

Removal of Heavy Metals from Industrial Acidic Effluents Using Electroless Plating

Thandiwe Sithole* and Freeman Ntuli

Abstract—Acid mine drainage (AMD) is one of the biggest issues faced by the mining and mineral processing industries in terms of removing heavy metals from the effluents. The present study investigated the effects of glyoxylic acid, hydrazine and dimethylamine borane as reducing agents and the effect of using Ni, Fe, basic oxygen furnace slag (BOFS) and granulated blast furnace slag (GBFS) as seeding materials to remove metals from acidic effluents respectively. The experiments were conducted using acidic mine effluent in a 0.5 L batch reactor using different seeding materials and reducing agents respectively. The study is the first of its kind to examine and compare all four seeding materials using different reducing agents respectively. X-ray diffraction (XRD) patterns, scanning electron microscope (SEM), and a Fourier Transform Infrared (FTIR) spectrometer were used to analyse the seeding material before and after Electroless plating. The study suggests that BOFS is a effective seed together with hydrazine reducing agent that yielded a 99.9% removal of Fe (III), whilst Ni and Fe powder failed to seed effectively. During reduction precipitation, nucleation and breakage were identified as the predominant particulate processes based on particle size distribution (PSD) evolution and its moments. There were significant mineral phases formed, such as bowenite $\text{Ca}_2(\text{Al}, \text{Fe})_2\text{O}_5$, which formed by replacing Si with Al and Fe in all tetrahedral coordinations between Al, Fe and Si, suggesting chemisorption being a dominant mechanism.

Index Terms—Electroless plating, heavy metal, reducing agents, seeding material

I. INTRODUCTION

A variety of industrial activities, including mining, metal reduction, and smelting, discharge acidic mineral effluents that contain iron as a major heavy metal and aluminum and manganese as minor metals [1]. Whenever such effluents are discharged into the aquatic system, minerals and salts are accumulated in the water bodies, the water is acidified, and metals are precipitated on the sediments. As a result of all these factors, aquatic ecosystems are adversely affected and water is not suitable for human consumption or agriculture without prior treatment. A significant amount of water and soil pollution occurs as a result of this acidic mineral effluent. Thus, it is important to remove metals from acidic wastewater. Metals have been removed from effluents using several technologies (adsorption, precipitation, and ion exchange) over the years, but the majority of these technologies do not recover metals for reuse. Instead, precipitation generates

metal-laden waste which needs to be disposed of. Furthermore, concentrated metal solutions cannot be handled by ion exchange due to organics and other solids in wastewater fouling the matrix. [2–4]. According to several authors [5–12], sorption is an efficient and effective method for removing organic and inorganic pollutants from wastewater streams, but it has low selectivity and produces waste. The efficiency, effectiveness and applicability of Electroless plating have attracted much attention in the recovery of heavy metal, as metals are recovered in their elemental state, allowing them to be re-used. In electroless plating, a complex compound and a chemical reducer react to deposit a continuous layer on a catalytic surface under controlled conditions. Studies on electroless plating in acidic effluents like acidic mine water are limited. In most studies, alkaline conditions (pH > 7) or mildly acidic conditions (pH 4) were used conditions [13–17]. Nickel powder and hydrazine have been investigated as seeding and reducing agent, respectively. According to Mashifana [13], removal efficiencies of over 99% for Ni and Co and about 98% for Cu, Ni, Cu, Co and Fe were effectively reduced to their elemental states. In a subsequent study [14], carried out a feasibility study by applying a reduction crystallization using hydrazine as the reducing agent. There were over 71% Fe, 14% Ti, 5.1% Mn, 4.12% Cu, and 2.4% Zn detected in the feedstock. Over 99% of heavy metals were effectively removed. Moreover, the removal and recovery of aluminium and manganese metal using hydrazine as a reducing agent was examined by [15]. The results showed that Mn can be effectively reduced by hydrazine with average reduction efficiencies of 99.8 and 99.5% when it is used as a single metal (Mn-only) reducing agent, rather than when used in a mixed metal system (Mn and Al). Naim *et al.* [16], examined the removal of pollutants from wastewater containing high levels of cyanide and metals using Electroless plating. Metal ions were effectively removed by Fe^{2+} reduction (for Cr^{6+}) and subsequent precipitation (for Cr^{3+} , Cu^{2+} , and Ni^{2+} ions), while cyanide was removed by forming insoluble complex compounds with Fe^{2+} . Lastly [17] also found that Ni powder seeding and sodium borohydride reducing agents were effective in removing over 99% of heavy metals. Thus, this study is the first to investigate and compare four different seeding materials and reducing agents respectively to remove and recover metals in their elemental state from acidic wastewater under acidic conditions. Furthermore, scarce research has been conducted on the use of Fe powder, basic oxygen furnace slag (BOFS), and granulated blast furnace slag as seeding materials and comparing them to Ni powder, which is commonly used in electroless plating. GBFS and BOFS are readily available by products that can be used as cheaper seeding material compared to Ni powder. Electroless

