

Role of Glycerol Oxidation Pathways in the Reductive Acid Leaching Kinetics of Manganese Nodules Using Glycerol

Aishvarya Venkataseetharaman,^{*,#} Geetanjali Mishra,[#] Malay Kumar Ghosh, and Goutam Kumar Das^{*}Cite This: *ACS Omega* 2021, 6, 14903–14910

Read Online

ACCESS |



Metrics & More

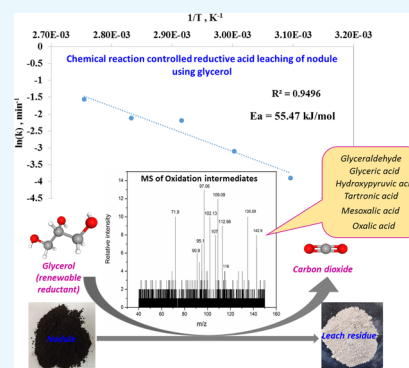


Article Recommendations



Supporting Information

ABSTRACT: Manganese nodules from ocean bed are potential resources of Cu, Ni, and Co for which land-based deposits are scarce in India. The present work describes a novel approach of using glycerol, a nontoxic biomass-derived reductant, for the reductive acid leaching of manganese nodules. Parameters such as acid concentration, time, temperature, and pulp density were optimized for leaching. The optimal leaching conditions were found to be 10% (w/v) pulp density and 10% (v/v) H₂SO₄ at 80 °C with 1% (v/v) glycerol yielding >95% of Ni and >98% Cu, Co, and Mn extraction within an hour. Kinetic analysis of the data based on the initial rate method showed that the leaching process was chemical reaction-controlled with an apparent activation energy of 55.47 kJ/mol. Various oxidation intermediates of glycerol formed during leaching were identified using mass spectrometry and Raman spectroscopy, and a probable oxidation pathway of glycerol during the leaching process has been elucidated based on the analysis. Glycerol was oxidized to glyceraldehyde, glyceric acid, tartronic acid, dihydroxyacetone, hydroxy pyruvic acid, glyoxalic acid, oxalic acid, and finally converted to CO₂ during leaching. The fast reaction kinetics, near-complete dissolution of manganese, and other associated metals in the nodule can be attributed to the participation of all intermediate products of glycerol oxidation in redox reactions with MnO₂, enhancing the overall reduction leaching efficiency.



1. INTRODUCTION

Ferromanganese nodules or polymetallic ocean nodules are a well-established source of valuable metals such as Co, Ni, Cu, Mn, and Zn, especially for India where exploitable land-based primary resources for Co and Ni are rare. These nodules are small rocks formed by the concentric layers of iron and manganese oxides/hydroxides in the ocean bed consisting birnessite (δ -MnO₂) and goethite (FeOOH) as the major minerals.¹ Manganese is the major constituent metal occurring up to 33% in the nodule matrix, along with small quantities of valuable metals such as Cu, Co, Ni, and Zn associated with aluminum silicate, clays, quartz, and other minerals present in the nodule. Nodules have a highly porous structure and retain significant moisture content. Low content of the valuable metals in the nodule, Ni (0.2–1.62%), Cu (0.1–1.7%), Co (0.02–1.15%), and Zn (0.1%), and high moisture content warrants a method of aqueous processing to recover these metals.² Fuerstenau and Han³ described that the constituent metals in the nodule matrix can be dissolved differently at different pH/Eh combinations and that sufficiently low pH and reducing conditions would enable solubilization of all metal oxides. In order to recover all the valuable metals through acid leaching, it is essential to convert Mn(IV) present in MnO₂ to soluble Mn(II) during leaching with the help of a reducing agent. Leaching of polymetallic nodules have been widely reported for Cu, Ni, and Co extraction in different leaching media such as sulfuric acid, hydrochloric acid, ammonia, etc. in

the presence of both inorganic and organic reducing agents. A summary of various leaching media and reducing agents used for the extraction of valuable metals from manganese nodules is shown in Table 1.

Conventionally used inorganic reducing agents such as pyrite, sodium sulfite/SO₂, carbon, sulfur, etc. (listed in Table 1) result in the formation of a residue or soluble compound in the leaching medium that necessitates treatment of tailings or effluents in the downstream processing after metal recovery. On the other hand, organic reducing agents have gained attention due to their benign nature, as they do not generate any toxic or hazardous solid/liquid waste during or after the process with the possibility of complete decomposition. In the context of nodule acid leaching, organic reducing agents such as oxalic acid, ascorbic acid, phenols, and glucose have been reported (Table 1). Apart from nodules, some of the organic reducing agents reported for acid leaching of low grade manganiferrous ores are glucose,¹⁸ starch,¹⁹ molasses,²⁰ sawdust, lactose,²¹ etc. Glycerol, a polyol and byproduct in

Received: February 9, 2021

Accepted: May 28, 2021

Published: June 7, 2021



Table 1. Overview of Reducing Agents Used in Manganese Nodule Leaching

s.no	ore	lixiviant	reducing agent	observations	reference
1.	Pacific Ocean nodules	H ₂ SO ₄ (0.93 g/g nodule)	phenols (hydroxybenzene) and aromatic amines (0.4 g/g nodule)	nearly 95% recovery of Mn, Cu, Ni, and Co	4, 5
2.	Pacific Ocean nodules	H ₂ SO ₃	SO ₂ (0.77 g/g nodule)	selective recovery >90% Mn, Ni, Co, and rejection of Cu	6
3.	Pacific Ocean nodules	ammonia/water	SO ₂ (quantity not available)	selective recovery of Ni, Cu, and Co with a NH ₄ OH + SO ₂ medium (>95%); water + SO ₂ extracted all metals with limited Mn and Fe	7
4.	Indian Ocean nodules	H ₂ SO ₄ (0.28 g/g nodule)-H ₂ O-(NH ₄) ₂ SO ₄ (0.5 g/g nodule)	SO ₂ (0.3 g/g nodule)	>98% Mn, Ni, Zn, >91% Co, 88% Cu, and 2–5% Fe extraction	8
5.	Indian Ocean nodules	dilute HCl (0.28 g/g nodule)	pyrite; Na ₂ SO ₃ ; carbon (1 g/g nodule)	pyrite effected >80% Mn and Co extraction; pyrite + carbon more effective than just carbon	9
6.	Pacific Ocean nodules	dilute HCl (0.73 g/g nodule)	Ni matte (1 g/g nodule)	>80% Co, >90 Ni, Cu, and Mn extraction	10
7.	Pacific Ocean nodules	dilute HCl (0.5 g/g nodule)	Zn matte (0.3 g/g nodule)	>90% Mn and Co extraction	11
8.	ferromanganese nodules	oxalic acid/H ₂ SO ₄	oxalic acid (3 g/g nodule)	2 stage leaching with oxalic acid and H ₂ SO ₄ to sequentially disrupt MnO ₂ and iron oxide matrices respectively	12
9.	Indian Ocean nodules	ammonia/ammonium chloride	glucose (0.2 g/g nodule)	100%Cu, >90% Ni, and >60% Co extraction	13
10.	Indian Ocean nodules	ammonia	Mn(II) (0.39 g/g nodule)	>90% Cu, Ni, Co with 20% Mn, and 2% Fe extraction	14
11.	Indian Ocean nodules	ammonia/ammonium sulfate	elemental sulfur (0.15 g/g nodule)	80% C, 95% Ni, and 70% Co	15
12.	Indian Ocean nodules	L-ascorbic acid	L-ascorbic acid (6.4 g/g nodule)	90% Cu, Ni, Co, and Mn extraction	16
13.	Indian Ocean nodules	H ₂ SO ₄	glycerol (0.63 g/g nodule)	>95% Mn, Ni, 87% Co, and >80% Cu	17

