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Reductive leaching behaviour of manganese and cobalt phases in laterite and manganese ores

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ABSTRACT

The reductive leaching behaviour of manganese (Mn) and cobalt (Co) in a laterite and a pure manganese ore was investigated by varying and optimising various leaching parameters for the recovery of Mn and Co. The effect of different reducing agents ($FeSO_4$, Na_2SO_3), sulfuric acid concentration, reductant/ore mass ratio, leaching time, and reaction temperature on the dissolution of Mn and Co from the laterite and manganese ores were studied. Furthermore, the kinetics of Mn and Co leaching from laterite ore was studied. The Mn and Co recovery from both ores increased with increasing H_2SO_4 concentration, reductant/ore mass ratio, leaching time, and reaction temperature. Based on the manganese and cobalt extraction efficiency, $FeSO_4$ was the best reductant among the two evaluated reductants. The optimum leaching of Mn and Co from the laterite ore occurred at a H_2SO_4 concentration of 0.51 M, a reductant/ore mass ratio of 2.7, a leaching time of 5 h, and a reaction temperature of 363.15 K. For the manganese ore the optimum leaching of these elements at the same temperature occurred at a higher H_2SO_4 concentration of 1.02 M, a reductant/ore mass ratio of 2.4, and a shorter leaching time of 2 h. The results from the optimization studies showed that the leaching trends of Mn and Co phases in the manganese ore are similar to those of the Mn and Co phases in the laterite ore. Moreover, Co was co-leached together with Mn suggesting a degree of correlation of cobalt to manganese mineral phases in both, the laterite, and the manganese ores. The kinetics of the reductive leaching of Mn and Co for the laterite ore could well be described by the Avrami model reflected by high correlation coefficient values of $R^2 > 0.95$. The leaching of Mn and Co occurred rapidly at the initial leaching stage but gradually slowed down with prolonged leaching time. This was indicated by the modal parameter (n) values that were <1, at varying reaction temperatures. The experiments showed further that Mn and Co leaching in laterite ore is a diffusion-controlled reaction, which was indicated by the apparent activation energy of 11.7 kJ mol^{-1} and 11.1 kJ mol^{-1}, respectively.

1. Introduction

Over the past years, there has been a drastic depletion of high-grade nickel (Ni) sulfide ores which has surged the urgency in the exploitation of laterite ores as an alternative for Ni and Co production. Stanković et al. (2020) predicted that, by 2022, 72% of Ni will be extracted from lateritic ores. Furthermore, the global annual production of Co from Ni laterite ores is estimated by Newsome et al. (2020) to be around 40% by 2022.

Nickel and cobalt are produced widely via a pyrometallurgical route from sulfidic and high-grade laterite ore (i.e. saprolite ore types). The low-grade limonitic laterite ore types are treated commonly via the hydrometallurgical route.

The leaching of cobalt from laterite ores has resulted in low recovery owing to the strong correlation of cobalt to manganese phases (Newsome et al., 2020) which hinders the full liberation of cobalt from its host ore. The close association of cobalt and manganese is due to their similarities in chemical properties (Alloway, 2013). It has been proposed that cobalt is absorbed and incorporated into the crystal lattices of different varieties of manganese oxide minerals, which may have resulted in the low recovery of cobalt from laterite ores (Alloway, 2013).

To improve the recovery of a metal from its host rock, it is imperative to study its mineralogical and geochemical properties and its leaching kinetics (Lambiv Dzemua et al., 2013). However, it has been extremely

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difficult to characterize the mineralogy of manganese phases in lateritic deposits due to the complex and diverse nature of laterite ores at macroscopic and microscopic scales. The manganese phases in laterite ores also have relatively small grain sizes, making it almost impossible to accurately examine the individual manganese phases by traditional methods of microscopy and image analysis (Lambiv Dzemua et al., 2013). Hence, little information on mineralogy and leaching behaviour of manganese phases in lateritic ores are available (Stanković et al., 2022).

Various studies have made use of a reductive leaching approach to characterize the extraction of manganese and cobalt from manganese oxide and Ni laterite ores, respectively, due to their various oxidation states. Manganese is insoluble in the +4 state but soluble in the +2 state. Therefore, insoluble manganese needs to be reduced to the soluble form to achieve its recovery from its ore. On the other hand, Co^{3+} which occurs in most cobalt-bearing minerals (asbolane, heterogenite, Co-lithiophorite) is unstable in solution. To dissolve cobalt of oxidation state thee, there is the need to reduce it to state two, which is more stable and soluble in acidic media. This is achieved by the addition of a reducing agent to facilitate the reduction of Mn^{4+} to Mn^{2+} and Co^{3+} to Co^{2+}. It can be clearly seen in Fig. 1 that, for effective conversion of Mn (IV) to Mn(II) and Co(III) to Co(II), leaching should be achieved in a reduced and acidic environment (lower redox potential (Eh) value) (Sinha and Purcell, 2019).

For example, Das and De Lange (2011) reported a rapid 95% cobalt and manganese recovery using reductive atmospheric leaching of West Australian nickeliferous smectite ore in SO_2 – H_2SO_4 solution. Jiang et al. (2003, 2004) described that hydrogen peroxide is crucial in the sulfuric acid leaching of manganese ore at room temperature. They observed the dual purpose of hydrogen peroxide as both, a leaching and reducing agent. Das et al. (1997a, 1997b), and Senanayake et al. (2011, 2015) have also reported that a reducing agent is very important in the facilitation of acid dissolution of laterite ores which resulted in the high recovery of nickel and cobalt. Table 1 gives a summary of the leaching of manganese and cobalt from laterite ores.

A previous study by Stanković et al. (2022) reported a low recovery for the chemical leaching of cobalt from laterite ores. Further analysis of the results indicated that cobalt was mostly located in the manganese mineral phases such as asbolane which could be one of the factors that influenced the low recovery of cobalt. This established the basis for this work to investigate the leaching behaviour of manganese and cobalt phases in laterite ores to understand the mechanism of co-leaching of Co with Mn from laterite ores. At the time of this work, little information on mineralogy and the co-leaching behaviour of Co with Mn phases in lateritic ores was available, hence the results from this work will provide some background information on the leaching behaviour of Mn and Co phases in lateritic and manganese ores. Knowledge from this study could then be transferred to the improvement of cobalt recovery from laterite and other cobalt-bearing ores in future studies.

In this work, a reductive leaching study was conducted to ascertain the leaching behaviour of manganese and cobalt phases in laterite ore using $FeSO_4$/ Na_2SO_3 as reductants in an acidic medium (sulfuric acid). In that, the effect of various leaching parameters such as different reductants, acid concentration, reductant/ore mass ratio, leaching time and temperature were investigated to optimize the leaching conditions.

