

Research Article

Synthesis and Characterization of Iron Nanoparticles from Acid Mine Drainage Using Sodium Borohydride as Reductant

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Abstract

The large volume of toxic acid mine drainage wastewater generated from the pyritic oxidation of coal and gold mine result in serious environmental pollution because of the problem of waste disposal. The aim of this study is to use iron-rich raw acid mine drainage (RAMD) as a substitute to commercial reagent grade iron salt to synthesize iron nanoparticles. Chemical reduction method was employed to synthesize iron nanoparticles using sodium borohydride as reductant. The synthesized iron nanoparticles from RAMD and reagent grade iron salt solutions were quantified and characterized using analytical techniques such as ion chromatography (IC), Inductively coupled plasma-optical-emission spectroscopy (ICP-OES), X-ray diffraction (XRD), high resolution scanning electron microscopy (HRSEM), High resolution transmission electron microscopy-Selected area electron diffraction (HRTEM-SAED), X-ray fluorescence (XRF), Brunauer-Emmett-Teller (BET), Fourier Transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM), and Thermogravimetric analysis (TGA). The ICP-OES result revealed high iron concentration (4784.13 mg/L) and IC sulphate concentration (27, 204. 72 mg/L that iron sulphate salt was present in the RAMD solution. XRD results identified magnetic pure iron mineral phase for both samples and the SEM results revealed spherical crystal particle morphology as long interwoven strand with beads. The HRTEM results revealed a bead-like necklace structure with average particle size of 28.48 ± 4.2 nm and 24.23 ± 2.17 nm for iron nanoparticles synthesized from RAMD (A) and ferric chloride (B) respectively. The XRF elemental composition of the synthesized nanoparticles revealed A (97.4%) and B (99.9%) iron (Fe). BET surface area results for A is 89 ± 3.13 m²/g and B is 93 ± 3.16 m²/g, FTIR results revealed O-H, CO₂, Fe and FeO absorption peaks and the AFM results revealed more agglomeration in sample A than in B. The TGA of both synthesized iron nanoparticles were thermally stable. In conclusion, the iron-rich RAMD wastewater was found to be a good substitute for reagent grade iron salt use for making quality iron nanoparticles.

Keywords

Raw Acid Mine Drainage, Chemical Reduction, Reductant, Iron Nanoparticles, Characterization

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1. Introduction

Acid mine drainage toxic wastewater is generated from mines as a result of the oxidation of metal pyrite mine wastes/tailings with oxygen in the presence of water [1]. AMD is characterized with low pH, high electrical conductivity (EC), total dissolved solids (TDS) and elevated sulphate concentration [2-5]. Coal and Gold mines consist of more ferrous and ferric pyrites rich also in other toxic metal ions in low concentration [6]. AMD is a waste that is associated with mining and mineral processing activities all over the world especially where coal and gold mine activities are common [7]; [8]. AMD is one of the most prevalent causes of environmental pollution due to its high acidity ($\text{pH} < 3$) and toxic metal content [8]. Acid mine drainage (AMD) is a serious environmental issue which is associated with mining because of its acidic pH and potentially toxic elements (PTE) content.

Iron is the fourth most abundant metal found on the earth crust that is used for several purposes [9]. Iron nanoparticle is a strong reducing agent and it is very reactive with heavy metals, inorganic and organic compounds, textile organic dyes, emerging contaminants such as antibiotics, plastics, polycyclic aromatic hydrocarbon (PAHs), polyhydrocarbons (PHCs), Pesticides, endocrine disruptors, etc. [10]. Iron nanoparticles have high tendency to react rapidly with oxygen and water to form agglomeration; this is why nanoparticles are usually capped with various inorganic and organic materials as a support to protect them [10-12]. Nanoparticle is an emerging product synthesized using nanotechnology and it varies for different materials for different fields as the particle sizes are smaller than the bulk material and more reactive [13, 14]. Nanotechnology is used to synthesize nanoparticles of small particle sizes than the bulk which exhibits better qualities such as reactivity, size and large surface area. of iron nanoparticles is the approach Synthesis of magnetic iron nanoparticles by reduction method has a long time historical period dated as far back in the seventies and eighties [15]. With the aid of nanotechnology, bulk material can be manipulated to make them stronger, lighter, durable, extremely reactive and conductive. The synthesis of iron nanoparticles can either be top-down or bottom-up approach but the top-down approach involves breaking down of large solid material to nano-sized particles using different routes/methods such as physical and chemical methods which have been used in the synthesis of magnetic iron nanoparticles. Physical methods such as etching or machining [16-22]; milling [23, 24]), and chemical methods such as chemical [25-27], microwave [28-30], chemical precipitation [24, 31-34]), Sol-Gel [35, 36]), hydrothermal [37, 38]), sonochemical [39-41]), thermal decomposition [42, 43]), Chemical precipitation is the most common synthesis approach that yields relatively good quantities with control over the size and the morphology of nanoparticles. The quality of the iron nanoparticle has been improved to obtain good controlled particle size and

morphology [44]. Fabrication of iron nanoparticle is very important for its potential use in wastewater treatment process and other applications [16]). The positive impact of nanotechnology is that it is a fast growing technology because of its remarkable potential and application of manipulating bulky materials to a nanoscale [45, 46]. The aim of this study is to use acid mine wastewater as a substitute to commercial reagent grade iron salt to synthesize of iron nanoparticles.