biodiesel production is widely used in synthesis as a precursor due to its simple yet multifunctional structure. It has also been reported as a reducing agent during the Mo-catalyzed chemoselective deoxygenation of sulphoxides (García et al., 2013).

Given the nontoxic, biomass-derived nature of glycerol with huge supply potential due to growing biodiesel industry²² and its reducing ability in an acid medium, the present work is focused on the optimization of leaching parameters and understanding the chemistry of glycerol oxidation during the nodule leaching process. Following a promising preliminary study on nodule leaching using glycerol as a reductant by Aishvarya et al., 2013,¹⁷ parameters such as pulp density, time, temperature, and acid concentration were optimized in the present work and glycerol oxidation accompanying the leaching process was elucidated using the Raman spectroscopy and liquid chromatography-mass spectrometry (LC-MS) studies of the leach liquor. Additionally, the rate-limiting step in the heterogeneous leaching reaction of the nodule using glycerol was better understood by studying the kinetics of the leaching process.

2. RESULTS AND DISCUSSION

The reductive effect of glycerol on the H₂SO₄ leaching of the manganese nodule is given in Table 2 under the test conditions

Table 2. Comparison of Metals Extraction without and with the Reducing Agent (Glycerol) under the Test Conditions of 2% Pulp Density (w/v), 2% H₂SO₄ (v/v), 80 °C, and 2 h

condition	% recovery				
	Mn	Co	Cu	Ni	Fe
without glycerol addition	8.2	4.4	68.8	70.4	61
with glycerol addition (1% v/v)	98	97.8	97.5	88	80

of 2% pulp density (w/v), 2% H₂SO₄ (v/v), 80 °C, and 2 h. The leaching in H₂SO₄ solution without any glycerol produced very poor Co and Mn dissolution (<10%) with 60–70% Cu, Ni, and Fe extraction, while with 1%(v/v) glycerol addition, all the metals were leached very effectively giving >97% Cu, Co, and Mn with 88% Ni extractions. The effect of glycerol concentration was reported in the previous study by Aishvarya et al., (2013).¹⁷ Accordingly, 1% (v/v) or 0.126 g glycerol per gram of nodule is used in the present work for the optimization of other parameters. Optimization study of the other leaching parameters (time, H₂SO₄ concentration, pulp density, and temperature) are discussed in this study along with the elucidation of leaching kinetics and various oxidation intermediates generated from glycerol.

2.1. Study of Leaching Parameters. 2.1.1. Effect of Time. The effect of reaction time on the metal recovery was estimated by carrying out an experiment keeping all other leaching parameters fixed, i.e., nodule pulp density at 10% (w/v), concentration of reducing agent glycerol at 1%(v/v), H₂SO₄ concentration at 10% (v/v), and temperature at 80 °C. Samples were collected at regular time intervals up to 3 h. The effect of time variation on extraction of different metals is shown in Figure 1. It can be observed that extraction of metals increases up to 1 h after which the increase in recovery is very marginal and time has practically no effect.

2.1.2. Effect of Acid Concentration. The concentration of lixiviant sulfuric acid was varied from 2% to 12.5% (v/v) while keeping glycerol concentration fixed at 1% (v/v), pulp density at 10%, and temperature at 80 °C. From the results, it was observed that the percentage of metal extraction increased with acid concentration (Figure 2). Maximum extractions of Co, Ni, and Cu were observed at 10% (v/v) acid, which are comparable with sulfuric acid leaching in the presence of phenols and sucrose reported for nodules (Table 1) and low

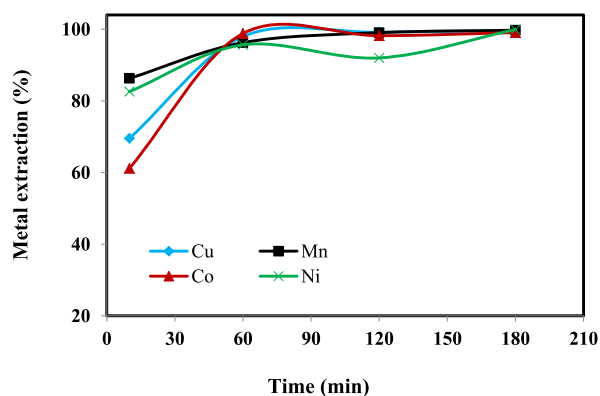


Figure 1. Effect of leaching time on metal extraction. Conditions: pulp density 10% (w/v), H₂SO₄ 10% (v/v), glycerol 1% (v/v), 80 °C.

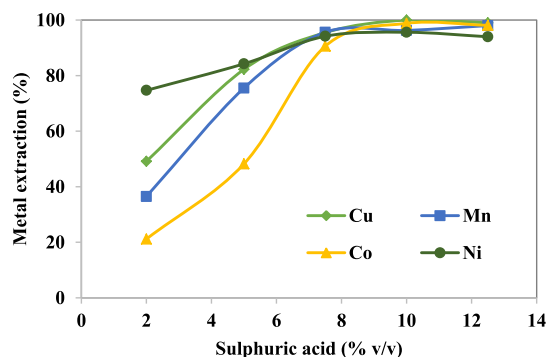


Figure 2. Effect of H₂SO₄ concentration on metal extraction. Conditions: pulp density 10% (w/v), glycerol 1% (v/v), 80 °C, 1 h.

grade manganese ores, respectively.^{5,18} At 10% (v/v) H₂SO₄ the extraction percentages of Co, Ni, and Cu were 98.8, 95.6, and 100, respectively, while Mn recovery was 95.6% at 7.5% (v/v) acid with a marginal increase at 10% (v/v). Further increase in acid concentration did not show a significant increase in extraction of targeted metals. Therefore, 10% v/v acid concentration was used for the other parameter optimizations.