To get a deeper insight into the effect of variables on leaching trends (Senanayake et al., 2011, 2015) of Mn and Co phases in different ore types, a manganese ore was also leached, and the results were compared to the leaching trends of the laterite ore. The comparison between these two ores was to especially explore the role of manganese phases being a minor component in laterites but dominant in the manganese ore on the recovery kinetics of cobalt.

Furthermore, a kinetic analysis was conducted to ascertain the appropriate kinetic model that would best describe the leaching of manganese and cobalt phases in only the laterite ore. However kinetic analysis of the leaching of manganese and cobalt phases in the manganese ore was not studied in this work and it is recommendable for future study.

2. Materials and methods

2.1. Samples

The laterite ore sample was obtained from the Barro Alto mine (Anglo-American) in the Goiás state in Brazil as described by Stanković et al. (2022). The ore sample Barro Alto Canal consisted of freshly sampled limonite (hereinafter referred to as sample BaC).

The manganese ore sample was taken from Ilfeld/Harz mountains, Thuringia, Germany and was provided by the Geoscientific Collections of the TU Bergakademie Freiberg.

2.2. Sample preparation

The laterite ore sample BaC was first sieved into two batches smaller than 2 mm to ascertain the sample's homogenous grain size distribution. During sieving, different stability of the aggregates was observed. To

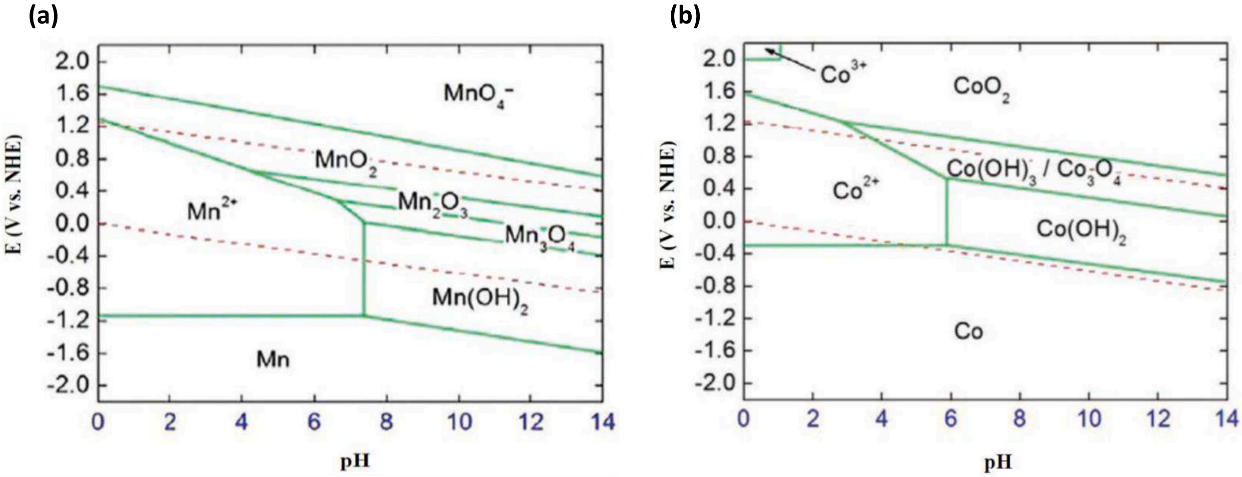

Fig. 1. Simplified Pourbaix diagram for a) Mn and b) Co in aqueous solution with dissolved species considered as having an activity of 1 at 25 °C. Green lines mark the boundaries of regions where the various species are thermodynamically stable. Red dashed lines represent the stability region of water; the upper red dashed line relates to the oxygen development reaction and the lower red dashed line relates to the hydrogen development reaction. Reproduced from Gao et al. (2021) with permission from John Wiley and Sons. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Leaching of Mn and Co from laterite ores.

Ore type	Optimum leaching conditions	Leaching medium	Reducing agent	Metal Recovery		Reference
				Mn (%)	Co (%)	
Limonitic ore	Time: 30 min, particle size: 90–125 µm, pulp density: 10% (*w/v*), H_2SO_4: 0.72 M, temperature: 90 °C, SO_2: 0.3 mol/L, agitation speed: 650 rpm	H_2SO_4	SO_2	90–100	90–100	Senanayake and Das, 2004
Limonitic ore	Time:5 min, temperature: 90 °C, $Na_2S_2O_3$: 10 g/L, H_2SO_4: 8% (*w/w*), liquid/solid ratio (L/S): 10:1	H_2SO_4	$Na_2S_2O_3$	80	91	Li et al., 2011
Limonitic ore	Time: 6 h, temperature: 90 °C, pulp density: 10% solids (*w/v*), SO_2: 0.6 dm^3 min^{-1}, H_2SO_4: 0.72 M	H_2SO_4	SO_2	99	99	Das et al., 1997a
Smectite ores (clay-based nontronite)	Pulp density: 35% (w/w), temperature: 90 °C, H_2SO_4: 700 kg/t ore, time: 10 h, SO_2 flow rate: 0.45 L/min, Cu(II): ~1 g/L	H_2SO_4	$Cu(II)/SO_2$	95	97	Senanayake et al., 2015
Nickeliferous smectite ore	Pulp density: 20% (w/w), temperature: 90 °C, H_2SO_4: 600 kg/t ore, time: 10 h, SO_2 flow rate: 0.45 L/min, Cu(II): ~1 g/L, particle size: - 0.106 µm	H_2SO_4	$SO_2/Cu(II)$	96	97	Das and De Lange, 2011
limonitic ore	Pulp density: 2.5 gdm^{-3}, temperature: 90 °C, H_2SO_4: 1 M, time: 10 min, $SO_2 = 0.1\ dm^3min^{-1}$, $Fe = 20\ g\ dm^{-3}$, $FeSO_4.7H_2O = 12\ gdm^{-3}$, particle size: 90–125 µm	H_2SO_4	SO_2, Fe, $FeSO_4$,	100	80–100	Senanayake et al., 2011
limonitic ore	Pulp density: 10% (*w/v*), temperature: 40 °C, HCl: 0.5 M, time: 60 min, $FeCl_2 = 0.01$ M, particle size: 90–125 µm	HCl	$FeCl_2$	70	68	Senanayake et al., 2011

reduce the grain size of aggregates, the sample was crushed using a laboratory-scale jaw crusher. During crushing, most of the sample disintegrated into grains of <2 mm with about 78% of the grains belonging to <0.020 mm size fraction with an average particle size of 0.018 mm (Stanković et al., 2022), showing only weak solidification of the aggregates. Therefore, the grain size fraction <2 mm was selected for this experiment. To ensure working with defined and representative material, the batches of the individual sample were mixed and thoroughly homogenized in roller drums. The material was split, using a laboratory scale ripple divider into batches for further processes. The sample was bagged and properly labelled.