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plating due to slags' increasing environmental impact, assessing how to use or repurpose these low-cost materials is an important issue [18]. The reducing agent hydrazine is commonly used in Electroless plating. Although the same technique could potentially be used with different seeding materials and reducing agents respectively, no study has been conducted to compare Fe powder, GBFS and BOFS performance with Ni powder. Therefore, this study evaluates the effectiveness of Fe powder, GBFS and BOFS together with different reducing agents to remove Fe from acidic effluents. Various metal cations can be reduced to an elemental state using reducing agents.

II. MATERIALS AND METHODS

A. Materials

Sigma Aldrich supplied $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, for the preparation of a 1000 ppm synthetic metal solution. For reducing agents, Sigma Aldrich supplied glycolic acid, dimethylamine borane (DMAB), and hydrazine. As seeding materials, Sigma Aldrich supplied nickel powder and iron powder along with ArcelorMittal South Africa supplied GBFS and BOFS. pH was adjusted with H_2SO_4 supplied by Rochelle Chemicals.. For AAS analysis, Fe, Mn, and Al standards of 1000 ppm were used as calibration standards. Sample digestion and preservation were carried out with HCl and HNO_3 HCl and HNO_3 were used for sample digestion and preservation.

B. Apparatus

The experiments were conducted in a 1000 mL batch reactor. Metler Toledo dual meters (Sevenduo pH/conductivity meter equipped with ISM electrode for pH and conductivity probe for conductivity) were used to measure pH and conductivity of all samples during Electroless plating. Electroless plating. After reduction Fe concentrations were measured using atomic absorption spectroscopy (AAS; ICE 3000 series). The elemental composition of the seeding material was determined using XRF (Rigaku ZSX Primus II). Using the laser diffraction technique, the PSD of the powder was determined with the Malvern Particle Analyser Mastersizer (2000). Prior to and after the Electroless plating experiments, the seeding material was characterized using FTIR (Thermo scientific IS10). Electroless plating. The seeding materials were analyzed by XRD to identify their mineral phases. To determine the effect of reducing agents, the powder morphology was captured using a scanning electron microscope (SEM; Tescan Vega 3 XMU 1).

C. Preparation of Synthetic Metal Solution

A 98% concentration of H_2SO_4 was used to acidify the RO water to pH 2. Reverse osmosis (RO) water was mixed with 4.83 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Dissolving the salt in the solution was achieved by stirring the solution. To make a 1000 ppm Fe^{3+} solution, 1500 mL of the resultant solution was made up to 1500 ml. Effect of using a different reducing agents system on reduction of Fe^{3+} .

According to Table I, in a mixed metal system, all metal ions must be reduced in stoichiometric amounts to achieve their metallic state: In order to determine the effect of

hydrazine, dimethylamine borane, and glyoxylic acid on mixed metal systems, the above procedure was repeated with each of these reducing agents.

TABLE I: REDUCING AGENT ADDED PER EXPERIMENTAL RUN

Types of reducing agents	Amount of reducing agents to be added (g)
Hydrazine	1.62
DMAB	1.84
Glyoxylic acid	3.15

D. Electroless Plating Experiments

1) Electroless plating of Fe^{3+} solution using different reducing agents

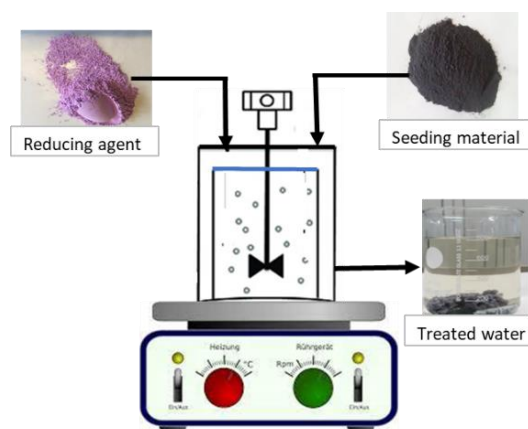


Fig. 1. Schematic diagram of electroless plating.