2.1.3. Effect of Pulp Density. In order to estimate the limiting solid to liquid ratio in extraction of metals, pulp density was increased from 2 to 12.5% (w/v) keeping other parameters constant such as sulfuric acid at 10% (v/v), temperature 80 °C, 1% (v/v) glycerol, and leaching time of 1 h. Figure 3 shows that extraction of target metals were satisfactory ($\geq 95\%$) without much variation for the increase of

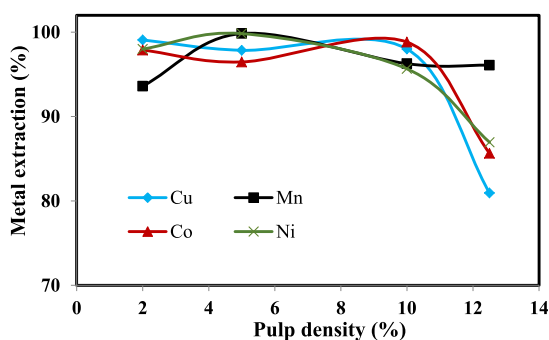


Figure 3. Effect of pulp density on metal extractions. Conditions: H₂SO₄ 10% (v/v), 80 °C, 1 h, glycerol 1% (v/v).

pulp density up to 10% (w/v) for the amount of reagents used. At 12.5% (w/v), there was a 10–12% decrease in recovery of metals especially of Cu, Co, and Ni.

This is attributed to the insufficiency of sulfuric acid, which was calculated from the pH of the liquor to be 0.14 M after 1 h of leaching at 12.5% (w/v). Since the leachability of metals is directly related to the extent of reduction and free acid content, it may hence be required to proportionately increase the amount of acid and glycerol for operations above 10% pulp density. Experiments carried out at higher acid and glycerol concentrations (shown in Table 3) ascertain this.

Table 3. Experiments at Higher Pulp Density with Enhanced Reagent Concentrations

s.no.	experimental condition	% recovery			
		Mn	Cu	Ni	Co
1	12.5% (w/v) pulp density; 12.5% (v/v) H ₂ SO ₄ ; 1.25% (v/v) glycerol; 80 °C, 1 h	93.0	97	98	98
2	15% (w/v) pulp density; 15% (v/v) H ₂ SO ₄ ; 1.5% (v/v) glycerol; 80 °C, 1 h	92.6	98	95.2	99

2.1.4. Effect of Temperature. Temperature influences the reaction kinetics strongly and it was necessary to optimize the same for reductive leaching in the presence of glycerol especially due to the organic nature of the reductant. Experiments were performed by varying the temperature from 50 to 90 °C while keeping other conditions constant such as pulp density at 10% (w/v), H₂SO₄ at 10% (v/v), glycerol at 1% (v/v), and leaching time 1 h, and the obtained results are presented in Figure 4. Close to 80% Cu, Ni, and Mn

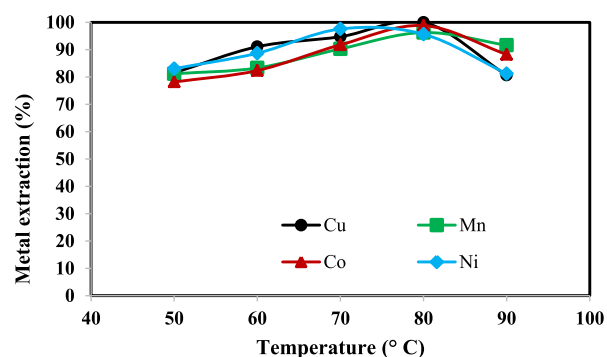


Figure 4. Effect of temperature on extraction of metals. Conditions: pulp density 10% (w/v), H₂SO₄ 10% (v/v), glycerol 1% (v/v), 1 h.

extractions were obtained at 50 °C and the extraction of the metals increased with the increase in temperature and reported a maximum at 80 °C with $>95\%$ extraction for all elements. Further increase in temperature to 90 °C led to a small decrease in metal recovery, possibly due to some retarding effect of higher temperature on the further reductive activity of intermediates during the leaching process; however, awaiting additional experiments to understand and ascertain the cause. Hence, for the chosen parametric conditions, 80 °C was found to be optimal.

At the end of the optimization experiments on pulp density, time, acid concentration, and temperature variation using 1% (v/v) glycerol, the suggested set of optimal parameters are 10%

(w/v) pulp density, 10% (v/v) H_2SO_4 at 80 °C for 1 h, and the glycerol used is thus 0.126 g/g under optimal conditions.

2.1.5. Kinetics. Leaching kinetics was studied by experimenting at 2% (w/v) nodule pulp density up to a time period of 1 h with intermittent sampling. The initial rate analysis method, which is an unbiased method of evaluating the rate-controlling step²³ was employed here specifically for kinetic data at different temperatures. The general leaching conditions for the kinetic study were 2% (w/v) pulp density, 2% (v/v) H_2SO_4 , 1% (v/v) glycerol, and the mean nodule particle size was 91 μm (for size range, $-106 + 75 \mu\text{m}$). Since MnO_2 is the major metal bearing phase in the nodule, Mn dissolution data were used for deducing kinetics. The fraction of Mn leached (X_{Mn}) versus time at different temperatures under the aforementioned conditions is shown in Figure 5. It can be

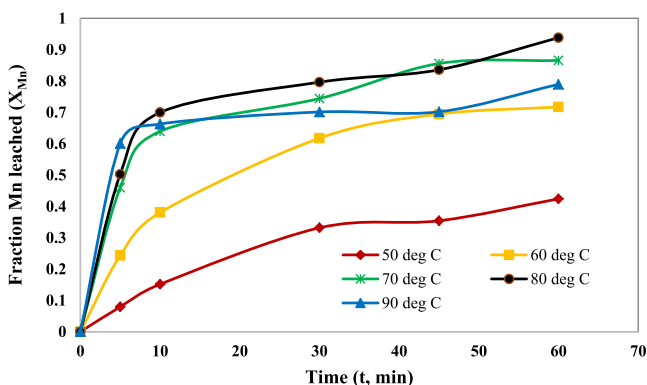


Figure 5. Fraction of manganese leached at different temperatures versus time. Conditions: pulp density 2% (w/v), sulfuric acid 2% (v/v), glycerol 1% (v/v), mean particle size 91 μm .

noticed that there is a steep rise in dissolution in the first 10 min of the reaction especially at higher temperatures followed by a relatively slow and steady increase up to 60 min. Nearly 80% of total dissolution seems to happen within the first 30 min, especially at elevated temperatures.