The manganese ore was washed using tap water to remove dirt and other physical impurities and left overnight to dry in the open air. Open-air drying was adopted to conserve the chemical structure of the ore. The manganese ore sample was dry crushed with a laboratory-scale jaw crusher, and ground with a laboratory-scale mill. After crushing and milling, the sample was dry screened to provide raw material sized into particle size fraction of 63–200 µm. The screening was aided by a vibration screening machine. The pulverized manganese ore sample was bagged and labelled.

2.3. *Instrumental methods, geochemical and mineralogical analyses*

The chemical composition of the laterite and the manganese ores was analyzed using a portable X-ray fluorescence spectrometer (XRF, BRUKER S1 Titan) in the laboratory of G.E.O.S. Ingenieurgesellschaft mbH Freiberg, Germany. The mineralogical composition analysis was carried out in the Mineralogical Laboratory of the TU Bergakademie Freiberg (TUBAF), Germany. Measurements were carried out with an X-ray diffractometer system Orion Comet P2 (XRD Eigenmann GmbH) with Co-Kα radiation, an automatic divergent aperture, and a Si-Drift detector. The angular range 5–80° 2θ was measured in the step-scan procedure with 0.02° increment, 2 s counting time per step. The pregnant liquors were analyzed using Microwave Plasma-Atomic Emission Spectrometry (MP-AES) method and spectrophotometer at the TUBAF mine water laboratory and G.E.O.S. Freiberg respectively.

2.4. *Leaching procedure*

For the laterite leaching experiments, 20 g of the laterite sample (BaC) of particle size <2 mm was introduced into a 2 L glass beaker. The calculated stoichiometric amount of reductant ($FeSO_4$/ Na_2SO_3) was measured and introduced into the glass beaker containing the laterite sample. A known volume of H_2SO_4 was added to the mixture to form a pulp with a pulp density of 17% (*w/v*). Mixing of the pulp was achieved by an impeller stirrer and leaching was performed for 24 h. Clarified leach liquors were taken at various leaching times and centrifuged at a speed of 9500 rpm for 10 min.

Manganese ore with a particle size of 63–200 µm and a calculated stoichiometric amount of reductant ($FeSO_4$/ Na_2SO_3) was filled into a 100 mL plastic bottle. A 2 g sample of ore was used in each leaching experiment. The reductants were added in solid form. The required volume of H_2SO_4 solution was added to the mixture to form a pulp with a pulp density of 9% (w/v). An overhead shaker with a speed of 21 rpm was used for the agitation of the solution.

It should be noted that, the mass of the ore samples, pulp density, and particle size distribution used in the laterite and manganese ore were not adjusted to be similar for the following reasons;

a. A 20 g sample of laterite was selected because the low grade of Mn in the laterite sample since Mn is a minor element in the laterite ore. Only a 2 g sample of Mn ore was selected due to the high grade of Mn in the Mn ore in comparison to the laterite ore. Also, Mn is a major element in the manganese ore.
b. Pulp density was selected based on the quantity of materials taken. However, a preliminary study conducted by Moro et al. (2021) on the effect of pulp density on Mn recovery for similar manganese ore showed maximum metal recovery for the selected pulp density used in this work.
c. A preliminary study on similar ore types showed Mn and Co enrichment in the selected particle size ranges in this work.

For both samples, the variation of the following leaching parameters was tested: different reductants, sulfuric acid concentration, reductant/ore mass ratio, and leaching time. The parameters were changed to investigate the optimal conditions for the leaching. Liquid samples from the leaching experiments were taken and filtered using a 0.45 µm filter syringe after each leaching period. The leaching experiments were conducted in batch mode.

3. Results and discussion

3.1. *Characterization of laterite and manganese ore*

The chemical composition of the laterite ore sample BaC (Stanković et al., 2022), and the manganese ore is shown in Table 2. The chemical composition of the laterite ore was characterized by a high content of Fe_2O_3 (61.4%). The ore contained 1.31% of nickel, 0.12% of cobalt and 0.71% of manganese. The high content of iron and low content of nickel characterized the laterite ore as a limonitic ore type. The ore also contained 7.63 mass% Al_2O_3 and 9.42 mass% SiO_2. The manganese ore contained 47.2% (*w*/w) Mn and low content of cobalt (0.52%) and nickel (0.01%). It also contained 6.23% Fe_2O_3, 6.51% SiO_2, 1.17% Al_2O_3 and 6.81% CaO.

Table 2
Geochemical composition of laterite and manganese ore samples used for experiments.

Components in ore	Concentration (mass %)	
	Laterite	Manganese
MgO	2.10	< LOD
Al_2O_3	7.63	1.17
SiO_2	9.42	6.51
P_2O_5	0.02	0.07
K_2O	0.02	0.38
CaO	0.09	6.81
Mn	0.71	47.18
Fe_2O_3	61.4	6.23
Co	0.12	0.52
Ni	1.31	0.01
Cr	2.18	0.03
Cu	–	0.09
As	–	< LOD

The results of the mineralogical analysis (XRD pattern) for laterite and manganese ore can be seen in Fig. 2. The mineral phase distribution (see supplementary material; Fig. A.1) in the laterite ore sample is in quite good agreement with a previous XRD analysis by Stanković et al. (2022). Fig. 2a shows that the laterite ore (BaC) contained mainly goethite, with a relatively low abundance of crystalline hematite/maghemite. Other mineral phases included quartz, serpentine mineral (e.g., lizardite), chlorite, talc, and spinel (chromite and/or hercynite). Classification of spinel in the laterite was relatively uncertain and it was rather difficult to distinguish between chromite and hercynite phases. The higher serpentine and chlorite content indicated a higher grade of Ni in this type of laterite deposit. The ore however showed an intermediate grade of Co with a relatively low amount of manganese phases. These properties may enhance the acid leachability of this type of laterite ore. Visual examination of the laterite ore generally showed conformity of the sample characteristics with the literature by Melfio et al. (1988). The laterite ore showed a second stage laterization representing "lateritic or oxidized nickel ore" with a high content of asbolane as a mineral phase. Manganese phases in this ore occurred as lithiophorite-asbolane which could confirm the binding of cobalt to manganese phases in this ore.

Based on the XRD pattern of the manganese ore (Fig. 2b), the manganese phase showed a relatively high grade of crystallinity. The manganese ore sample contained mainly manganite as the major manganese phase, with no minor manganese phase. Calcite was also detected. The analysis suggested some unaccounted mineral phases, which were amorphous according to XRD. Quartz was not detected in this sample, possibly due to the low SiO_2 concentration in the ore sample as seen in Table 2.