2. Experimental

2.1. Sample Collection

Raw acid mine drainage (RAMD) water samples were collected from Randfontein gold mine in Gauteng Province in the Republic of South Africa in 5L plastic containers and stored in a refrigerator at 4 °C. The RAMD samples were filtered with 0.45 μm membrane filter to remove particulate matter present. Nitrogen gas was bubbled into the deionized water so as to de-oxygenate it for about 30 minutes before use. All chemicals used include ferric chloride, absolute alcohol, sodium borohydride which are reagent grade chemicals purchased from Kimix chemicals and used without further treatment or purification.

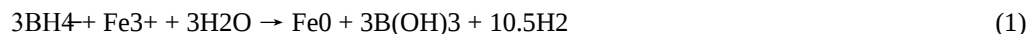
2.2. Synthesis

(A) The iron nanoparticle was synthesized at room temperature by reductive precipitation of iron-rich raw acid mine drainage (RAMD) with Sodium borohydride solution (NaBH_4). A volume of 100 mL of iron-rich RAMD sample solution was measured and poured into a 250 mL beaker and nitrogen gas was bubbled into the mine solution before subjecting to constantly stirring with the aid of a magnetic stirrer at the rate of 350 rpm. A concentration of 0.5 M sodium borohydride solution was added into 100 mL RAMD solution in drops which results in the formation of black crystal particles. The black crystal particle was separated from the solution mixture with the aid of a strong external bar magnet. The supernatant was separated from the residue and washed with 100 mL de-ionized water twice and 50 mL absolute alcohol once and sonicate for 10 - 15 minutes for proper dispersion of the particles. The residue was collected in a beaker and dried with nitrogen gas until a constant weight was obtained.

(B) A concentration of 0.1 M solution of commercial reagent-grade ferric chloride was prepared in a 500 mL beaker. A volume of 100 mL of the ferric salt solution was measured into a 250 mL beaker and saturated it with nitrogen gas for 30 minutes before subjecting it to constant stirring with a magnetic stirrer at 350 rpm. A concentration of 0.5 M NaBH_4 solution was added drop wise into the ferric chloride solution to form black precipitate. The black precipitate obtained was separated with a strong bar magnet, washed with 100 mL of deionized water twice and

rinsed with 50 mL absolute alcohol once and sonicated for 10 - 15 minutes to make the particles to disperse well. The precipitate was dried with nitrogen gas, weighed and recorded. The

drying and weighing process was repeated until a constant weight was obtained.



2.3. Characterization

The chemical composition of the iron-rich RAMD was determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Variance Liberty II) and a Dionex DX-120 Ion Chromatography (IC) was used to determine cations and anions respectively. The iron oxide crystallinity and mineral phases in the iron nanoparticle was identified using a Bruker D8 Advance X-ray diffractometer with Cu K α radiation (45 kV, 40 mA, $\lambda = 1.542 \text{ \AA}$). Scan was carried out from the range of 200 to 800 (2 θ). The elemental composition of iron nanoparticle was conducted using Phillips PW 1480 X-ray spectrometer. The structure and particle size of the nanoparticles were examined with both high resolution scanning electron microscopy (SEM-EDS) and transmission electron microscopy (TEM-EDX). The surface structure of iron nanoparticle was conducted using a SEM HITACHI S-4700 electron microscope. The TEM inner structure of the nanoparticle was determined using Phillips Tecnai F20 super-twain. The FTIR spectroscopy was used to determine functional groups present in the nanoparticles with attenuated total reflectance (ATR). The particle was dried inside a regulated oven at 105 °C for 24 hours to remove any trace of moisture present in the synthesized nanoparticles. BET surface area of the iron nanoparticle was measured at a temperature of 77.35K using a quantachrome NOVA 2000 surface analyzer. Atomic force microscope (AFM, Veeco, Nanoscope) was used to determine the Particle size and morphology of the synthesized iron nanoparticles.

3. Results

3.1. Analysis of AMD

Figure 1 present the concentrations of all the dissolved metals and anions in the RAMD solution. The ICP results indicated 71.10% iron content as the predominant and most abundant metal with the highest concentration while Aluminium (9.9%), Calcium (8.4%), Magnesium (6.59%), Manganese (1.90%), Sodium (1.26%) and Silicon (0.75%) composition. The IC results identified these anions NO $_3^-$, Cl $^-$, and SO $_4^{2-}$ concentrations in the RAMD solution to be 56.72 mg/L, ND and 22, 587 mg/L respectively. This implies that RAMD sample was rich in iron and sulphate which could be a good source of iron (Fe) salt that can be used as feedstock raw material for making iron nanoparti-

cles. The ICP-OES and IC results are presented in Figures 1 and 2 respectively.