In order to determine the initial rate, polynomial regression was performed to fit the experimental X_{Mn} versus t plots corresponding to different temperatures. The correlation coefficients of the regression equations were more than 0.99. The initial rate was determined from the slope of the regression equations at time $t = 0$, by taking first order differential (dX_{Mn}/dt , at $t = 0$) corresponding to each temperature. This initial rate is in fact the apparent rate constant " k_s ,"²³ which was further used to estimate the activation energy from the slope of the straight line plot (Arrhenius plot) of $\ln(k_s)$ versus $1/T$.

As shown in Figure 6, the activation energy estimated from the slope of the Arrhenius plot ($-Ea/R = -6672.3$, $R^2 = 0.9496$) was found to be 55.473 kJ/mol. The high activation energy is indicative that the process is controlled by the chemical reaction at the surface of the particle.^{24,25} Other reports of nodule leaching kinetics in the H_2SO_4 medium in the presence of a solid inorganic reducing agent²⁶ show a reaction-controlled and product diffusion-controlled kinetics due to the buildup of solid residues (such as sulfur) in the process. It is clear that the absence of additional solid residue generation in the case of glycerol presents advantageous leaching kinetics for metal recovery from the nodule.

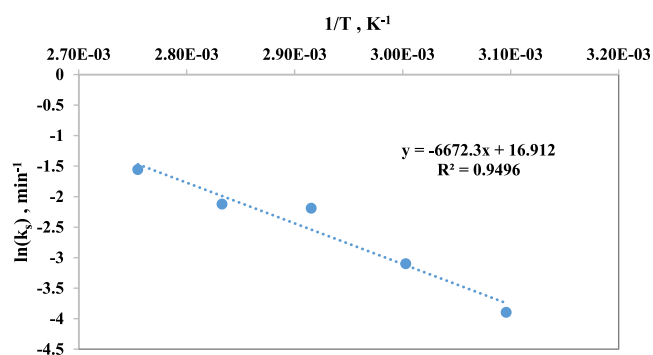


Figure 6. Arrhenius plot for manganese nodule leaching in H_2SO_4 using glycerol as the reductant.

2.2. Mineralogical and Morphological Characterization. The characteristic X-ray diffraction (XRD) pattern of the nodule sample (Figure 7) clearly shows the presence of

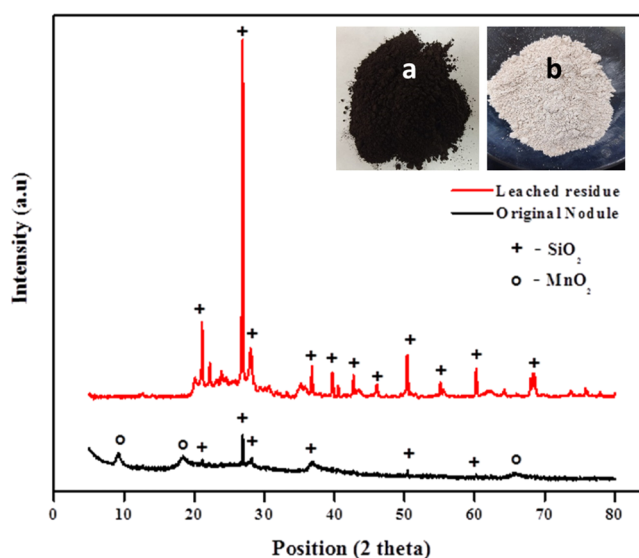


Figure 7. XRD pattern of the original nodule and the leached residue; (inset image) digital photographs of (a) original nodule powder and (b) leached residue.

MnO_2 (JCPDS Ref. no. 03-065-1298) and SiO_2 (JCPDS Ref. no. 89-8934) peaks. Iron in the manganese nodule was reported to be present as goethite,² which is not detected in the original nodule being amorphous in nature. A typical leach residue from the optimized leaching condition, i.e., 10% (w/v) pulp density, 10% (v/v) H_2SO_4 , 1% (v/v) glycerol, at 80 °C for 1 h, was analyzed for residual mineral phases. The diffraction pattern of the leached residue confirms the absence of MnO_2 peaks (Figure 7) signifying that nearly all the manganese in the nodule has been successfully leached out leaving behind SiO_2 in the residue. The difference in the physical appearance between the leached residue and the original nodule powder can also be seen (Figure 7), showing an almost white-colored residue. Change in surface morphology of the ore before and after leaching can be seen from Figure 8. The leached residue shows a reacted and weathered surface with increased roughness. Following the optimization of parameters in the present study and the leaching kinetics, it can be confirmed that glycerol is an effective reducing agent to achieve a near-complete recovery of manganese (>99%) from

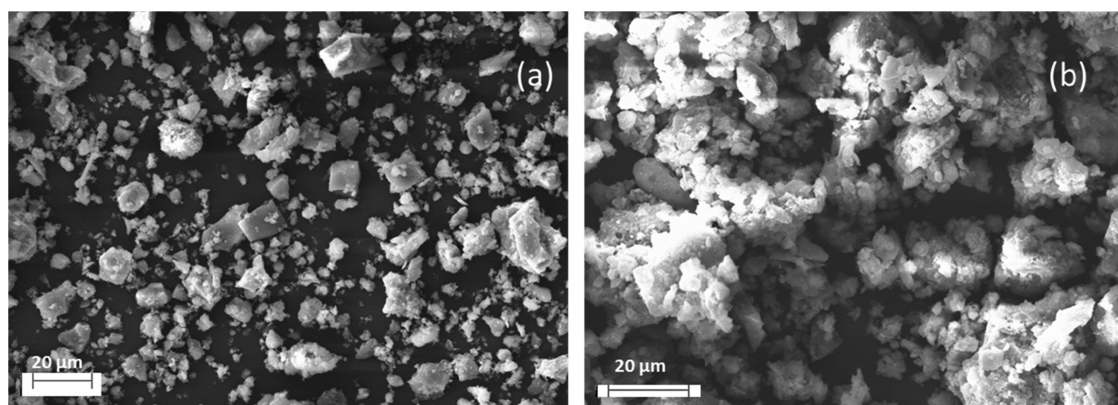


Figure 8. Scanning electron microscopy image showing morphological differences between (a) nodule powder and (b) leached residue.

the nodule and at significantly low requirement (0.126 g/g nodule) as compared to other cited reducing agents (Table 1).