3.2. *Leaching behaviour*

3.2.1. *Effect of different reductants*

Fig. 1 shows the important role of a reducing agent in the optimal leaching of manganese and cobalt from its host ore. In this regard, the two reducing agents, iron sulfate ($FeSO_4$) and sodium sulfite (Na_2SO_3), were selected to compare their reducing effect on the leaching efficiencies of manganese from both the laterite and manganese ores. The results of this experiment are shown in Fig. 3. Overall, $FeSO_4$ showed a relatively higher extraction efficiency than Na_2SO_3 for the leaching of Mn from both ores which could be explained based on their respective standard electrode potential values (E_o). In view of this, $FeSO_4$ was selected as the optimal reductant for the subsequent leaching experiments, as also reported by Senanayake et al. (2011).

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad E_o = -0.77 \text{ V} \tag{1}$$

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^- \quad E_o = -0.20 \text{ V} \tag{2}$$

3.2.2. *Effect of acid concentration*

In the case of the laterite sample, the concentration of H_2SO_4 varied from 0 to 2.55 M and the other leaching parameters were fixed. An increase in acid concentration resulted in an increase in metal recovery for Mn, Ni and Co (Fig. 4a). However, the highest recovery was achieved at 0.51 M H_2SO_4 for Mn (74.2%) and Co (74.6%). Nickel on the other hand showed a continuous increase in recovery with the increase in H_2SO_4 concentrations beyond 0.51 M, however, the recovery was still lower compared to that of Mn and Co. At 2.55 M H_2SO_4, the recovery of Ni was 20% compared to 80.9% and 78.4% for Mn and Co respectively. Higher acid concentrations tended to improve recovery of Mn and Co, but did not significantly increase the recovery of Ni. This suggested that a high extraction of Ni is achievable at higher acid concentrations. This can be a potential clue for sequential leaching of Mn, Co, and Ni from laterite ores owing to the fast-leaching rate of Mn and Co even at relatively low acid concentrations. In that, Mn and Co could be leached first using a reductive leaching approach at relatively low acid concentration, followed by the leaching of Ni by increasing the acid concentration since Ni doesn't leach better at low acid concentrations. It is worth noting that, even without H_2SO_4 addition, Mn and Co recovery reached 33.7 and 34.3% respectively. This indicates that Mn and Co related acid consumption in the leaching of limonite ores is relatively low.

In the experiment with the manganese ore sample (Fig. 4b), the acid concentration varied in the range of 0.51–2.55 M H_2SO_4 with the other leaching conditions being fixed. The results in Fig. 4b demonstrated that

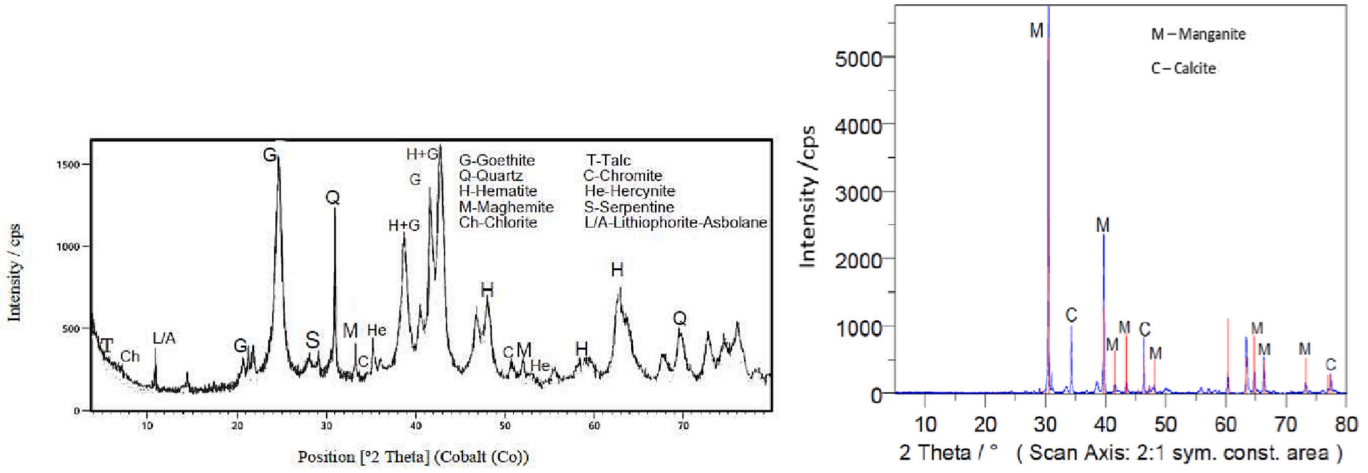

Fig. 2. a) XRD pattern of the laterite ore (modified after Stanković et al., 2022) and b) manganese ore.

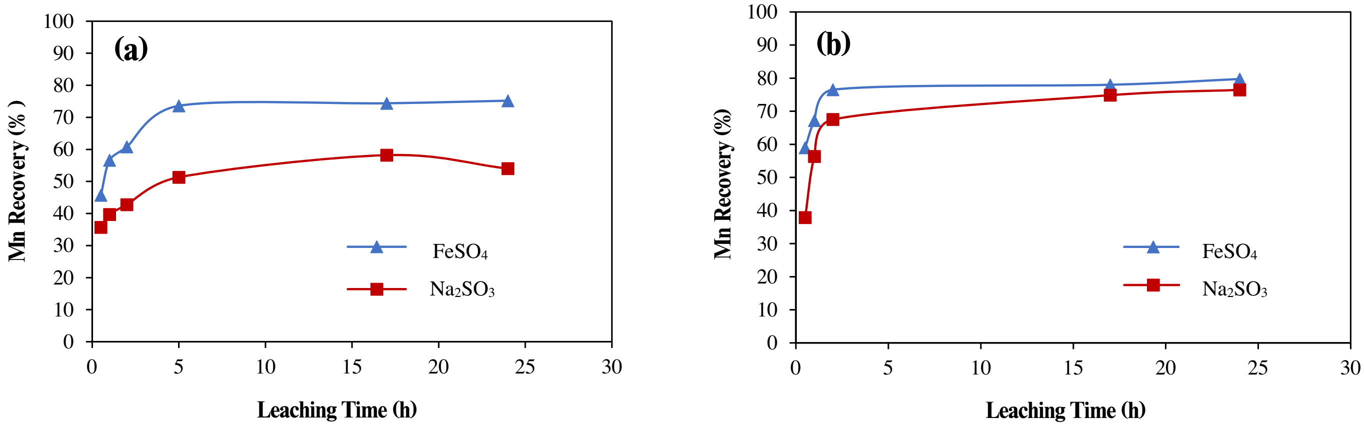

Fig. 3. The effect of $FeSO_4$/Na_2SO_3 on the leaching recovery of Mn from (a) laterite (b) manganese ore in H_2SO_4; Leaching conditions: particle size: < 2 mm for laterite ore and 63–200 μm for Mn ore; acid concentration = 0.51 M for laterite ore and 1.02 M for Mn ore; pulp density = 17% (*w*/*v*) for laterite ore and 9% (w/v) for Mn ore; reductant/ore mass ratio = 2.7 for laterite ore and 2.4 for Mn ore; leaching time = 24 h; temperature = 24 °C.

