 KeV and 7.1 KeV but the one with the intense peak is 6.4 KeV which is a typical characteristic of zerovalent iron nanoparticles as reported by Prema, *et al.*, 2011. Presence of Silicon was noticed in ARH-nZVI at energy level of 1.8 KeV, there is a dispersion of the iron nanoparticle powder throughout the surface of the ash rice husk (Frost, *et al.*, 2010; Zhu *et al.*,2011). The presence of other elements in these samples are negligible. Although, they could result from the reagents or the additives used for coating during the SEM-EDX analysis, however, their presence could enhance adsorption of heavy metals via ion exchange mechanism. Nevertheless, report has been published on ARH-nZVI nanocomposite, therefore, it a novel, promising and potential adsorbent relevant in environmental remediation. A summary of the surface atomic distribution, chemical elemental composition couple with the percentage composition are clearly stated on table 2 and 3.

### TEM analysis



The Transmission electron microscope, TEM, is also one of the great tools for characterization of nanoparticles and nanocomposites because it unravels the size, shape and morphology of the samples. It further confirms the characteristics discovered through SEM.

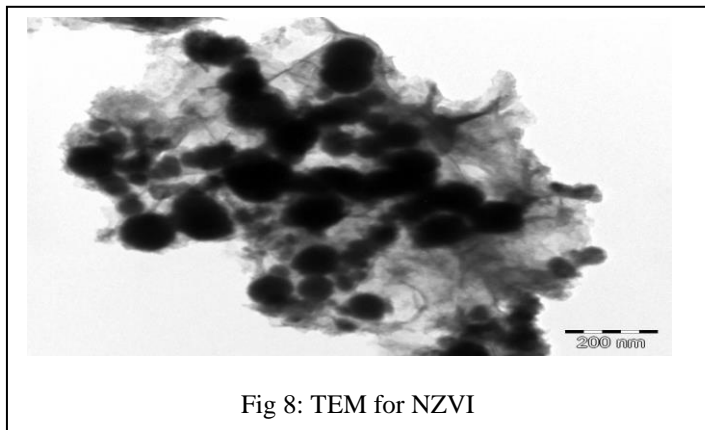


Fig 8: TEM for NZVI

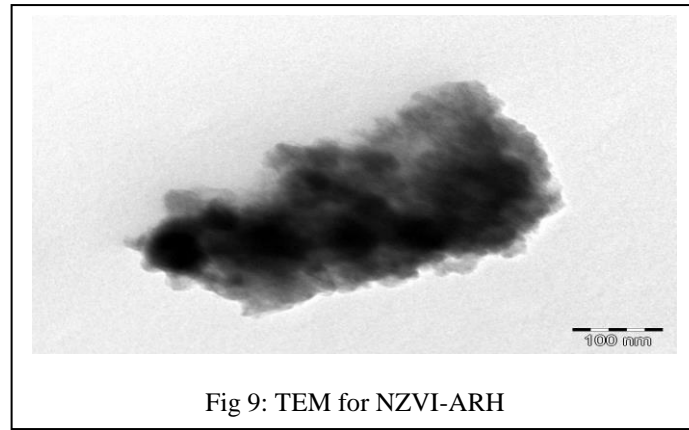


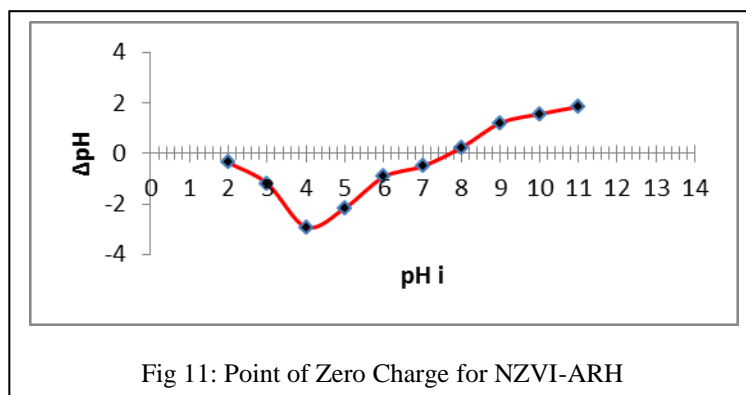
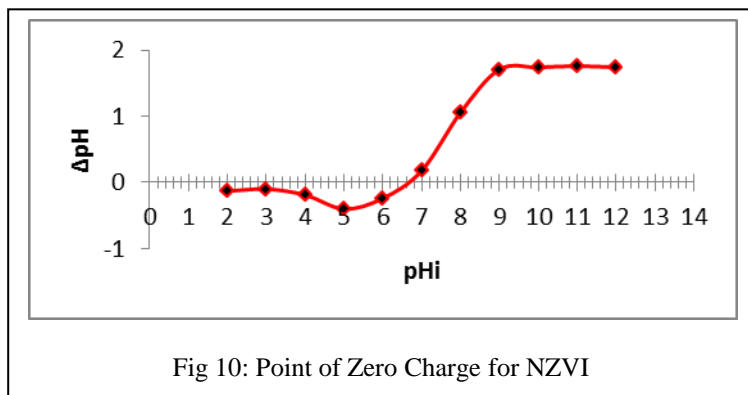
Fig 9: TEM for NZVI-ARH

Generally, in NZVI, particles are spherical, snake-like and chain-like because of the magnetic and vander waal forces in  $Fe^0$ . The size ranges from 5nm to 15 nm (Fan *et al.*, 2009; Sushil *et al.*, 2006). ARH-nZVI nanocomposites show some dispersion of zerovalent iron nanoparticles on the ash rice husk base material which may be due to ultrasonic effect but it can also be observed that there are traces of snake-like and chain-like attribute of  $Fe^0$  nanoparticles (Xi, *et al.*, 2011; Fan *et al.*, 2009). However, when  $Fe^0$  was dispersed onto the surface of ash rice husk, significant differences can be observed using TEM, which showed chains were not predominant anymore, instead, these basic units were separated and presented as individual spherical shaped particles, as shown on Fig. 9 compared to Fig 8. Size variation of iron nanoparticle can be achieved by varying the amount of iron salt added; this knowledge is utilized for scaling up of nanoparticles/nano-composites (Fan *et al.*, 2010).

### Point of Zero Charge

Fig. 10 and 11 showed the point of zero charge for both nZVI and ARH-nZVI at 6.80 and 7.80 respectively. The significance of this kind of plots is that an adsorbent will have positive charge at solution pH values less than the pzc and thus be a surface on which anions may adsorb. On the other hand, adsorbent will have negative charge at solution pH values greater than the pzc and thus be a surface on which cation may adsorb. There is no much difference in the values of nZVI and ARH-nZVI. The information provided from the pzc will help to know the pH at which the sorption experiment can take

place for heavy metal ion and other toxicants like dyes. This finding is similar to the report in by Srivastava *et al.*, 2005.



## Conclusion

The synthesis of nZVI and ARH-nZVI were carried out by chemical reduction in an anaerobic environment. The UV-VIS reveals the absorption band of nZVI. FT-IR showed the molecular environment while the morphological changes were revealed by SEM. After ARH was dispersed on nZVI, the snake-like, chain-like and spherical shapes of zerovalent iron were observed which was further confirmed by TEM. The EDX spectrum showed a well dispersion and good distribution of nZVI on the surface of ARH. The points of zero charge (PZC) provide strong information for the utilization of nZVI and ARH-nZVI for adsorption studies. The special features possessed by nZVI and ARH-nZVI showed that they are promising, potential and novel adsorbents for toxicant removal from the environment.

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