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Research Article

Synthesis of Nano Zero Valent Iron Using Magnetic and Decantation Separation Techniques

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Abstract: This paper presents a simple, easy and convenient separation technique for obtaining nano zero valent Iron from Sodium tetrahydroborate (NaBH_4) and Iron (II) Chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), using the wet chemistry method. Three samples, A, B, and C were prepared using molar ratio of NaBH_4 and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 4:5, 2:3, and 3:2 respectively. Nano particles were obtained from samples A, B, and C applying the commonly used vacuum filtration and the proposed magnetic and decantation method. Vacuum filtration separation was used for sample A and B; while magnetic and decantation separation method was used for sample C. All the samples, A, B, and C were characterized using X-Ray Diffraction (XRD) and Energy Dispersion X-ray spectroscopy (EDX). There was no observation of distinct peaks for sample A and B; but sample C had seven distinct peaks indicating synthesized nano zero valent iron (nFe^0) particles. Sample C was further subjected to EDX, and the result revealed a distinct peak. A nano particle size of 54.28nm was obtained for sample C using Scherrer's equation. A simple and easy to operate laboratory separation techniques are hereby suggested for the synthesis of nano zero valent iron.

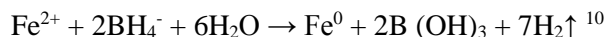
Keywords: Magnetic and decantation, Nanoparticles, nano zero valent iron, Vacuum filtration, oxidation, XRD and EDX.

INTRODUCTION

Zero valent iron (Fe^0) is an elemental iron in zero oxidation state. This simply refers to iron in an uncombined state. Fe^0 facilitates reliable and effective degradation of waterborne pollutants in the environment – groundwater¹. The use of zero valent Iron as a cheap reducing agent for the treatment of wide range of environmental contaminants and in iron wall remediation has been reported². Furthermore, Fe^0 is referred to as a green material due to the quantity of Iron readily available as recycled materials; its capability to degrade most contaminants with little or no contamination; and its mild toxicological features³. The evolution of nanoscale dimension of Fe^0 has created a unique class of Fe^0 material with tremendously improved reactivity due to its extremely small size and large surface area. Nano zero valent Iron (nFe^0) therefore refers to elemental iron in nano-scale (one billionth) metre level. In the past years, nFe^0 has attracted much attention for its potential application for the treatment of polluted soil and impure groundwater. Zhu *et al*⁴ stated that various technologies were available to extract toxic metals from water, but nanoscale zero valent Iron was reported an ideal and more effective material for the in-situ remediation due to its large reactive surface area and high affinity for toxic metals. The nano zero valent Iron has capability to transform the injurious materials to non-injurious materials; it can also be used to promote the reduction and precipitation of harmful and carcinogenic metals such as chromium (VI), Cr^{6+} to more stable state of chromium (III), Cr^{3+} .⁵ The wet chemistry method of synthesizing nano zero valent iron (nFe^0) was first developed in the mid-1990s by Zhang and his colleagues⁶. Ever since, varying wet chemistry synthesis methods and characterization techniques have been evolving. In this work two compounds were used as main chemicals; Iron (III) Chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and Sodium borohydride (NaBH_4). NaBH_4 (0.2 M) which served as a reductant was added into $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.05 M) solution at approximately 1: 1 volume ratio⁷. Below is the chemical equation:



From this chemical equation, it is explicit how Sodium borohydride reduced iron (III) Fe^{3+} to zero valent iron, Fe^0 . Rashmi *et al.*⁸ also synthesized nFe^0 by using chemical reduction method similar to the one developed by Zhang. Nonetheless, a different molar concentrations 5 : 1 of NaBH_4 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were used as against 4 : 1 by Zhang⁶. Furthermore, Yaacob *et al*⁹ reported a wet chemistry method of synthesizing nFe^0 by reducing Iron II Chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) with NaBH_4 .



All the researchers mentioned above used vacuum filtration method of separation to obtain nano zero valent Iron from the final mixture after the reaction. In this research, nano zero valent iron (nFe^0) was synthesized using different ratios of Iron (II) Chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and NaBH_4 . The commonly used vacuum filtration was applied to obtain nano particles as well as magnetic and decantation separation techniques. Characterization was done using EDX and XRD analysis.

EXPERIMENTAL

All chemicals used are of analar grade.

De-ionized water was used to prepare the sample solutions;

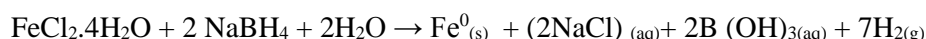
A bar magnet was used during the samples separation;

EDX Model EDXRF Spectrophotometer (EDX3600B) was used to characterize sample-C; and XRD Model GBC Enhanced Mini Material Analyzer (EMMA) X-Ray was used for all the samples characterization.