2.3. Identification of Glycerol Oxidation Intermediates. Glycerol oxidation comprises a complex series of reactions as many reaction centers are created in the polyol structure during its oxidation. In order to predict the pathway of glycerol oxidation and to identify all the oxidation reaction intermediates before formation of CO_2 , the leach liquor was intermittently analyzed by LC-MS and Raman spectroscopy. For this purpose, a typical leach liquor obtained from the optimized parametric conditions, i.e., 10% (w/v) pulp density, 10% (v/v) H_2SO_4 , and 1% (v/v) glycerol at 80 °C for 1 h was used.

2.3.1. Raman Spectroscopy of the Leach Liquor. The Raman active vibration modes corresponding to different stretching and bending vibrations of various functional groups present in glycerol and its oxidation products are reflected from the Raman spectra shown in Figure 9. For the purpose of carrying out Raman spectroscopy, a leaching experiment was carried under the abovementioned optimized conditions with intermittent sampling at 10, 30, 45, and 60 min and compared against 1% (v/v) glycerol in water as the blank. The characteristic asymmetric stretching of C–H and O–H groups and CH_2 deformation of glycerol can be noticed in Figure 9 matching with standard glycerol spectra.²⁷ The band at 329 cm^{-1} corresponds to C–C bending vibration of the carbon chain and can be seen in both glycerol as well as the products in the leach liquor. The broad line at 470 cm^{-1} is produced due to the C–CO rocking of the quaternary carbon atom in one of the oxidation products, which is absent in the blank. Similarly, the bands at 1762 and 1654 cm^{-1} are due to the carbonyl ($>\text{C}=\text{O}$) stretching vibration of carboxylic acids. The line at 2947 cm^{-1} is possibly due to antisymmetric C–H stretching vibrations of the aliphatic chain seen in both glycerol and oxidation products.^{27–29} The band at 2426 cm^{-1} could not be matched to any particular vibration but is found to occur in all intermittent liquor samples collected as well as in the blank (glycerol). However, it is evident from the Raman spectra of the leach liquor that glycerol is oxidized to different aldehydes and aliphatic acids during the Mn-nodule leaching process.

2.3.2. LC-MS Analysis of the Leach Liquor. During the leaching process in the presence of sulfuric acid, MnO_2 present in the manganese nodule accomplishes the oxidation of glycerol to several partially oxidized intermediates, which can be confirmed from the mass spectrum obtained from a typical leach liquor sample of 30 min (under optimized conditions) as

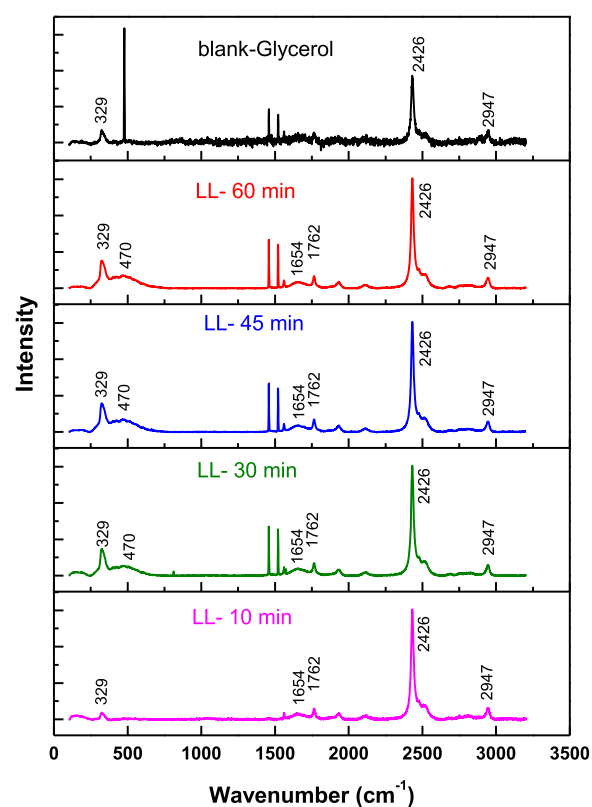


Figure 9. Raman spectra of the nodule leach liquor under optimized conditions collected at different time intervals.

shown in Figure 10. The spectrum obtained shows peaks of mass to charge ratio (m/z) values of 72, 91, 97, 102, 107, 113, 116, and so on, which can be indexed to various oxidation intermediates as explained below.

In an acidic environment glycerol, becomes the radical cation as it loses one hydrogen to form the nearest radical having an m/z value of 91. The m/z value of 102 corresponds to the hydroxy pyruvate ion. The hydroxy pyruvic acid (m/z 104) forms from dihydroxy acetone (m/z 90) which is formed from glycerol on oxidation. This hydroxy pyruvic acid loses two hydrogen forming hydroxyl pyruvate ions (m/z 102).²⁹

The m/z value of 107 may be attributed to the formation of 1,3,2,2 tetrahydroxy propane (m/z 108) from glycerol after losing one hydrogen from the second carbon or from a hydrated oxalic acid molecule (m/z 108). The peak at m/z 116 corresponds to the mesoxalate ion after losing two hydrogen

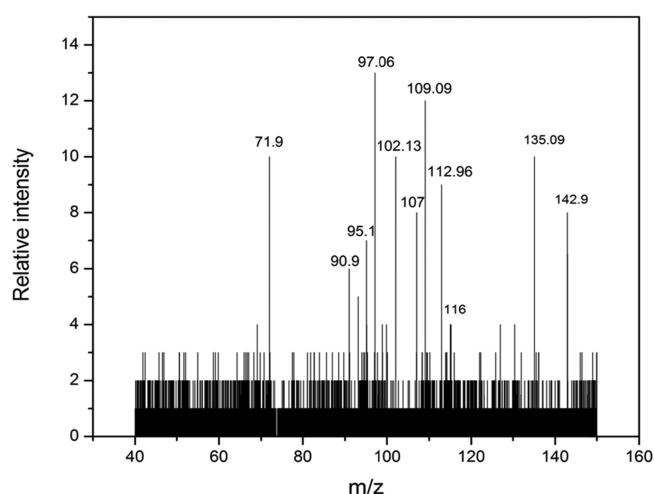


Figure 10. Mass spectrum of the leach liquor after 30 min of leaching.