3.1.1. Inductively Coupling Plasma Optical Emission Spectroscopy (ICP-OES)

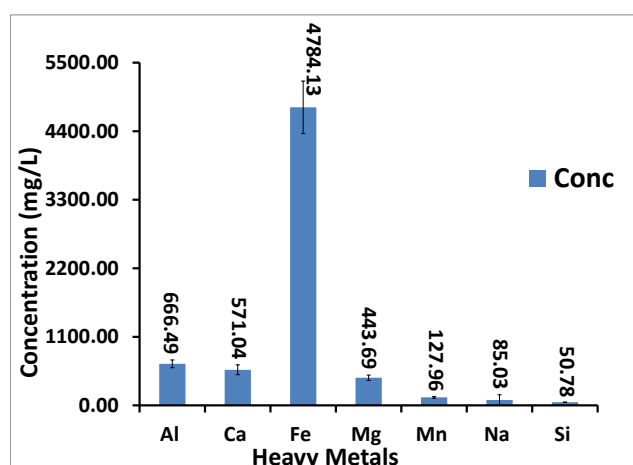


Figure 1. ICP concentration (mg/g) of major species in RAMD. Experimental conditions: concentration of RAMD = 4784.13 mg/L, pH = 2.06, EC = 7.92 and TDS = 6/14, n = 3.

3.1.2. Ion Chromatography (IC)

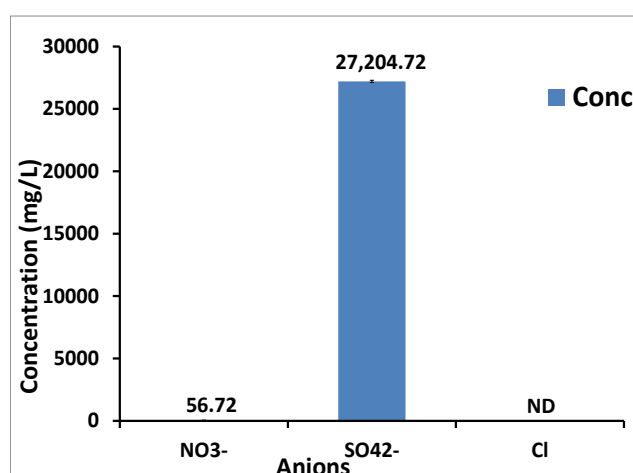


Figure 2. IC concentration (mg/g) of major anions in RAMD. Experimental conditions: concentration of RAMD SO $_4^{2-}$ anions = 27, 204.72 mg/L, pH = 2.06, EC = 7.92 and TDS = 6.14, n = 3.

3.2. Characterization

3.2.1. XRD

Figure 3 showed the powder XRD patterns of the synthesized iron nanoparticles BAI and BFCI. Similar diffraction pattern was obtained for both synthesized iron samples and all the peaks obtained from the XRD pattern can be indexed to body-centered cubic Fe. The diffraction pattern of the BAI (A) and BFCI (B) at the reflection angle was identified as pure iron (α -Fe) mineral phase indexed at angle of diffraction of 44-45° which indicate the presence of zerovalent iron according to [31]. The spectral peaks indexed at angle 2θ of 44.5° and 35.1° or 65.2° for the BAI and BFCI samples indicate the presence of both zerovalent iron (α -Fe) and iron oxide (FeO) crystalline mineral phases respectively [18, 30, 47-49]. The JCPDS file was used to identify the diffraction. The core of magnetic iron nanoparticles are composed of metallic iron (α -Fe) and the surface shell is formed as iron oxides (FeO) is the protective shell layer which agrees with the report of [50]. The shell layer was formed due to the exposure of the core nano zero-valent iron (nFe0) particles to the air after magnetic separation and drying process [51]. The diffraction peaks at angles 44.5° and 65.2° can be indexed to (110) and (200) lattice plane of cubic Fe mineral phase. The results obtained in this study agree with some of previous studies by (Li et al., [52]; Lin et al., [48]; Wang and Zhang, [53]). The XRD pattern presented in Figure 3 reveals that the Fe(0) characteristic peaks of $2\theta = 44.59$ and 64.62 , which indicates that the crystallization of the iron nanoparticles. The nanoparticles revealed relatively broad peak with smaller particle sizes and lower crystal structure. The good aspect of this study is that RAMD was successfully used directly to synthesize magnetic iron nanoparticles without any pretreatment. The synthesized iron nanoparticles from RAMD cited in the literature used caustic soda and sulphuric acid pretreatment process to generate the ferric ion solution before using ammonium hydroxide to synthesize the nanoparticles. Wei & Viadero Jr, [44], and Cheng et al. [54] reported the recovery of iron from synthetic RAMD using fuel cell technologies. Menezes et al. [55] used the alkali and acid pretreatment approach to generate ferric iron salt solution before using sodium borohydride to synthesize magnetic iron oxide nanoparticles which was characterized and identified as magnetite (Fe_3O_4) mineral phase.