Three different samples: sample-A; sample-B; and sample-C, were prepared using different combination of materials and separation techniques in the synthesis of nano zero valent iron (nFe^0). Wet chemistry method was used throughout the synthesis of nano zero valent iron (nFe^0). This method involved a reduction of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ using NaBH_4 . (delete sentence)

Samples Preparation: Sample-A was prepared by titrating 2M NaBH_4 against 50ml aqueous solution of 2.5M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4:5), sample-B was prepared by titrating 2M NaBH_4 against 50ml aqueous solution of 3M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2:3) and sample-C was prepared by reacting 100ml aqueous solution of 1.5M NaBH_4 with 1M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3:2). All the reactions were carried out with continuous agitation at room temperature. In each case NaBH_4 was added in excess to accelerate the reaction and ensure uniform growth of Iron particles. Each preparation procedure comprised four stages which were mixing, washing, separating, and drying.

The equation below shows the reaction equation:



Immediately after the first drop of reducing agent into the Iron solution, black particle appeared; then further addition in excess produced the maximum yield of black iron particles.

Sample-A and sample-B were then subjected to vacuum filtration separation technique, while sample-C was subjected to magnetic and decantation separation techniques. At the completion of reduction reaction of sample-C in a beaker, a magnet bar was placed by the side of the beaker to magnetize the magnetic particles. Those particles that adhered to the magnet were separated by decantation from the non-magnetic materials. This method is referred to as magnetic and decantation separation techniques. The magnetic particles were then oven dried, and then kept in a dessicator for characterization.

The samples were characterized by subjecting them to XRD and EDX analyses at NASENI Centre of Excellence in Nanotechnology and Advanced Materials, Akure, Nigeria.

The size of the nano zero valent iron (Fe^0) was calculated using two equations:

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (\text{i})$$

Where d is particle size; k is peak shape coefficient; λ is radiation wavelength in nanometre; β is integral breadth derived from “full width at half maximum” (FWHM); and θ is Bragg angle. The equation (i) above is known as Scherrer’s equation.

$$\beta = 0.5 * FWHM \left(\frac{\pi}{\ln 2} \right)^{1/2} \quad (\text{ii})$$

Where FWHM is full width at half maximum; and π has a constant value, 3.142...

RESULTS AND DISCUSSION

I – XRD Analyses

The results of the characterized samples: sample-A; sample-B and Sample-C are presented below.

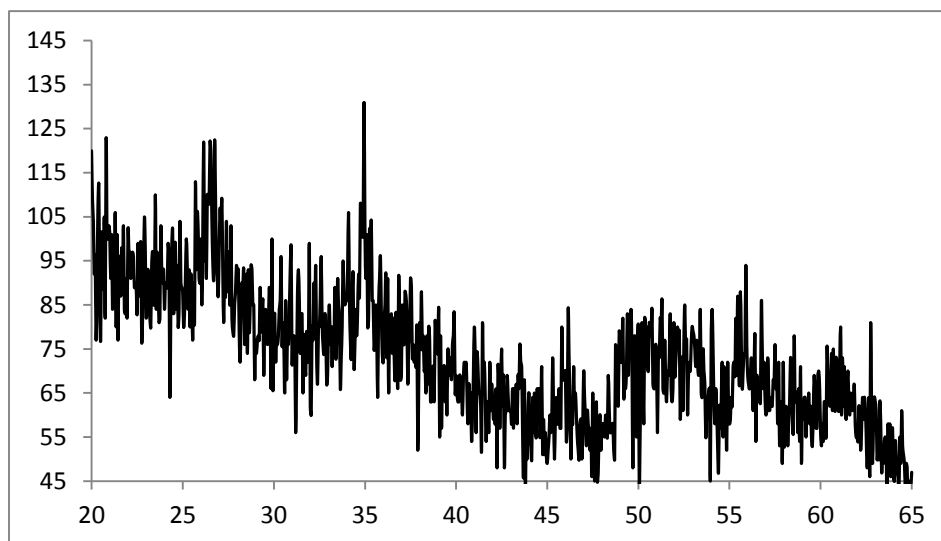


Figure 1: Sample-A XRD Pattern.

The XRD patterns of sample-A is shown in **figure 1**. The pattern showed no major peak. The peak indicating nano zero iron should have appeared at 2 theta value of approximately 44.7° ¹¹ but as evident in **figure 1**, such peaks are non-existence. Many factors influence the XRD pattern of nanoparticles, like, temperature, pH value during its synthesis and also presence of impurities. All these may change the original structure of the specimen. The black colour formed during the analysis faded and changed to brown during vacuum filtration process an indication that some of the synthesized $n\text{Fe}^0$ may have been oxidized to form Fe^{3+} .