atoms from mesoxalic acid (m/z 118). The m/z value of 72 corresponds to the formation of the glyoxalate ion from glyoxalic acid (m/z 74) upon removal of two hydrogens. Similarly, the tartronate ion forms through oxidation of glyceraldehyde (m/z 90) to glyceric acid (m/z 106) and from glyceric acid to tartronic aldehyde (m/z 104) which further oxidizes to tartronic acid (m/z 120). This tartronic acid when loses two hydrogen ions forms the tartronate ion (m/z 118).³⁰ The mass spectrum of glycerol in plain water (Supporting Information Figure S1) can be seen showing the characteristic base peak from protonation (m/z 93) and with Na^+ ions (m/z 115).^{31,32}

2.4. Glycerol Oxidation Pathway during Leaching.

Glycerol oxidation in the sulfuric acid medium generates several oxidation products due to the reactive polyol structure of the reductant and the extent of intermediate products formed depend on the strength of the oxidizing agent.^{33,34} MnO_2 which is present in the nodule, is a strong oxidizing agent and results in CO_2 , H_2O , and Mn(II) formation by reacting with acid and glycerol as given below:

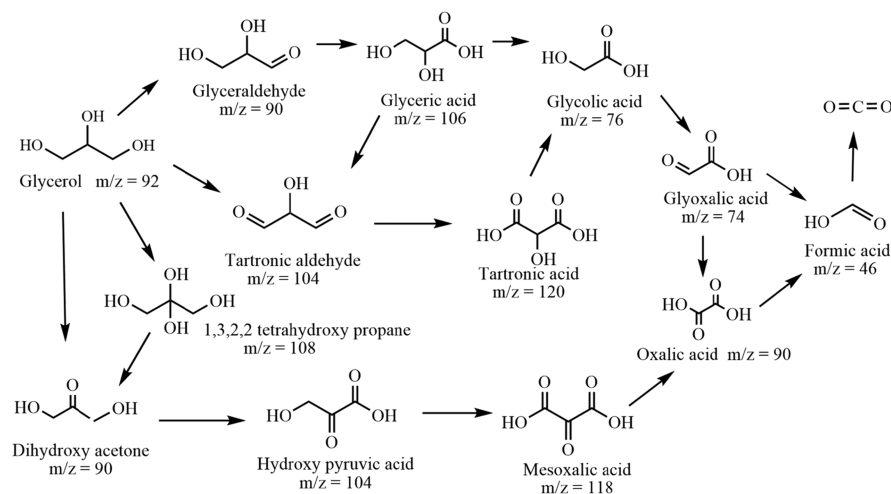
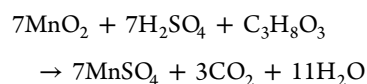


Figure 11. Schematic of probable oxidation pathways of glycerol during reductive leaching of the polymetallic nodule.

The intermediate oxidation products of glycerol such as aldehyde, ketone, or acids formed during the oxidation as evidenced from both Raman spectra and LC-MS analysis further oxidize in the acid medium forming CO_2 as the final product.³⁴ The formation of CO_2 was confirmed in the present study by passing the evolved gas through a water of lime solution (aq. Ca(OH)_2). For this test, an experiment was carried out at optimized leaching parameters in a sealed autoclave with a vent provision. Generation of CO_2 was confirmed with the formation of CaCO_3 which changed the lime solution to appear milky white.

Given that the formation of oxidation intermediates of glycerol is ascertained based on the mass spectrometry and Raman spectroscopy analysis (Figures 9 and 10), and the final oxidation product was confirmed to be CO_2 , it is possible to derive the probable pathway of oxidation during the leaching process due to the well-known and simple polyol structure of glycerol. An overall scheme of various oxidation pathways is represented in Figure 11 with all possible major and minor intermediates based on the leach liquor analysis presented.^{30,35}

Glycerol is oxidized to several partial oxidation intermediates such as glyceraldehydes, glyceric acid, dihydroxy acetone, tartronic aldehyde, tartronic acid, glycolic acid, glyoxalic acid, hydroxy pyruvic acid, mesoxalic acid, oxalic acid, formic acid, and finally CO_2 during nodule leaching. As seen from the kinetic data, nearly 80% of the total dissolution happens within the first 30 min of the reaction (Figure 5), during which many oxidation intermediate formation can be seen (Figures 9 and 10). Each of the intermediate is further capable of reducing MnO_2 in the process of its own oxidation as evidenced by their reductive action elsewhere.³⁵ This reductive action of multiple intermediates formed during glycerol oxidation may be attributed as the reason for a near-complete MnO_2 dissolution resulting in leaching of metals from the nodule, especially using a much lower quantity of the reducing agent as compared to other reductants (Table 1). Further studies on stoichiometric consumption of glycerol and its oxidation products may help establish the role of each intermediate involved. Clearly, glycerol is an attractive candidate as a green reductant for maximizing metal recovery from nodules en route to achieving an efficient leaching process.

3. EXPERIMENTAL SECTION

3.1. Raw Material. Polymetallic Indian Ocean nodules used in this study were supplied by CSIR-National Institute of Oceanography, Goa, India. The nodules were crushed, ground, and sieved to obtain a size fraction less than 150 μm . The chemical analysis of the representative sample is given in Table 4 which shows high Mn and Fe content, while the valuable

Table 4. Elemental Composition of the Polymetallic Nodule Used in the Study

elements	Cu	Fe	Mn	Co	Ni
%	0.93	5.6	18.75	0.085	1.15

metals Ni and Cu were ~ 0.9 – 1.2% and Co was $<0.1\%$. The major phases present were MnO_2 and SiO_2 as seen from the XRD pattern (Figure 7). For convenience, the XRD pattern of the manganese nodule is compared with the XRD of leach residue and included in Figure 7. The chemicals (H_2SO_4 and glycerol) used in this work were of analytical reagent grade. The specification of glycerol used in the study are provided in Table 5.