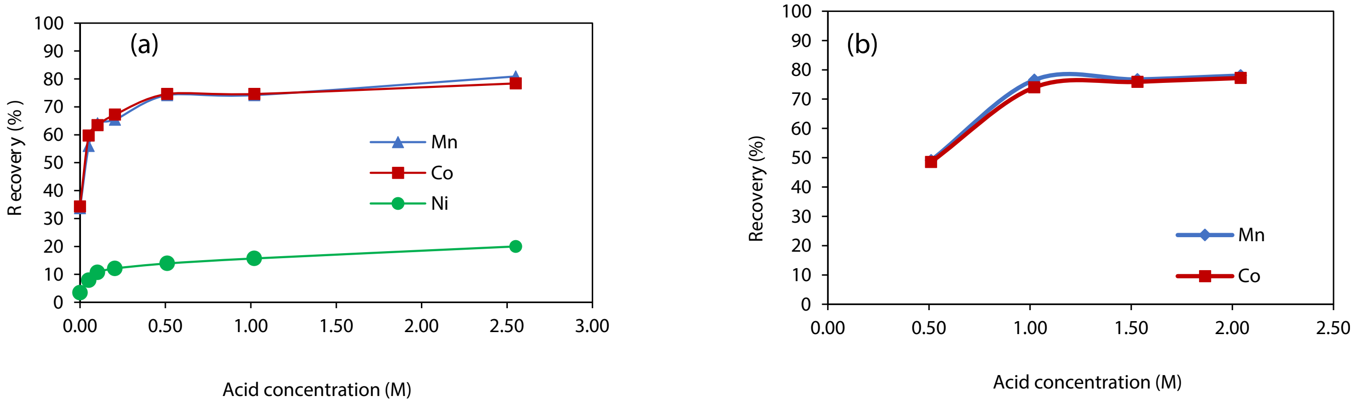

Fig. 4. The effect of sulfuric acid concentration on the recovery of Mn, Co, and Ni from (a) laterite (b) manganese ore in H_2SO_4; Leaching conditions: particle size: < 2 mm for laterite ore and 63–200 μm for Mn ore; pulp density = 17% (*w*/*v*) for laterite ore and 9% (w/v) for Mn ore; reductant/ore mass ratio = 2.7 for laterite ore and 2.4 for Mn ore; leaching time = 5 h for laterite ore and 2 h for Mn ore; temperature = 24 °C.

the recovery of Mn and Co increased from ~49% to 75.3% as the acid concentration increased from 0.51 M to 1.02 M, however it reached a plateau from 1.02 M to 2.04 M H_2SO_4 (Mn and Co recovery were around 77.6%). Hence, at 1.02 M H_2SO_4 the extraction of Mn and Co was almost complete.

Low metal recovery for both, the laterite, and the manganese ore sample, indicated that the chemical reaction was impeded at lower acid concentrations. However, increasing the acid concentrations resulted in higher metal recovery. This is because an increasing acid concentration promoted the availability of leaching agents to react with the minerals at reaction sites (Moro et al., 2021; Yi et al., 2015).

3.2.3. *Effect of reductant/ore mass ratio*

The effect of reductant/ore mass ratio was investigated for the

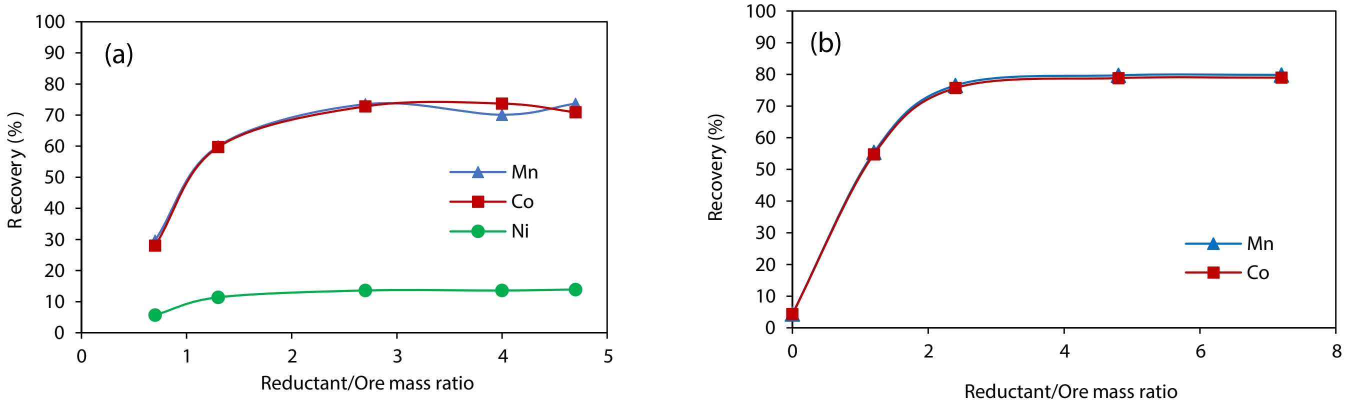

Fig. 5. The effect of reductant/ore mass ratio on the recovery of Mn, Co, and Ni from (a) laterite (b) manganese ore in H_2SO_4; Leaching conditions: particle size: < 2 mm for laterite ore and 63–200 μm for Mn ore; acid concentration = 0.51 M for laterite ore and 1.02 M for Mn ore; pulp density = 17% (*w*/*v*) for laterite ore and 9% (w/v) for Mn ore; leaching time = 5 h for laterite ore and 2 h for Mn ore; temperature = 24 °C.

maximum metal recovery from the laterite ore sample by varying the mass ratio of $FeSO_4$ and laterite ore from 0.7 to 4.7. All the other leaching parameters remained the same. The results are given in Fig. 5a. A steep increase of Mn and Co recoveries from ~28% to 73.2% for the increase in reductant/ore ratio from 0.7 to 2.7 is clearly shown in Fig. 5a, followed by a steady increase beyond this point and a plateau. However, the effect of the reductant/ore mass ratio on the recovery of Ni was very minimal. Hence, the ratio of 2.7 was considered as an optimum for this experiment.

The effect of reductant/ore mass ratio was studied for the maximum recovery of Mn and Co from the manganese ore under room temperature with all other parameters being fixed. In this experiment, the mass ratio of $FeSO_4$ and manganese ore was changed from 0 to 7.2 and the results are given in Fig. 5b. The results demonstrated a steep increase in Mn and Co recovery from ~4.3% to 76.1% with an increasing reductant/ore mass ratio from 0 to 2.4. However, there was no appreciable increase in metal recovery beyond this ratio, hence 2.4 was selected as the optimum reductant/ore mass ratio in this study.