3.2.2. SEM-EDS

The SEM morphology and spectral analysis of the synthesized iron nanoparticles are presented in Figure 4. The SEM images clearly showed the growth of chainlike aggregate of

the samples with spherical bead-like structures attached to one another in a thread like manner called a nanonecklace [56]. Similar structure was synthesized from ferric chloride using sodium borohydride solution by Wang & Zhang, [53]. The morphology of BAI (A) and BFCI (B) nanoparticles were spherical and the BAI (A) particle size ranged from 52-150 nm while the BFCI (B) particle size ranged from 49-140 nm. The spectral analysis of BAI (A) revealed the composition of the elements present in the synthesized nanoparticles to be O, Al, C, S, Fe, and Cu while the BFCI (B) contained O, C, Fe, and Cu. It was observed that the iron from RAMD was contaminated with Al and S but the Cu is from the grid where the sample was coated and the C is from the coating material on the grid. Figure 3 revealed the surface morphology of the synthesized iron nanoparticles from different iron salt sources measured at the same magnification revealed that their images were similar. The SEM-EDS chemical composition of BAI (A) and BFCI (B) nanoparticles identified iron as 71.69% and 78.52% respectively. This implies that iron (Fe) particles constitute the bulk of the iron nanoparticles formed from the reduction precipitation process. The SEM-EDS elemental analysis of the synthesized iron nanoparticles in Table 1 revealed that the RAMD sample contained some other elements like sulphur and aluminium which are some of the components of the RAMD sample identified from the ICP and IC analysis. The EDS and spectral analysis of the iron nanoparticles obtained from RAMD and commercial reagent grade iron chloride salt revealed that the same type of elements is present in Table 1.

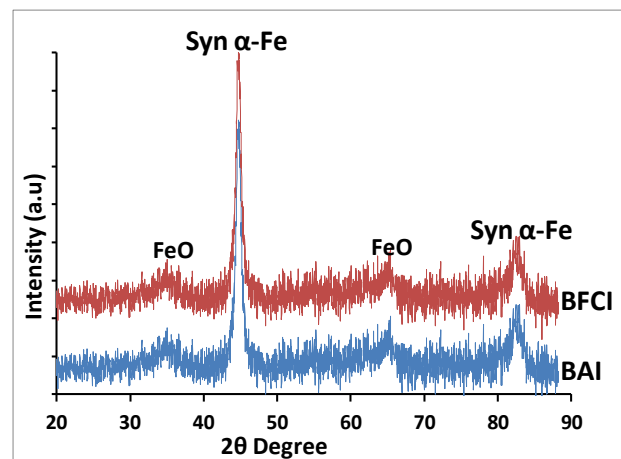


Figure 3. Powder X-Ray Diffraction pattern of synthesized iron nanoparticles BAI and BFCI. Experimental conditions: concentration of RAMD SO_4^{2-} anions = 27, 204.72 mg/L, pH = 2.06, EC = 7.92 and TDS = 6.14, n = 3.