In the reactor, 500 mL of synthetic solution containing 1000 ppm Fe^{3+} was added. In addition, 30 g of seeding material were added. A temperature of 60 °C was then applied to the solution. An experimental run involved adding 0.43 g of 98% concentrated hydrazine. pH measurements were taken every 30 s during the 3 min Electroless plating reaction. Electroless plating Once the solution had been agitated for 3 min, it was cooled and the heating was stopped. Clear supernatants were carefully decanted from the reactor after settling. They were left behind as seeding material. AAS was used to analyze the supernatant sample. A fresh Fe^{3+} solution was used two times with the same seed from the previous reduction cycle. A solid product was discharged from the reactor after the third densification (batch reduction). Following the filtering, 100 mL of the sample was examined with an AAS to determine the residual metal concentration. As a comparison step, dimethylamine borane and glyoxylic acid were used to determine their effect on a single metal system (Fe^{3+}).

E. The Effect of Using Different Seeding Material

Different seeding materials were investigated using the same procedure, including Ni powder, Fe powder, BOFS, and GBFS. In all experiments, 30 g were used for each seeding material.

Samples were prepared for Metal analysis by quantitatively transferring 100mL of the Fe^{3+} sample into a 250 mL volumetric flask; the sample digestion was performed. To acidify the sample, 2 mL of 1:1 HNO_3 were added to 1 ml of 1:1 HCl, then added to the mix. After heating to 358.15 K, the volumetric solution was evaporated to 20

mL. In order to make this solution up to volume, the solution was cooled, transferred to a 50mL volumetric flask, and reverse osmosis (RO) water was added to fill to volume. AAS was then used to analyze the sample along with calibration standards prepared by appropriate dilutions of Fe, Al and Mn stock solutions.

III. RESULTS AND DISCUSSIONS

A. Effect of Fe and Ni Powder as Seeding Materials

Fig. 2 shows the concentration of metals after Electroless plating.

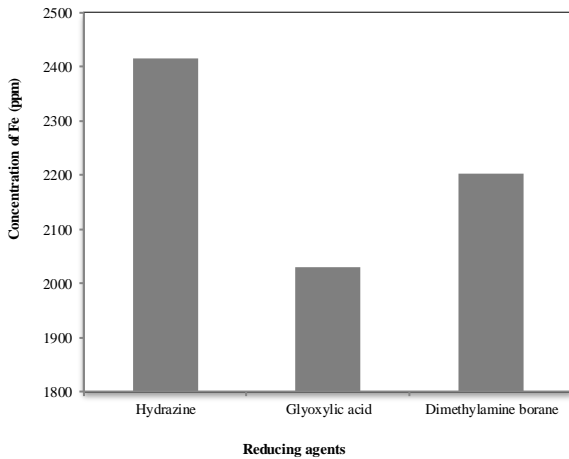


Fig. 2. Concentration of Fe using Fe powder as a seed.

Fe concentrations increased in all experiments, as shown in Fig. 2. As a result of the solution's acidity (pH = 2), Fe has been leached from the seeding material. A further study was then conducted using Ni and Fe powder as seeding material to determine whether pH affected seeding material leaching behaviour as shown in Fig. 3.

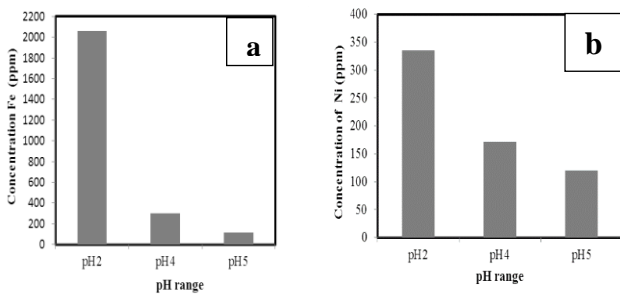


Fig. 3. (a) Concentration of Fe using Fe powder as a seeding material, (b) Concentration of Ni in Fe³⁺ solution using Ni as a seeding material.