Table 5. Specification of Glycerol Used in the Study

linear formula	$\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$
molecular mass, g/mol	92.09
assay, %	>99.5
water, %	0.5 (max)
ignition residue, %	0.005 (max)
boiling point, $^\circ\text{C}$	290
melting point, $^\circ\text{C}$	18
flash point, $^\circ\text{C}$	160
density, g/cm^3	1.261

3.2. Methodology. Experiments were carried out in a double-walled glass reactor attached to a hot water bath with circulator arrangement (Julabo, Germany) which maintained the reactor at a given temperature (± 0.2 $^\circ\text{C}$). A required amount of H_2SO_4 solution of known concentration was placed in the reactor and heated up to the desired temperature with agitation using a magnetic stirrer. Once the temperature was attained, the required amount of nodule and glycerol were added to the reactor. Few experiments were also carried out in a 1 L autoclave (make: Parr Instrument company, USA) to confirm CO_2 generation. After leaching, the leach slurry was filtered, and the residue was washed thoroughly with distilled water and dried in an oven. Phase identification of the powdered nodule sample and a typical leach residue was carried out by a Rigaku Ultima IV X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54$ \AA) in the range of 10 to 80° (2θ) at a scan rate of $3^\circ/\text{min}$. The surface morphology information of the ore and leached residue was obtained from scanning electron microscopy (SEM, ZEISS-EVO18).

The metal ions in the leach liquor were analyzed by atomic absorption spectroscopy (AAS, Perkin Elmer). The leach liquor was immediately analyzed for oxidation byproducts of glycerol by using LC-MS and Raman spectroscopy. The mass spectra analysis was performed using a Bruker micrOTOF-Q II mass spectrometer equipped with an electron spray ionization (ESI) source. The Raman spectra were observed using a dispersive type micro-Raman spectrometer (Renishaw-InVia Raman microscope, UK).

4. CONCLUSIONS

Reductive leaching of Mn, Co, Cu, and Ni from the polymetallic sea nodules was successfully accomplished using glycerol as a reducing agent in a sulfuric acid medium. Glycerol is a process-friendly organic renewable reductant that does not generate solid or liquid wastes in the process. Reductive leaching of Indian Ocean nodules was performed and the optimal parameters were found to be 10% (v/v) H_2SO_4 , 1% (v/v) glycerol, 10% (w/v) pulp density, 80 $^\circ\text{C}$ temperature, and 1 h duration. Nearly complete recoveries of all the metals, i.e., $>95\%$ of Ni and $>98\%$ of Mn, Cu, and Co were achieved in 1 h at the optimized condition. Kinetic analysis reveals that the leaching process was chemical reaction-controlled with an apparent activation energy of 55.47 kJ/mol . XRD of the leach residue showed no detectable manganese peaks indicating that MnO_2 has been leached out from the nodule. The probable oxidation pathways of glycerol were elucidated indicating the oxidation products based on the analysis of the leach liquor by LC-MS and Raman spectroscopy. The analyses revealed that glycerol was oxidized to multiple partial oxidation products such as glyceraldehyde, glyceric acid, tartronic acid, dihydroxy acetone, hydroxy pyruvic acid, glyoxalic acid, oxalic acid, and finally converted to carbon dioxide. The fast dissolution kinetics and near-complete dissolution of MnO_2 in the manganese nodule are attributed to the participation of these intermediate oxidation products arising from the unique structure of glycerol, resulting in maximum leaching of metals at a very low reductant to nodule quantity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c00730>.

Mass spectrum of glycerol in plain water (Figure S1) (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Aishvarya Venkataseetharaman – Academy of Scientific and Innovative Research (AcSIR), CSIR-Institute of Minerals and Materials Technology Campus, Bhubaneswar 751013, India; Hydro & Electrometallurgy Department, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar 751013, India; orcid.org/0000-0003-4294-4686; Phone: +91-7735849811; Email: aishvarya@imtm.res.in

Goutam Kumar Das – CSIRO Mineral Resources, Waterford, Western Australia 6152, Australia; Phone: +61 8 9334 8933; Email: Goutam.Das@csiro.au; Fax: +61 8 9334 8001

Authors

Geetanjali Mishra – Hydro & Electrometallurgy Department, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar 751013, India

Malay Kumar Ghosh – Academy of Scientific and Innovative Research (AcSIR), CSIR-Institute of Minerals and Materials Technology Campus, Bhubaneswar 751013, India; Hydro & Electrometallurgy Department, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar 751013, India

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsomega.1c00730>

Author Contributions

#A.V. and G.M. made equal contribution to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are thankful to the Director, CSIR-IMMT, Bhubaneswar for his kind permission to publish this work. The authors appreciate the support of Ms. Swagatika Mohanty, Dr. B.B. Palei, Dr. Monojit Das, and Mr. Ajit Dash for the assistance rendered in characterization techniques. The financial support for the project from the Ministry of Earth Sciences, Govt. of India (GAP-301) is gratefully acknowledged.