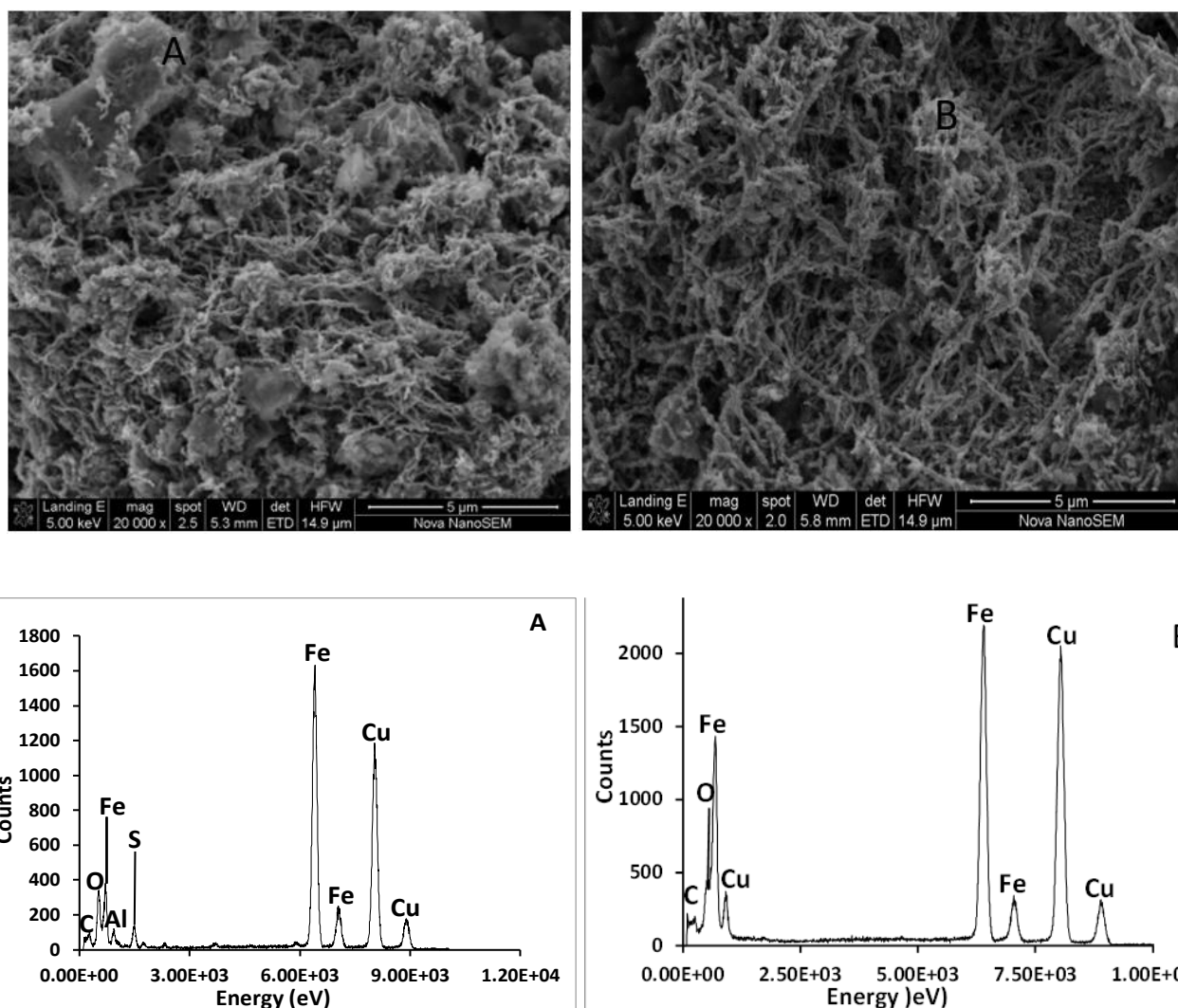


Figure 4. SEM image and EDS spectral analysis of BAI (A) and BFCI (B) nanoparticles. Experimental conditions: concentration of RAMD SO_4^{2-} anions = 27, 204.72 mg/L, pH = 2.06, EC = 7.92 and TDS = 6.14, n = 3.

Table 1. SEM-EDS elemental composition of BAI and BFCI nanoparticles. Experimental conditions: concentration of RAMD SO_4^{2-} anions = 27, 204.72 mg/L, pH = 2.06, EC = 7.92 and TDS = 6.14, n = 3.

ELEMENTS	BAI (% atomic wt)	BFCI (% atomic wt)
Fe	70.08 ± 5.85	75.8 ± 3.96
O	20.04 ± 0.6	24.11 ± 1.38
S	8.26 ± 0.03	ND
Al	1.66 ± 0.01	ND

3.2.3. Hrtm-saed

The synthesized nanoparticles formed a chainlike, aggregated structure because they have the natural tendency to remain in the more thermodynamically stable state during oxidation and corrosion to Fe(III) oxide/hydroxide [56]. The particle size, morphology and crystallinity of the BAI (A) and BFCI (B) na-

noparticles were determined by HRTEM-SAED. Figure 5 present the HRTEM-SAED morphology of the synthesized BAI and BFCI results revealed that they are spherical (nanospheres) in shape and joined together to form a chain-like structure called core-shell Fe-FeO nanonecklace with average particle size of 28.48 ± 4.2 nm and 24.23 ± 2.17 nm for A and B nanoparticles respectively [30]. The ring-type patterns of the selective area

electron diffraction (SAED) spots of A and B particles indicated that the nanonecklace structure were polycrystalline iron core with an amorphous iron oxide shell in both cases. The shape of the iron nanoparticles obtained in this study agrees with the results of previous studies [31]. The HRTEM revealed agglomeration in the synthesized iron nanoparticles from A and B which is more common than bare iron nanoparticles can be attributed to the drying process or high surface energy [58]. The spherical shape of the iron nanoparticle is characteristic of particles that are precipitated in solution. The similarities in the synthesized iron nanoparticles A and B morphology, particle sizes and SAED revealed both materials were almost similar in quality, even though BAI was prepared from waste effluent whereas the BFCI was prepared from reagent grade iron chloride.

The particle size distribution of A and B nanoparticles presented in Figure 5 was obtained using imageJ software. The histogram of A and B nanoparticle sizes was determined using imageJ software plot of HRTEM technique to show the crystal distribution of A and B have an average crystal size of 28.48 ± 4.2 nm and 24.23 ± 2.17 nm respectively. The crystal size of synthesized nanoparticles A is a little bit bigger than B particle. The XRF elemental composition of Fe for B was 99.6% while the EDS composition was 78.52% and XRF for A was 96.8% while the EDS composition was 71.69%. The results showed that the XRF analysis gave larg-

er composition of Fe than the EDS samples A and B nanoparticles. The sample A contained Al and S co-precipitated with the synthesized iron nanoparticles from RAMD while sample B particles synthesized from FeCl_3 contained no Al and S. This co-precipitation of S can be attributed to the composition of sulphate anion associated with the iron-rich RAMD used for the synthesis. Traces of sulphur and aluminium in the RAMD were found in the synthesized iron nanoparticles.