As shown in Fig. 3(a), seeding material leached at pH 2. Higher pH suppresses Fe dissolution from seeding materials, therefore reducing Fe leaching. Fig. 2(b) shows Ni leaching into Fe³⁺ solution from the seeding material. The concentration of Ni leached decreased, as pH increased. The dissolution of seeding material under acidic conditions has led to the conclusion that Ni and Fe powder cannot be used as seeding materials. Thus, In order to favor Electroless plating under acidic conditions, further research was conducted using alternative seeds. Hence, the effect of using different slags was investigated.

B. Effect of Using GBF and BOF Slags as Seeding Material

Fig. 4(a) shows residual Fe concentrations using GBFS as a seeding material; where as compared to other reducing agents, hydrazine produced the lowest residual content. In spite of 76% removal by hydrazine, Fe concentrations were still above the guidelines' limit as outlined in volume 1 [19]. A variation in residual concentration is shown in Fig. 4(b) using BOFS as a seeding material. Based on the results, the use of BOFS significantly reduced Fe concentration by 98%. This is owing to BOFS being a reduction catalyst due to its high Fe content and also the presence of CaO, which neutralizes the solution and allows Fe to be removed. Using the various reducing agents, all residual concentrations were below 20 mg/L, which is an acceptable concentration for disposal into sewers and rivers. The BOFS showed a significant reduction as compared to GBFS, suggesting that it could be used as alternative seeding material.

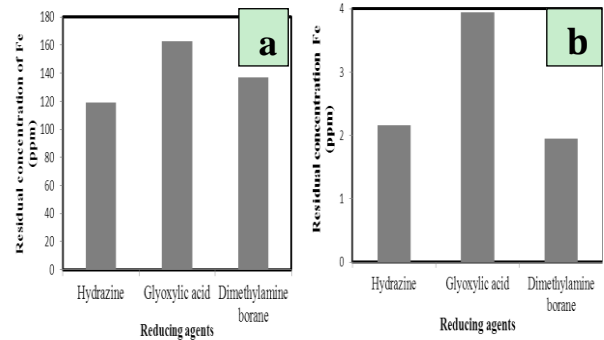


Fig. 4. (a) Fe residual concentrations after seeding with GBFS and using different reducing agents, (b) Fe residual concentrations after seeding with BOFS and using different reducing agents.

The subsequent experiments were conducted using BOFS as a seeding material since it was able to remove the highest percentage of Fe at pH 2 when used as a seeding material.

C. Metal Removal from a Single Metal System Using BOFS as a Seeding Material

1) Effect of using BOFS as a seeding material with different reducing agent on Fe reduction

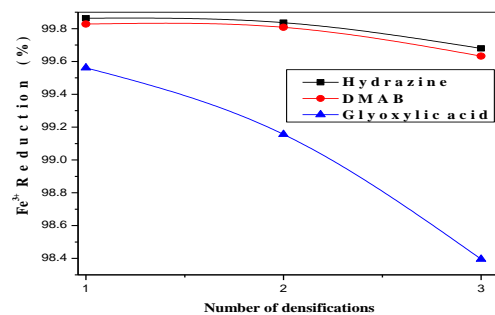


Fig. 5. % Reduction of Fe³⁺ using BOFS as a seeding material and three different reducing agents.

The percentage of Fe³⁺ removed by subsequent batch reductions referred to as densifications, is shown in Fig. 5. In comparison with the other reducing agents, hydrazine removed the most metal. For all the reducing agents, the % reduction of Fe³⁺ decreased from the 1st to the 3rd densification. There was, however, a significant increase in

the removal of dimethylamine and hydrazine borane in all three densifications compared to glyoxylic acid, which had the lowest removal rate of 98.4%. For this to occur, there must be a more negative anodic reaction than a more positive cathodic reaction in order to ensure that the reaction proceeds spontaneously by using a thermodynamic consideration which states that anodic reactions should be more negative than cathodic reactions. Dimethylamine borane ($E^0=-1.10$ V) and hydrazine ($E^0=-1.17$ V) have more negative redox potentials than Fe^{3+} ($E^0=-0.06$ V). In comparison to the metal being reduced, the potential of glycolic acid (1.07 V) is positive, indicating glyoxylic acid was non spontaneous. Table II shows the ANOVA test results indication that the metal removals comparing the reducing agent (DMAB, hydrazine and glyoxylic acid) were insignificantly difference since $F < C_{critical}$