The results in Fig. 5 show that Mn and Co recovery increased with an increasing reductant/ore mass ratio. This confirms the fact that the complete conversion of Mn^{4+}/Mn^{3+} to Mn^{2+} and Co^{3+} to Co^{2+} in a reduced environment is thermodynamically feasible at relatively high reductant/ore mass ratios (Morcali, 2015). However, a further increase in the reductant/ore mass ratio did not show any significant effect on Mn and Co recovery, because the conversion process had been completed. The need for a reducing agent for the leaching of Mn and Co was also evident from the low recovery of Mn and Co at the low reductant/ore mass ratio without the addition of $FeSO_4$ (Lasheen et al., 2014, see Fig. 5b). The chemical reactions during the reductive acid leaching of MnO_2 and Co_2O_3 in the presence of $FeSO_4$ can be expressed as follows:

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + 2H_2O \quad (3)$$

$$Co_2O_3 + 2FeSO_4 + 3H_2SO_4 \rightarrow 2CoSO_4 + Fe_2(SO_4)_3 + 3H_2O \quad (4)$$

3.2.4. *Effect of leaching time*

With all other leaching parameters fixed, the effect of leaching time was investigated on the maximum metal ion (Mn, Co, and Ni) recovery from the laterite sample during leaching at room temperature. Therefore, the leaching time varied from 0.5 to 24 h. Fig. 6a. shows the effect of leaching time on the metal recovery from the laterite ore. An initial rapid increase in Mn and Co recoveries from ~45% to 74.6% with increasing leaching time from 0.5 to 5 h occurred. Afterwards, the recovery values remained unchanged. Therefore, 5 h was chosen as the optimum leaching time. After 17 h of leaching time, Co recovery declined which might be caused by precipitation effects.

A series of experiments was also conducted to ascertain the effect of leaching time (0–24 h) on the recovery of Mn and Co from the manganese ore. The results shown in Fig. 6b. indicated a rather fast leaching process at the beginning from 0.5 to 2 h, afterwards, the reaction became slow even for the prolonged leaching time of 24 h. Therefore, 2 h was selected as the optimum leaching time for the leaching of metals from the manganese ore.

The initial rapid increase in the recoveries of Mn and Co from both, the laterite and the manganese ore imply that the reactivity of metal oxides of Mn and Co towards H_2SO_4 is very high in the initial stages of the leaching reaction (Muzayanha et al., 2020). This confirms several publications which showed a maximum Mn and Co recovery at the initial stage of leaching (Das et al., 1997a, 1997b; Su et al., 2008; El Hazek et al., 2006).

3.2.5. *Recovery correlation*

Figs. 4, 5, and 6 clearly show for both types of ore (laterite and manganese ore) that Mn and Co recoveries are strongly correlated. Leaching recovery trends were relatively similar for both ores. Thus, Fig. 7 summarizes that the R^2 values for the correlation of Mn and Co recovery reached 0.97 for the laterite and 0.99 for the manganese ore. Similar correlations have been reported for nickel laterite ores (Senanayake et al., 2011). This indicated that the leaching of Mn and Co is strongly correlated in both cases. Hence, Co seems to be nearly completely bound to Mn phases in both ores, as shown by Stanković et al. (2022) for the laterite ore and discussed in section 1 above. The

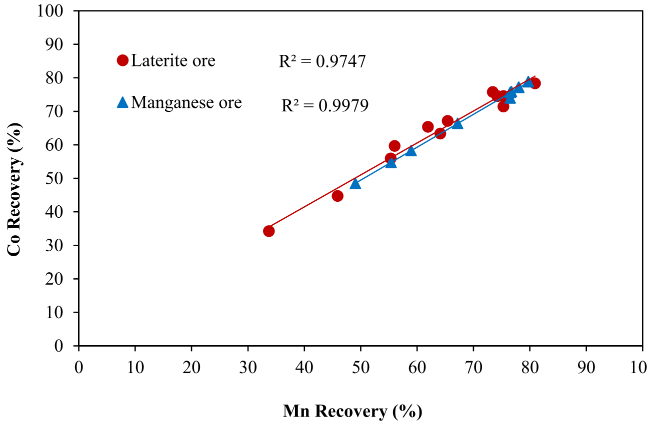

Fig. 7. Correlation between the recoveries of Mn and Co from the laterite and the manganese ore.

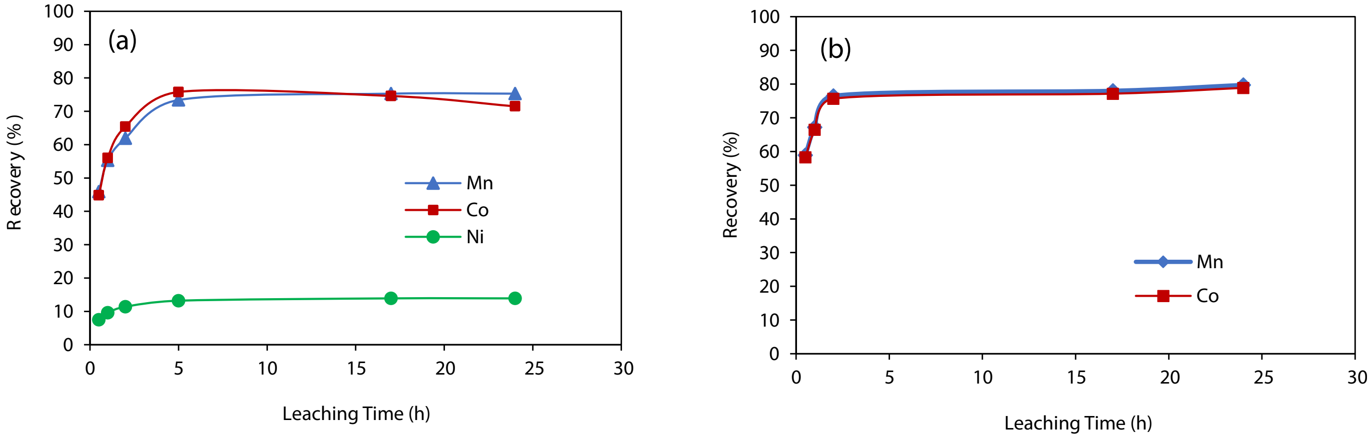

Fig. 6. The effect of leaching time on the recovery of Mn, Co, and Ni from (a) laterite (b) manganese ore in H_2SO_4; Leaching conditions: particle size: < 2 mm for laterite ore and 63–200 μm for Mn ore; acid concentration = 0.51 M for laterite ore and 1.02 M for Mn ore; pulp density = 17% (*w/v*) for laterite ore and 9% (w/v) for Mn ore; reductant/ore mass ratio = 2.7 for laterite ore and 2.4 for Mn ore; temperature = 24 °C.

strong association of cobalt with manganese mineral phases in the laterite ore BaC and other laterite ore samples was shown by a combination of scanning electron microscopy with Mineral Liberation Analysis (MLA) software and laser ablation-inductively coupled plasma-time of flight mass spectrometry (LA-ICP-TOFMS) by Stanković et al. (2022). It is worth noting that in all the leaching experiments Ni showed a very low recovery. There was dominant selective leaching of Mn and Co against Ni. With reference to Table 1, the leaching efficiency of Mn and Co was not significantly high for both the laterite and manganese ores. Similar Co recovery results have been reported by Stanković et al. (2022) for the same laterite ore, and this needs to be further investigated to improve upon their respective recoveries.