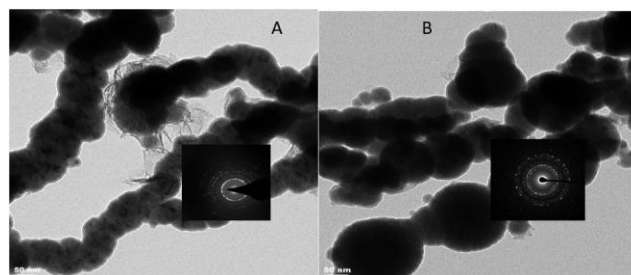


Figure 5. HRTEM-SAED morphology of BAI (A) and BFCI (B) nanoparticles. Experimental conditions: concentration of RAMD SO_4^{2-} anions = 27, 204.72 mg/L, pH = 2.06, EC = 7.92 and TDS = 6.14, $n = 3$.

3.2.4. XRF

Table 2. XRF elemental composition of iron nanoparticles A and B synthesized from RAMD and reagent grade iron chloride salt solutions with NaBH_4 as reductant. Experimental conditions: concentration of RAMD SO_4^{2-} anions = 27, 204.72 mg/L, pH = 2.06, EC = 7.92 and TDS = 6.14, $n = 3$.

Sample	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO
BAI	97.4 ± 0.01	0.07 ± 0.01	0.68 ± 0.01	0.15 ± 0.01
BFCI	99.6 ± 0.03	ND	ND	ND

ND = Not detected

The XRF elemental composition of the synthesized A and B iron nanoparticles presented in Table 2 confirmed the presence of Fe, Si, Ca and Al in sample A. The XRF confirmed the presence of Fe, O, Al and S in BAI while that of BFCI contained only Fe which implies that BFCI is purer than BAI sample. The presence of SiO₂, Al₂O₃ and CaO in the BAI can be attributed to the presence of impurities from the source of the iron salt.

3.2.5. BET

Figure 6 presents the N₂ adsorption-desorption isotherms of the synthesized iron nanoparticles A and B. The hysteresis loops of the iron nanoparticles A and B belong to adsorption classification of H3 with adsorption-desorption classification of Type

H2 which indicate mesoporosity [56, 57]. The structures of these synthesized iron nanoparticles A and B revealed a large surface area within a relatively small volume of the powdered particles. The surface area of A and B are 89 ± 3.13 m²/g and 93 ± 3.16 m²/g respectively while the surface area for samples A and B have higher values than some synthesized iron particles reported in the literature [49, 53, 58, 59]. The BET of the synthesized iron nanoparticles A and B have less value than some reported in the literature [60]. The iron nanoparticles A, synthesized from iron-rich RAMD had smaller surface area value than the B synthesized from reagent grade iron chloride purchased in the market. The BET results of the synthesized iron nanoparticles A and B are similar to what was obtained in some literatures [47, 56, 61].

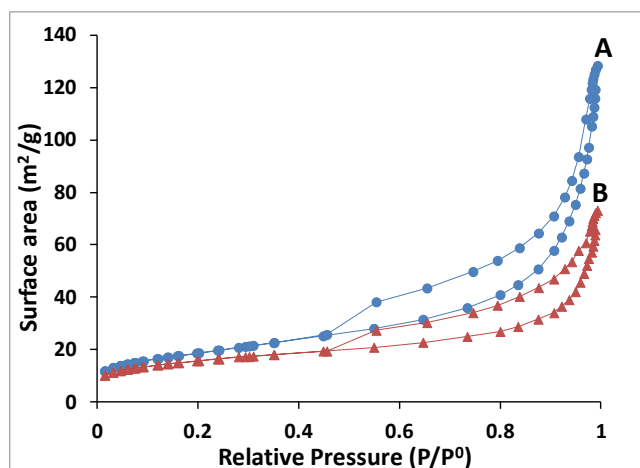


Figure 6. BET surface area N₂ adsorption-desorption hysteresis loop of BAI and BFCI nanoparticles. Experimental conditions: concentration of RAMD SO₄²⁻ anions = 27, 204.72 mg/L, pH = 2.06, EC = 7.92 and TDS = 6.14, n = 3.