TABLE II: STATISTICAL ANOVA TEST

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	10.27	2	5.13	5.00	0.052	5.14
Within Groups	6.15	6	1.025			
Total	16.42	8				

2) The variation in pH and reduction potential on Electroless plating

TABLE III: REDUCTION POTENTIAL AND pH USING HYDRAZINE AND GLYOXYLIC ACID

	Hydrazine				Glyoxylic acid			
	1st run		2nd run		1st run		2nd run	
Time	pH	mV	pH	mV	pH	mV	pH	mV
30	11.3	-281	11.4	-288	10.5	-135	10.6	-134.8
60	11.2	-285	11.4	-287	10.6	-137	10.7	-136.3
90	11.3	-286	11.4	-289	10.9	-137	10.8	-136.9
120	11.3	-286	11.4	-289	10.9	-137	10.8	-136.9
150	11.3	-285	11.4	-288	11.0	-136	10.8	-135.7
180	11.3	-284	11.3	-286	11.0	-136	10.8	-135.1

TABLE IV: REDUCTION POTENTIAL AND pH USING DIMETHYLAMINE BORANE

	Dimethylamine borane			
	1st run		2nd run	
Time	pH	mV	pH	mV
30	11.4	-280	11.5	-276
60	11.4	-280	11.5	-275
90	11.4	-279	11.5	-276
120	11.4	-278	11.5	-275
150	11.4	-277	11.5	-274
180	11.3	-275	11.5	-274

A linear relationship between the acidity of the solution and the reduction potential is shown in Table III and Table IV. In comparison to dimethylamine borane, hydrazine shows a greater reduction efficiency, as its reduction potential is more negative. DMAB and hydrazine have the highest reducing capacities between pH ranges of 8–11 and 6–10, respectively, so their percentage reduction was higher. The increasing pH in BOFS is caused by the neutralization of solution by CaO, the basic constituent. With glyoxylic acid, the pH increased, indicating that the reduction slowed with time, resulting in

the lowest percentage reduction. With increasing pH, reducing agents have a greater reduction potential.

3) The effect of Electroless plating on BOFS PSD

TABLE V: MOMENTS OF THE PSD BEFORE AND AFTER REDUCTION

	Before reduction		After Reduction	
	BOFS seed	Hydrazine	Glyoxylic acid	Dimethylamine borane
$0^{th}(m^{-3} \times 10^{14})$	3.54	15.9	6.78	10.0
$2^{nd}(m^2m^{-3} \times 10^3)$	1.75	12.6	4.76	10.1

Table V shows that the particle number and external surface area are represented by the 0th and 2nd moments, respectively. All reducing agents showed increased number and surface area compared to the seed before reduction, indicating nucleation or breakage. Compared to glyoxylic acid, hydrazine and dimethylamine borane showed greater increases than glyoxylic acid, indicating that nucleation dominated.

4) Effect of Electroless plating on particle morphology

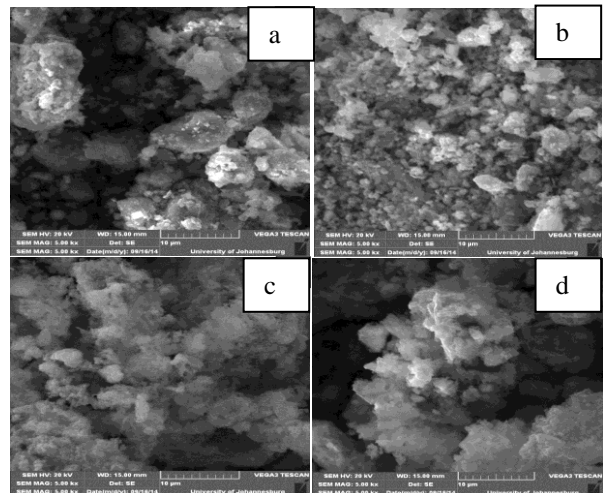


Fig. 6. SEM of the BOFS (a) before reduction, (b) BOFS obtained using Hydrazine; (c) BOFS obtained using dimethylamine borane; (d) BOFS obtained using glyoxylic acid.

As shown in Fig. 6, there is a change difference between the micrographs before and after Electroless plating on BOFS (seed). A smaller particle size was observed in micrograph (b) than in micrograph (a). Images (c) and (d) show porous, dense aggregates formed by spherical crystals.