3.3. *Leaching kinetics*

3.3.1. *Effect of temperature*

McDonald and Whittington (2008) reported that one of the strategies to improve metal (e.g., Co and Ni) recovery is to increase the reaction temperature. The influence of temperature was investigated for the optimum Mn and Co recovery from the laterite ore sample BaC, by varying the reaction temperature in the range of 303.15 K – 363.15 K. Fig. 8 shows an increase in Mn and Co recovery with the increase in temperature. Thereby Mn and Co reached a maximum recovery of 87.7% and 93.2% respectively at a temperature of 363.15 K. Leaching under elevated temperatures improves the reaction rate (Muzayanha et al., 2020). This was an indication of the important role of temperature in the recovery of Mn and Co from their ores.

To have a better understanding and control of a leaching process, it is important to establish the leaching kinetic equation and the activation energy (E_a) to predict the leaching behaviour of Mn and Co in the laterite ore. The experimental data in Fig. 8 was applied to the most frequently used kinetic models i.e., Avrami equation (Eq. 5), shrinking core (Eq. 6–8), and logarithmic rate law (Eq. 9). However, all the curves (kinetic equation and Arrhenius plot) did not show high values of R^2 (> 0.95) for the shrinking core model and the logarithmic rate law, hence it is irrelevant to this study as shown by the data provided in supplementary material Fig. A.2-A.9. Fig. 9 and Fig. 10 show the curves of the Avrami equation and Arrhenius plot for the calculation of E_a, respectively, for Mn and Co leaching from the laterite ore. All the curves exhibited high values of R^2 (> 0.95) for the leaching of Mn and Co from the laterite ore, suggesting a good fitting of the Avrami equation for this study.

Avrami equation:

$$ln\left(-ln(1-X)\right) = lnk + nlnt \tag{5}$$

Shrinking core model:

$$X = k.t \tag{6}$$

$$1-(1-X)(1-X)^{\frac{1}{3}} = k.t \tag{7}$$

$$1-\frac{2}{3}X-(1-X)^{\frac{2}{3}} = k.t \tag{8}$$

Logarithmic rate law:

$$\left(-ln(1-X)\right)^2 = k.t \tag{9}$$

Eq. 5 expresses the Avrami model as reported by Ding et al. (2019). In Eqs. (5–9), k is the rate constant, t is leaching time, n is the model parameter which indicates the leaching behaviour of metals as indicated by Muzayanha et al. (2020) and X is the fraction leached.

The Avrami equation has been used successfully to explain the leaching kinetics of many metals by other authors. Li et al. (2011) used this model to successfully study the leaching behaviour of Mn and Co in an acidic thiosulfate medium. Zhang et al. (2018) also used this model to study the kinetics and mechanism of reductive dissolution of manganese oxide ores using EDTA/EDTA-2Na as reductants.

Fig. 9 shows a plot of ln (−ln (1–X)) against lnt which indicates linear relationships according to eq. 5 which allows the determination of *lnk* and *n* from the intercept and slope, respectively. This information can be used to reveal the reaction order (n) and calculate the activation energy (E_a) using the Arrhenius equation.

From Fig. 9, the n-values for temperatures of 303.15, 333.15, and 363.15 K are 0.35, 0.34, and 0.33 for the reductive leaching of Mn from laterite ore and 0.35, 0.37, and 0.37 for the reductive leaching of Co from laterite ore. This indicated that the leaching of Mn and Co from the laterite ore occurred rapidly at the very beginning but gradually slowed down with extended leaching time. According to Senanayake et al. (2011, 2015), changes in mineral composition and low remnant acid could be possible reasons for the slow leaching at prolonged leaching time.

The activation energy was further calculated using the Arrhenius equation; $k = Ae^{-Ea/RT}$, where k: rate constant (1/min); A: frequency factor (min^{-1}), E_a: activation energy of reaction ($J\ mol^{-1}$), R: universal gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$), and T: temperature (K).

The plot of *lnk* against 1/T gives a straight line where the slope is ($-E_a/R$). From Fig. 10 the value of E_a/R was found to be 1402 and 1332 for Mn and Co respectively, hence the apparent activation energy value was calculated to be 11.7 $kJ\ mol^{-1}$ for Mn and 11.1 $kJ\ mol^{-1}$ for Co.

Zhang et al. (2018) reported that diffusion-controlled leaching processes are characterized by an apparent activation energy value in the range of 5–15 $kJ\ mol^{-1}$. Therefore, the reductive dissolution of Mn from the laterite ore using $FeSO_4$ as the optimum reductant is a diffusion-controlled reaction which is also evident in the leaching of Co owing to the strong correlation between these two metals. This further suggests that the leaching mechanism is governed by diffusion through the product layer (Faraji et al., 2022).

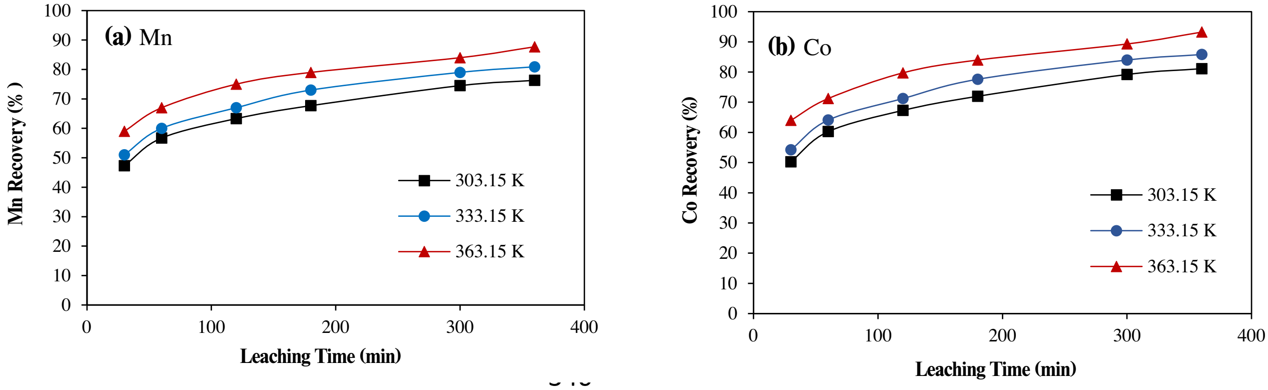

Fig. 8. Effect of reaction temperature on the recovery of (a) Mn and (b) Co from laterite ore in H_2SO_4; Leaching conditions: particle size: < 2 mm; acid concentration = 0.51 M; pulp density = 17% (*w/v*); reductant/ore mass ratio = 2.7; leaching time = 6 h.