In this work, the vacuum filtration was not effectively done due to the peculiar environment of the researchers, e.g irregular supply of electric power. Furthermore, samples were transferred to distant laboratory for characterization. All these may have contributed to the oxidation of the sample, and subsequent XRD pattern observed. Sample A was prepared using a molar ratio of 4:5 NaBH_4 and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. This molar ratio of reagents may not have been conducive for obtaining nano zero valent iron. In short, nano particles were not produced in sample A.

The XRD pattern of sample-B is shown in figure 2. Although peak broadening reduced slightly there was still no identifiable peak for nano zero valent iron. This slight improvement may have been due to the addition of the chelating agent (EDTA). Chelating agents are known as stabilizers for nano particles¹². Experimental parameters such as reactant concentration, stirring speed, external temperature etc. can to some extent influence composition and surface properties of Iron nano particles¹³.

The molar ratio of reagents for sample B was 2:3 this represents a concentration lower than that of sample A. During the synthesis, there was formation of few clusters of Iron particles in the deep black coloured solution. The black colour persisted till washing stage. Sample-B was also subjected to vacuum filtration; however, the sample got oxidized before vacuum filtration was complete. Particles obtained after drying appeared to be completely oxidized to Fe^{3+} . Once again the molar ratio 2:3 and the vacuum filtration method did not yield zero valent iron nano particles as expected.

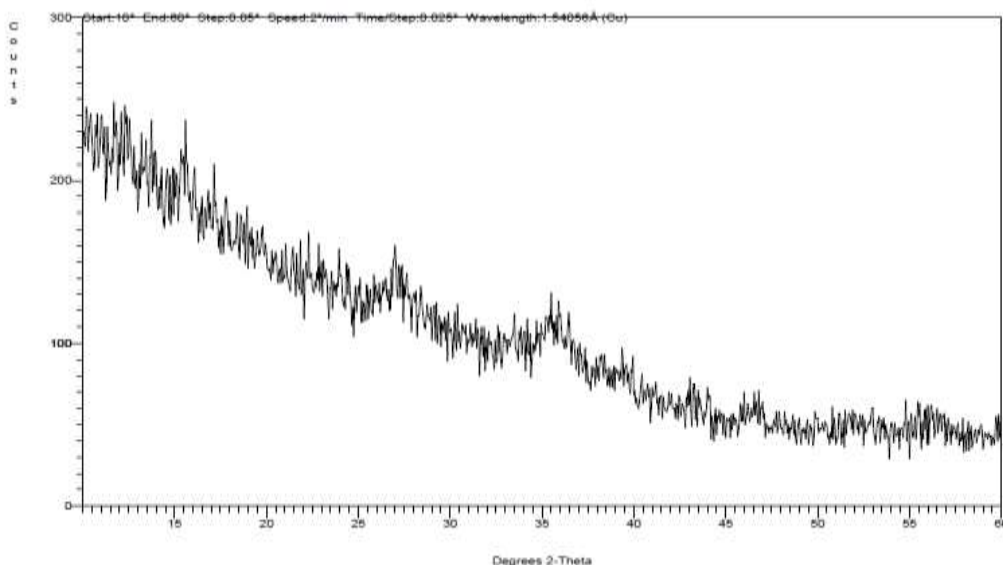


Figure 2: Sample-B XRD Pattern

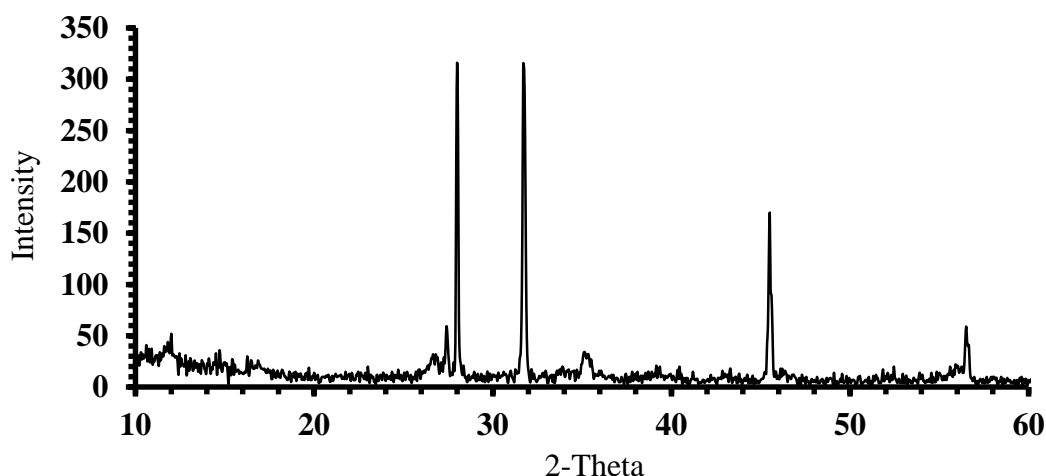


Figure 3: Sample-C XRD Pattern.