5) Effect of Electroless plating on BOFS chemical composition

A comparison of BOFS composition before and after Electroless plating can be seen in Table VI. Due to dissolution, the basic oxides MgO and CaO decrease which results in neutralization and pH dramatically increases. Fe content increases as a result of Fe being removed from solution or precipitated. As a result of the change in relative proportions of other elements, SiO₂ content was not significantly affected during reduction. Fig. 7 shows the FITR spectra of the BOF slag before and after reduction.

TABLE VI: ELEMENTAL COMPOSITION OF BOFS BEFORE AND AFTER REDUCTION

Elements	REDUCTION			
	Before reduction	Hydrazine	Glyoxylic acid	Dimethylamine borane
P ₂ O ₅	0.99	0.99	0.78	0.99
MgO	3.30	2.63	2.57	2.45
Al ₂ O ₃	6.63	6.90	7.32	7.17
SiO ₂	14.8	14.2	14.4	14.2
CaO	41.1	37.2	35.6	34.8
MnO	3.91	4.07	4.05	3.99
Fe ₂ O ₃	27.3	32.2	33.5	32.8

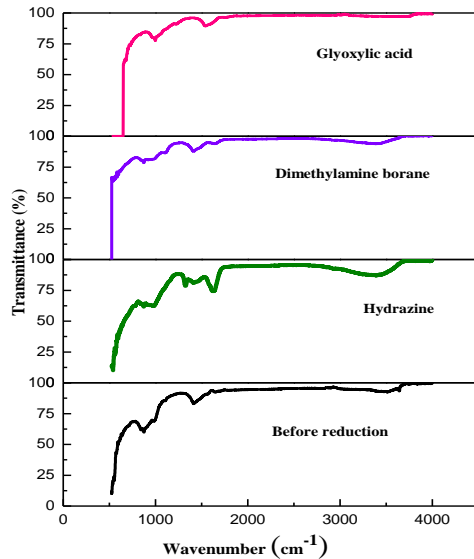


Fig. 7. FTIR Spectra for BOFS before reduction and after reduction with different reducing agent.

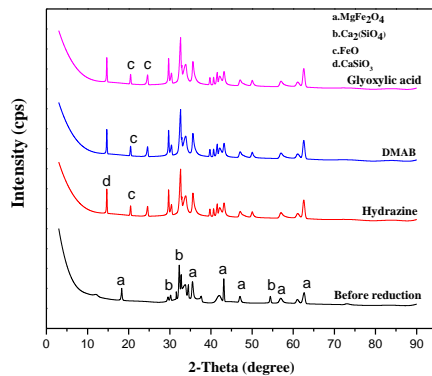


Fig. 8. XRD patterns before and after reduction.

Fig. 7 shows whether hydroxides precipitated after the Electroless plating. FTIR spectra were not indicative of the presence of Mn-OH, Fe-OH, and Al-OH bands as the bands at 1550–1850 cm⁻¹, 3365–3618 cm⁻¹ and 3360 cm⁻¹ respectively, in BOFS before and after reduction [20, 21]. BOFS spectra before and after reduction are quite similar, mainly between 1800 and 4000 cm⁻¹ in the mid-IR range. There are bands at 1000 cm⁻¹ that indicate the presence of P₂O₅ [22]. As compared to before reduction, there was a shift to the right and an increase in intensity at 810 cm⁻¹. Consequently, this band can be used as an indicator of heavy metal sorption. Its intensity relates to the ion exchange in a lower extent. During reduction, the wavenumber of CaSiO₃ moved from 1500cm⁻¹ to 1660cm⁻¹. A chemisorption mechanism is strongly suggested by this shift [23]. Fig. 8 shows the XRD spectra for BOFS.

Fig. 8 shows that magnesium ferrite (MgFe₂O₄) and larnite Ca₂(SiO₄) were the only two major phases identified in the BOFS before and after Electroless plating. These similar dominant phases of BOFS have been reported by several authors [24, 25]. The intensities of the peaks indicate the quantity of minerals present in the samples, indicating that these phases were major. The XRF and SEM/EDS results confirm that FeO is one of the main mineral phases in BOFS before reduction, though the figure before reduction had a lower FeO content. The increase in FeO after reduction is supported by the results of XRF and SEM/EDS. FTIR results in Fig. 7 indicate that chemisorption dominates, as CaSiO₄ was reduced to CaSiO₃ after reduction.