REFERENCES

- (1) Kanungo, S. B.; Das, R. P. Extraction of Metals from Manganese Nodules of the Indian Ocean by Leaching in Aqueous Solution of Sulphur Dioxide. *Hydrometallurgy* **1988**, *20*, 135–146.
- (2) Senanayake, G. Acid Leaching of Metals from Deep-Sea Manganese Nodules - A Critical Review of Fundamentals and Applications. *Miner. Eng.* **2011**, *24*, 1379–1396.
- (3) Fuerstenau, D. W.; Han, K. N. Metallurgy and Processing of Marine Manganese Nodules. *Miner. Process. Extr. Metall. Rev.* **1983**, *1*, 1–83.
- (4) Zhang, Y.; Liu, Q.; Sun, C. Sulfuric Acid Leaching of Ocean Manganese Nodules Using Aromatic Amines as Reducing Agents. *Miner. Eng.* **2001**, *14*, 539–542.
- (5) Zhang, Y.; Liu, Q.; Sun, C. Sulfuric Acid Leaching of Ocean Manganese Nodules Using Phenols as Reducing Agents. *Miner. Eng.* **2001**, *14*, 525–537.
- (6) Khalafalla, S. E.; Pahlman, J. E. Selective Extraction of Metals from Pacific Sea Nodules with Dissolved Sulfur Dioxide. *JOM* **1981**, *33*, 37–42.
- (7) Kawahara, M.; Katayama, K.; Mitsuo, T. Leaching of Manganese Nodules Using Sulfur Dioxide as a Reductant. *Shigen-to-Sozai* **1991**, *107*, 871–876.
- (8) Acharya, R.; Ghosh, M. K.; Anand, S.; Das, R. P. Leaching of Metals from Indian Ocean Nodules in $\text{SO}_2\text{-H}_2\text{O-H}_2\text{SO}_4\text{-(NH}_4\text{)}_2\text{SO}_4$ medium. *Hydrometallurgy* **1999**, *53*, 169–175.
- (9) Kanungo, S. B.; Jena, P. K. Reduction Leaching of Manganese Nodules of Indian Ocean Origin in Dilute Hydrochloric Acid. *Hydrometallurgy* **1988**, *21*, 41–58.
- (10) Hsiaohong, C.; Chongyue, F.; Di-ji, Z. Reduction Leaching of Manganese Nodules by Nickel Matte in Hydrochloric Acid Solution. *Hydrometallurgy* **1992**, *28*, 269–275.
- (11) Kuh, S. E.; Kim, J. W.; Kim, D. S.; Choi, K. S. Extraction of Metal Values from Manganese Nodules in the Ocean Environment Using Zinc Matte as a Reductant. *Environ. Technol.* **2001**, *22*, 881–887.
- (12) Zeitlin, H.; Fernando, Q. Oxalic Acid Leaching of Marine Nodule. US4259295A, December 1979.
- (13) Das, R. P.; Anand, S.; Das, S. C.; Jena, P. K. Leaching of Manganese Nodules in Ammoniacal Medium Using Glucose as Reductant. *Hydrometallurgy* **1986**, *16*, 335–344.
- (14) Acharya, S.; Das, R. P. Kinetics and Mechanism of the Reductive Ammonia Leaching of Ocean Nodules by Manganous Ion. *Hydrometallurgy* **1987**, *19*, 169–186.
- (15) Mohanty, P. S.; Ghosh, M. K.; Anand, S.; Das, R. Leaching of Manganese Nodules in Ammoniacal Medium with Elemental Sulphur as Reductant. *Trans. Inst. Min. Metall., Sect. C* **1994**, *103*, C151–C154.
- (16) Mukherjee, A.; Raichur, A. M.; Modak, J. M.; Natarajan, K. A. Dissolution of Cu, Co and Ni from Ocean Nodules by L-Ascorbic Acid. *Chem. Eng. Process.* **2005**, *44*, 754–759.
- (17) Aishvarya, V.; Mishra, G.; Ghosh, M. K.; Subbaiah, T. Reductive Acid Leaching of Polymetallic Manganese Nodule with Polyol: Preliminary Study. In *XIII International Seminar on Mineral Processing Technology Vol. - I*; 2013; pp. 825–829.
- (18) Trifoni, M.; Vegliò, F.; Taglieri, G.; Toro, L. Acid Leaching Process by Using Glucose as Reducing Agent: A Comparison among the Efficiency of Different Kinds of Manganiferous Ores. *Miner. Eng.* **2000**, *13*, 217–221.
- (19) Hariprasad, D.; Ghosh, M. K.; Anand, S. Starch - A Potential Reductant for Manganese Ore Leaching. In *International seminar on Mineral Processing Technology (MPT)*; 2008; pp. 156–159.
- (20) Su, H.; Wen, Y.; Wang, F.; Sun, Y.; Tong, Z. Reductive Leaching of Manganese from Low-Grade Manganese Ore in H_2SO_4 Using Cane Molasses as Reductant. *Hydrometallurgy* **2008**, *93*, 136–139.
- (21) Ismail, A. A.; Ali, E. A.; Ibrahim, I. A.; Ahmed, M. S. A Comparative Study on Acid Leaching of Low Grade Manganese Ore Using Some Industrial Wastes as Reductants. *Can. J. Chem. Eng.* **2008**, *82*, 1296–1300.
- (22) Quispe, C. A. G.; Coronado, C. J. R.; Carvalho, J. A. Glycerol : Production , Consumption , Prices , Characterization and New Trends in Combustion. *Renew. Sustain. Energy Rev.* **2013**, *27*, 475–493.
- (23) Ghosh, M. K.; Das, R. P.; Biswas, A. K. Oxidative Ammonia Leaching of Sphalerite Part II: Cu(II)-Catalyzed Kinetics. *Int. J. Miner. Process.* **2003**, *70*, 221–234.
- (24) Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; John Wiley & Sons: New York, 1999.
- (25) Habashi, F. *Principles of Extractive Metallurgy: Vol 1*; Gordon and Breach Science publishers, New York, 1969.
- (26) Hsiaohong, C.; Chongyue, F. Kinetics of Leaching Manganese Nodules in the Presence of Zinc Sulfide. *Miner. Process. Extr. Metall. Rev.* **1995**, *15*, 101–114.
- (27) Mendelovici, E.; Frost, R. L.; Klopogge, T. Cryogenic Raman Spectroscopy of Glycerol. *J. Raman Spectrosc.* **2000**, *31*, 1121–1126.
- (28) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; 1999.
- (29) Silverstein, R.M., Webster, F.X., Kiemle, D.J., Bryce, D. L. *Spectrometric Identification of Organic Compounds*, 8th ed.; Wiley, 2014.
- (30) Suramane, P.; Poompradub, S.; Rojanathanes, R.; Thamyongkit, P. Effects of Reaction Parameters in Catalysis of Glycerol Oxidation by Citrate-Stabilized Gold Nanoparticles. *Catal. Lett.* **2011**, 1677–1684.
- (31) Field, F. H. Fast Atom Bombardment Study of Glycerol : Mass Spectra and Radiation Chemistry. *J. Phys. Chem.* **1982**, *86*, 5115–5123.
- (32) Mcintosh, T. S.; Davis, H. M.; Matthews, D. E. A Liquid Chromatography – Mass Spectrometry Method to Measure Stable Isotopic Tracer Enrichments of Glycerol and Glucose in Human Serum. *Anal. Biochem.* **2002**, *300*, 163–169.
- (33) Carrettin, S.; McMorn, P.; Johnston, P.; Griffin, K.; Kiely, C. J.; Attard, G. A.; Hutchings, G. J. Oxidation of Glycerol Using Supported Gold Catalysts. *Top. Catal.* **2004**, *27*, 131–136.
- (34) Zhou, C. H.; Beltramini, J. N.; Lu, G. Q. Chemoselective Catalytic Conversion of Glycerol as a Biorenewable Source to Valuable Commodity Chemicals. *Chem. Soc. Rev.* **2008**, *37*, 527–549.
- (35) García, N.; García-García, P.; Fernández-Rodríguez, M. A.; García, D.; Pedrosa, M. R.; Arnáiz, F. J.; Sanz, R. An Unprecedented Use for Glycerol: Chemoselective Reducing Agent for Sulfoxides. *Green Chem.* **2013**, *15*, 999–1005.