3.2.6. FTIR

The FTIR absorption spectra of synthesized iron nanoparticles A and B presented in Figure 6 were scanned between 4000 cm⁻¹ and 400 cm⁻¹. The spectrum for pure FeO is characterized by a broad region composed of vibration bands at 693 cm⁻¹, and 540 cm⁻¹ [62, 63]. The absorption spectra of the iron nanoparticle A and B showed peaks at 540 cm⁻¹ and 693 cm⁻¹ and the band at 693 cm⁻¹ was an indication of iron oxides. The band at 625 cm⁻¹ can be assigned to Fe—O stretching vibrations [64], and it was detected in the two iron nanoparticle samples A & B. Roonasi, [65] reported that the bands of iron nanoparticle is around 360 cm⁻¹ and 570 cm⁻¹ corresponded to the bending and stretching vibrations of Fe—O bonds that are characteristic of the crystalline lattice of Syn iron. Therefore, the sample B showed strong absorption peaks at 449 cm⁻¹ and 554 cm⁻¹ which fall within the range of magnetic iron absorption band [65, 66]. The samples A and B iron nanoparticles shows broad absorption stretching bands of O—H at 3248 cm⁻¹ which can be attributed to the presence of O—H in the water or alcohol used in washing the synthesized iron [67]. The absorption band at 1621 cm⁻¹ of the synthesized iron nanoparticles confirmed traces of water H—O—H bending [68]. The stretching absorption bands at 1093 and 1117 cm⁻¹ of the synthesized iron nanoparticles C—O confirmed the presence of O—H in the iron nanoparticles which could be due to the fact that the particles were washed with water and ethanol before drying. The synthesized iron nanoparticles A and B showed a C=O absorption stretching band at 2164–2045 cm⁻¹ which revealed that the iron nanoparticles have strong affinity for CO₂ gas [69]. The synthesized iron nanoparticle BAI and BFCI absorption bands appear at almost the same wave numbers.

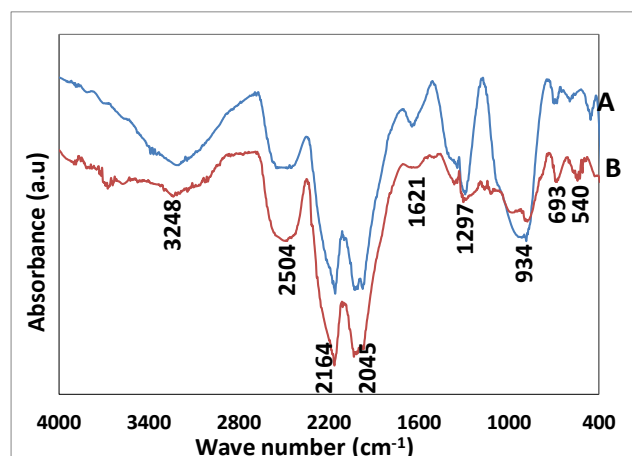


Figure 7. FTIR spectral analysis synthesized magnetic iron nanoparticles BAI (A) and BFCI (B). Experimental conditions: concentration of RAMD SO₄²⁻ anions = 27, 204.72 mg/L, pH = 2.06, EC = 7.92 and TDS = 6.14, n = 3.

3.2.7. AFM

The atomic force microscopy (AFM) presented was used to determine the smoothness/roughness of magnetic iron nanoparticles presented in Figure 8. Sample A showed more agglomeration than B with particle size ranging from 64–67 nm when measured. The particle size above 10 nm cannot be used to obtain the morphology of the magnetic iron nanoparticles but it will require the use of SEM and TEM.

3.2.8. TGA and DSC

TG and DSC curves of the synthesized iron nanoparticles are presented in Figure 9. The samples showed continuous weight loss as the temperature increased from room temperature to 900 °C. The gradual decrease in weight of the samples until close 300 °C before a sharp fall to around 490 °C before it attain thermal stability to 900 °C. All the curves revealed a common region of weight loss, which is accompanied by an endothermic process at the temperature range around 300 °C to 490 °C, by indicating the loss of physically absorbed water. The weight loss at can be attributed to the dehydration present on the surface of the nanoparticles [70]. However, an endothermic process occurs at around 300 °C, which is the temperature assigned to the dehydration process [11]. All the curves present a common region of weight loss, accompanied by an endothermic process at the temperature range from 300 °C to 490 °C, which indicates the loss of physically absorbed water [29]. The main weight losses at 200–350 °C are attributed to the decomposition of organic components, which were present on the surface of the nanoparticles [71]. Both synthesized iron nanoparticles are thermally stable.