TABLE VII: CHEMICAL COMPOSITIONS OF MINERALOGICAL PHASES HYDRAZINE AND DMAB

Before reduction		Hydrazine		DMAB	
Phase name	Content (%)	Phase name	Content (%)	Phase name	Content (%)
MgFe ₂ O ₄	38	CaSiO ₃	35	CaSiO ₃	38
Ca ₂ SiO ₄	39	Ca(OH) ₂	1.3	Ca(OH) ₂	3.1
FeO	13	FeO	30	FeO	27
CaFe ₄ O ₅	05	CaFe ₄ O ₅	1.0	CaFe ₄ O ₅	1.3
-	-	Ca ₂ (Al,Fe) ₂ O ₅	22	Ca ₂ (Al,Fe) ₂ O ₅	21
-	-	MnO	4.7	MnO	4.8
-	-	Ca ₂ Fe ₂ O	4.9	Ca ₂ Fe ₂ O	4.9
-	-	-	-	-	-

TABLE VIII: CHEMICAL COMPOSITIONS OF MINERALOGICAL PHASES OF GLYOXYLIC ACID

Before reduction		Glyoxylic acid	
Phase name	Content (%)	Phase name	Content (%)
MgFe ₂ O ₄	38	CaSiO ₃	38
Ca ₂ SiO ₄	39	Ca(OH) ₂	2.2
FeO	13	FeO	24
CaFe ₄ O ₅	5	CaFe ₄ O ₅	2.0
-	-	Ca ₂ (Al,Fe) ₂ O ₅	21
-	-	MnO	3.9
-	-	Ca ₂ Fe ₂ O	4.3
-	-	SiO ₂	2.4

BOFS chemical compositions before and after heavy metal incorporation are shown in Table VI. MgFe₂O₄ and Ca₂SiO₄ were the major phases in the BOFS before reduction, while FeO and CaFe₃O₅ were minor phases due to their low relative proportions. Ca(OH)₂, CaSiO₃, FeO, Ca₂(Al,Fe)₂O₅, MnO and SiO₄ were formed after reduction, supporting the results. In addition to the reduction of CaSiO₄ to CaSiO₃, MgFe₂O₄ to FeO, it can also be observed that Fe from AMD incorporated in the BOFS through reduction has contributed to the increase of its content after reduction. Due to the reduction of Mn from AMD, MnO was also formed and incorporated into BOFS. The formation of Ca(OH)₂ was caused by the dissolution of CaO in solution (AMD) Because of the heavy metals present in the solution, tetrahedral coordination on the BOFS formed Ca(Al,Fe)₂O₅ by substituting Si with Al and Fe [26]. As Mn is found on the polyhedral coordination surface, it did not participate in the substitution.

IV. CONCLUSION

This study evaluated the effectiveness of using different

seeding materials (Ni powder, Iron powder, GBFS and BOFS) with different reducing agent (Hydrazine, DMAB, and glyoxylic acid. Metal removal efficiency was used as a criterion to evaluate the effectiveness of the seeding material together with the reducing agents. Ni and Iron powder as seeding materials did not favour Electroless plating but leached under acidic conditions therefore they cannot be used to facilitate the Electroless plating process. On the other hand metals were successfully removed by Electroless plating using BOFS and GBFS as seeding materials, however BOFS outperformed GBFS. With the use of BOFS over 99% of Fe was removed whilst GBFS achieved approximately 90%. The dominant mechanism of Fe removal was chemisorption. Electroless plating

When compared to Glyoxylic acid, Hydrazine and DMAB were the most effective reducing agents with over 99% metal removal with BOFS as a seeding material. The percentage metal removals did not differ significantly between both reducing agents because reduction was thermodynamically feasible. It was not thermodynamically feasible to reduce with glyoxylic acid, so only a very small percentage of Fe was removed as compared to DMAB and hydrazine. The treated effluent meets the minimum statutory limit of water discharge into the rivers.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest

AUTHOR CONTRIBUTIONS

Freeman Ntuli: Supervision, Conceptualization, Methodology, Investigation, Writing – Review and Editing, Visualization. Thandiwe Sithole: Conceptualization, Methodology, Investigation, Writing – Review and Editing, Visualization, Administration, Funding acquisition. All authors had approved the final version.

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