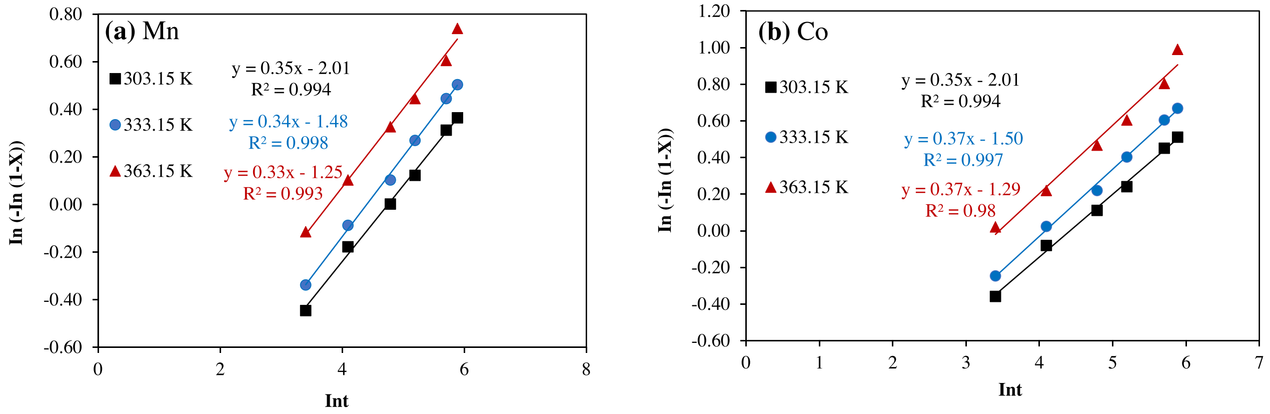

Fig. 9. The kinetic curve of (a) Mn and (b) Co leaching from laterite ore sample BaC, using the Avrami model (result based on data in Fig. 8).

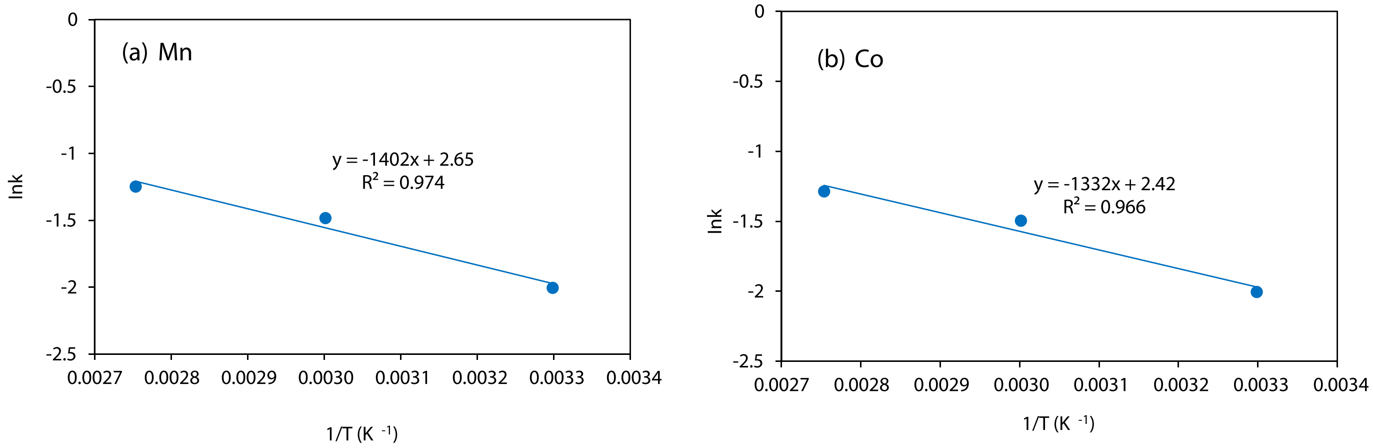

Fig. 10. Arrhenius plot for the leaching recovery of (a) Mn and (b) Co from laterite ore sample for the calculation of E_a (results are based on data in Fig. 9).

4. Conclusion

The reductive leaching behaviour of manganese and cobalt phases in limonitic laterite and manganese ores has been successfully studied using H_2SO_4 as a leaching reagent in the presence of $FeSO_4$ as a reducing agent. The effect of different reductants, acid concentration, reductant/ore mass ratio and leaching time were studied for the leaching of Mn, Co, and Ni from the laterite ore and Mn and Co from the manganese ore. The Mn and Co recovery increased with increasing acid concentration, reductant/ore mass ratio, leaching time, and reaction temperature. It is important to mention that other leaching parameters such as particle size, and agitation of the pulp can affect the recovery of Mn and Co, but these parameters were not studied in this work, and it is worth studying in future research. To understand the leaching variability of different manganese and cobalt phases in different ore types, the leaching of Mn and Co from laterite and manganese ores has been investigated and compared in terms of their recovery curves. Comparatively, Mn and Co recoveries showed similar leaching trends for the leaching of both laterite, and manganese ores.

The kinetic behaviour of the reductive leaching of manganese and cobalt from the laterite ore in an acidic medium in the presence of $FeSO_4$ followed the Avrami model. This model suggested that the leaching rate was rapid at the initial stage of leaching time but gradually slowed down with prolonged leaching time. The apparent activation energies of manganese and cobalt leaching from the laterite ore were calculated to be 11.7 kJ mol^{-1} and 11.1 kJ mol^{-1} respectively, indicating a diffusion-controlled leaching process. This confirms a probable strong association of cobalt with manganese mineral phases in the laterite ore.

CRediT authorship contribution statement

Kofi Moro: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Frank Haubrich:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing. **Mirko Martin**: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing. **Marlies Grimmer**: Investigation, writing – review & editing. **Nils Hoth**: Supervision, Writing – review & editing. **Axel Schippers**: Resources, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

Co-author is an editorial board member of Hydrometallurgy - Axel Schippers.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.hydromet.2023.106101.

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