Sample C was subjected to magnetic and decantation method instead of vacuum filtration. The molar ratio of NaBH_4 : $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was also interchanged to 3:2. The XRD pattern of the particles presented in figure 3 showed distinct and obvious peaks. During titration (synthesis), a deep black solution was formed, and after the reaction was complete, clear clusters of magnetic particles were formed in the solution. These separation techniques were very fast, cheap, and easy to carry out. Unlike vacuum filtration, the sample was exposed for a shorter time to the atmospheric oxygen. Unfortunately, during drying stage, major parts of the sample got oxidized.

Nevertheless, the sample-C XRD presents major peaks of Fe^0 at $2\theta = 45^\circ$ which indicates the presence of zero valent iron; while 2θ values of 28° , 32° , and 56° indicate the presence of Iron corrosion

products according to¹³ The peaks were found to have high intensity which shows the presence of a crystalline Iron phase¹⁴.

The size, 54.28nm of zero valent iron (Fe^0) was calculated using Scherrer's equation. This is close to the nano zero valent Iron TEM images obtained by Sun *et al.*¹³.

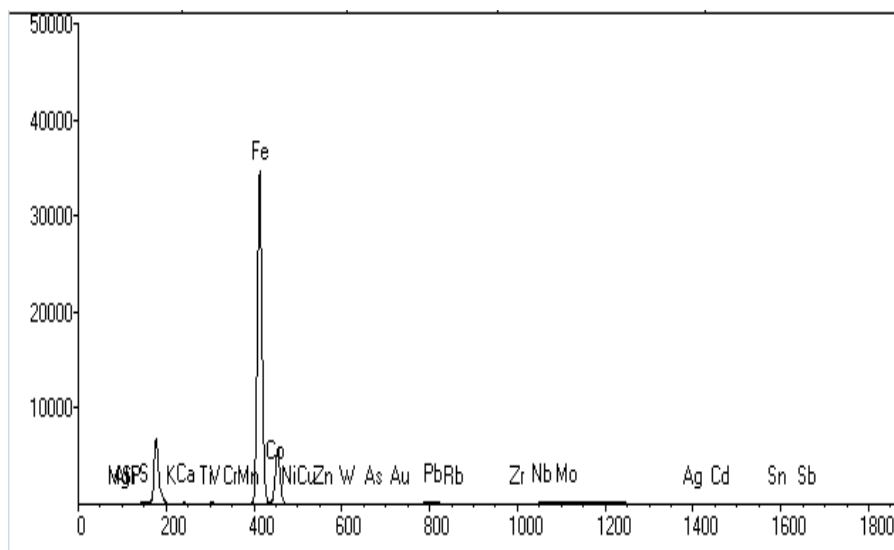


Figure 4: Sample-C EDX Pattern

II –EDX Analysis: The Sample-C EDX analysis was the only one done because of its satisfactory XRD pattern. The EDX pattern from figure 4 showed the distinct peak of Fe^0 with high intensity. The EDX pattern shows other peaks different from that of Fe^0 , which indicates the presence of minute quantity of other elements in the sample. Unlike XRD analysis, the EDX analysis determined the elemental components of the sample obtained.

CONCLUSION

The synthesis of nano zero valent Iron (nFe^0) using wet chemistry method was very challenging particularly at the separation and drying stages. This was due to the fact that, the zero valent iron (Fe^0) was easily oxidized by environmental oxygen. The results of sample-A and sample-B did not confirm that nano zero valent iron was synthesized considering their XRD patterns. However, the XRD and EDX patterns of sample-C showed that nano zero valent iron was successfully synthesized by using the same Sodium borohydride (NaBH_4) and Iron (II) Chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$).

The magnetic and decantation separation techniques used to produce sample C greatly prevented its oxidation; unlike samples A and B which were oxidized during vacuum filtration. The magnetic and decantation separation techniques were fast and easy. It is therefore suggested that this method can be added to the other existing separation techniques to produce nFe^0 using wet chemistry method. This new technique reduces oxidation of zero valent iron to a considerable extent.

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