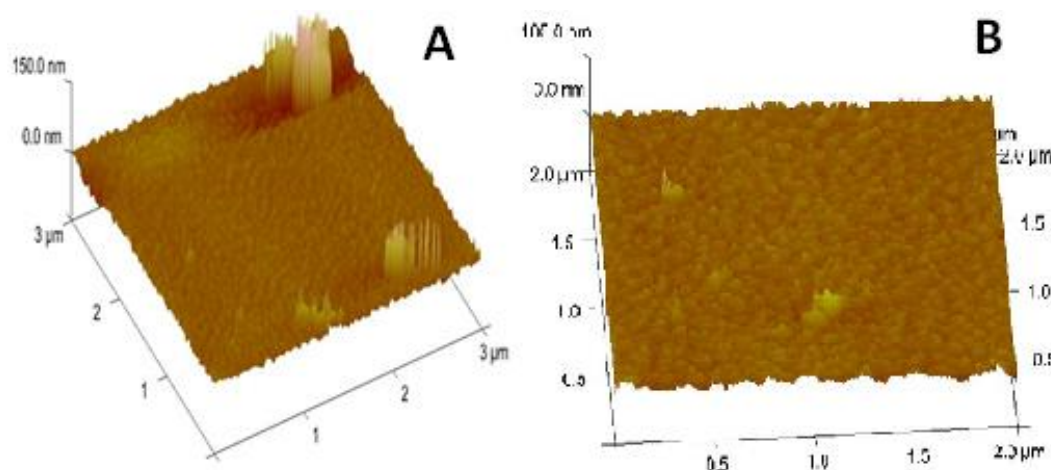


Figure 8. AFM analysis of synthesized magnetic iron nanoparticles BAI (A) and BFCI (B). Experimental conditions: concentration of RAMD SO_4^{2-} anions = 27, 204.72 mg/L, pH = 2.06, EC = 7.92 and TDS = 6.14, $n = 3$.

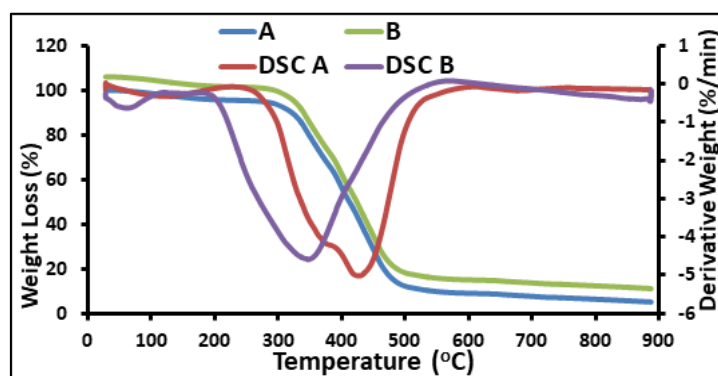


Figure 9. TGA analysis of synthesized magnetic iron nanoparticles BAI (A) and BFCI (B). Experimental conditions: concentration of RAMD SO_4^{2-} anions = 27, 204.72 mg/L, pH = 2.06, EC = 7.92 and TDS = 6.14, $n = 3$.

3.3. Conclusion

Iron-rich RAMD which is an environmental nuisance has been found to be a good source of ferric iron salt, a raw material for the synthesis of magnetic iron nanoparticles. This study used iron-rich RAMD as a cheap ferric iron salt feed-stock to synthesize magnetic iron nanoparticle so as to save cost instead of purchasing expensive commercial reagent grade iron salt which is an expensive chemical. The synthesized iron nanoparticles from RAMD and Commercial reagent grade ferric chloride salt were characterized with several techniques such as ICP, IC, XRD, SEM-EDS, HRTEM-SAED, XRF, BET, FTIR, AFM and TGA/DSC. Pure iron mineral phase was identified for both synthesized iron nanoparticles A and B in the XRD revealed crystallinity and the particle sizes of A was 23.7 nm and B was 26.4 nm. Both iron nanoparticle samples have similar morphology for HRSEM and the HRTEM. The HRTEM of the samples A and B particle sizes were obtained using ImageJ are: 28.48 ± 4.2 nm and 24.23 ± 2.17 nm respectively. The XRF elemental composition for A (97.4%) and B (99.6%) showed

high amount of pure iron content, both particles showed absorption stretching and bending of Fe and FeO at different bands with characteristic peaks at certain wave number. BET surface area results for iron nanoparticles A is 89 ± 3.13 m²/g and B is 93 ± 3.16 m²/g, and the AFM revealed that the synthesized iron nanoparticles from iron-rich RAMD had some agglomeration identified by the HRTEM image which can be attributed to impurities present in the acid mine water. The TGA of the samples revealed strong thermal stability. It is also possible to synthesize magnetic iron nanoparticles of high quality with the use of wastewater like AMD that is a serious environmental problem. The iron nanoparticles synthesized from two different iron salt sources had almost similar qualities when characterized with various techniques. In conclusion, the iron-rich AMD is composed of iron sulphate from the ICP and IC analysis, and it is a good substitute of commercial reagent grade iron salt to synthesize magnetic iron nanoparticles as its application in the treatment of environmental problems like AMD and others applications.

Acknowledgments

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Abbreviations

RAMD	Raw Acid Mine Drainage
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
HRSEM	High Resolution Scanning Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
BET	Brunauer-Emmett-Teller
FTIR	Fourier Transform Infra-red Spectroscopy
AFM	Atomic Force Microscopy
TGA	Thermogravimetric Analysis
AMD	Acid Mine Drainage
PTE	Potentially Toxic Elements
PAHs	Polycyclic Aromatic Hydrocarbons
PHCs	Polyhydrocarbons
NaBH ₄	Sodium Borohydride
ATR	Attenuated Total Reflectance
BAI	Borohydride AMD Iron Nanoparticles
BFCI	Borohydride Ferric Chloride Iron Nanoparticles
SAED	Selective Area Electron Diffraction
EDS	Energy Dispersive Spectroscopy
EDX	Energy Dispersive X-ray
DSC	Differential Scanning Calorimetry

Conflicts of Interest

The authors declare no conflicts of interest.

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