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Hydrometallurgical leaching and kinetic modeling of low-grade manganese ore with banana peel in sulfuric acid

Sajjad Ali[1)], *Yaseen Iqbal*[1)], *Inamullah Khan*[1)], *Ansar Ullah*[1)], *Muhammad Sadiq*[1)], *Muhammad Fahad*[2)], *and Khizar Hussain Shah*[3)]

1) Materials Research Laboratory, Department of Physics, University of Peshawar, 25120 Peshawar, Pakistan
2) Department of Electrical and Computer Engineering, COMSATS University Islamabad, Abbottabad Campus, University Road 22060 Abbottabad, Pakistan
3) Department of Chemistry, COMSATS University Islamabad, Abbottabad Campus, University Road 22060 Abbottabad, Pakistan

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Abstract: Manganese was leached from a low-grade manganese ore (LGMO) using banana peel as the reductant in a dilute sulfuric acid medium. The effects of banana peel amount, H_2SO_4 concentration, reaction temperature, and time on Mn leaching from the complex LGMO were studied. A leaching efficiency of ~98% was achieved at a leaching time of 2 h, banana peel amount of 4 g, leaching temperature of 120°C, manganese ore amount of 5 g, and sulfuric acid concentration of 15vol%. The phase, microstructural, and chemical analyses of LGMO samples before and after the leaching process confirmed the successful leaching of manganese. Furthermore, the leaching process followed the shrinking core model and the leaching rate was controlled by a surface chemical reaction ($1 - (1 - x)^{1/3} = kt$) mechanism with an apparent activation energy of 40.19 kJ·mol^{-1}.

Keywords: low-grade manganese ore; glucose; leaching; kinetics; activation energy

1. Introduction

Manganese is an important industrial metal and is widely used in the manufacturing of steel, alloys, fertilizers, paints, and chemicals [1–3]. The hydrometallurgical leaching of low-grade manganese ore (LGMO) has attracted significant interest in the last decade. Mn is typically obtained via the reductive leaching of manganese oxides using various reductants such as aqueous sulfur oxide (highly toxic), pyrite, iron sulfate, iron metal, and oxalic acid [4–8]. However, these reductants are expensive, hazardous, non-environment friendly, and less efficient, making industrial-scale production of manganese non-viable. These drawbacks have led to alternative routes and materials that are not only environmentally friendly, low cost, and efficient but also economical for manganese production. In this regard, the abundance and availability of cellulose-rich agricultural by-products can be utilized for manganese leaching owing to their low cost, effectiveness, and environment-friendly nature. Mn has been leached from manganese oxide ores in sulfuric acid medium using various agricultural by-products and plant powders, e.g., tea waste, molasses, corn-stalk, corncob, and sawdust [9–13]. Banana peel is another raw material, which is rich in cellulose (25.5wt%), and can be used as an efficient reductant for leaching manganese from LGMO. Banana peels are abundantly found in fruit markets and can be easily collected from such places, making them ideal for industrial applications.

From a geological perspective, the chemical composition of Mn-ores varies with its location and source, thus affecting the reaction pathway for the recovery of Mn from LGMO. Previous studies on the reductive leaching kinetics of pyrolusite reported that the relevant reaction is controlled by diffusion via a product layer, using a shrinking core model (SCM) [14–15].

The annual production/consumption of bananas in Pakistan is more than 154000 t, of which >30% is wasted in the form of peels. This disposal is costly and also pollutes the environment. Such problems can be addressed by developing a hygienic disposal system or transforming the waste into a useful raw material. Researchers are working towards recycling and utilizing banana peels for various purposes such as production of absorbents, preparation of porous carbon foams, and production of fillers and lingo-cellulose nano-

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Corresponding authors: Sajjad Ali E-mail: sajjad2485@yahoo.com; Khizar Hussain Shah E-mail: khizarshah@cuiatd.edu.pk

particles [16].

The present study aims at investigating the leaching potential of banana peels as a reductant for extracting manganese from its ores. The effects of processing parameters, such as banana peel amount, H_2SO_4 concentration, reaction temperature, and time, on the leaching rate of manganese were investigated. In addition, to derive the dissolution rate constant and determine the apparent activation energy (E_a), various kinetic models were applied and investigated.

2. Experimental

Samples of raw LGMO were collected from Prang Ghar, Mohmand district, Pakistan. Banana peels were obtained from a banana seller in a local market. The collected samples were properly washed with deionized water and dried in a hot-air oven (FREAS 605, Thermo Fisher Scientific, USA) at 90°C overnight and then crushed and grinded using a stainless-steel mortar and pestle system.

All the leaching experiments were performed in a fume hood (LFH-120 SCI, LabTech, Vietnam) using 250 mL glass beaker in a precision constant-temperature water bath with a magnetic stirrer on a hot plate (PC-420D, USA). In a typical experiment, 5 g of the LGMO sample (200 mesh) and 1–4 g of sieved (100 mesh) banana peels were added to 50 mL aqueous H_2SO_4 solution (5vol%–20vol%) while stirring (300 r/min) at a temperature range of 60–100°C (333–373 K) for 20–120 min. After the pre-determined time for the experiment, the slurry was cooled at room temperature and filtered via a Whatman filter paper. The slurry was properly washed and dried in a drier at 90°C for 2 h. In all the experiments, the pregnant leach solution containing a high concentration of manganese in the form of manganese sulfate was examined for manganese content using atomic absorption spectroscopy (AAS 700, Perkin Elmer, USA). For the phase, microstructural, and chemical analyses of the leftover manganese content, X-ray diffractometer (XRD; X'Pert^3 Powder, PANalytical, Netherland), scanning electron microscopy (SEM; JEOL JSM 5910, Japan) and X-ray fluorescence spectroscopy (XRF; EDX-7000 unit, Shimadzu, Japan) were applied, respectively. The yield was determined using Eq. (1):

$$\text{Yeild} = \frac{\text{Leached Mn}}{\text{Available Mn}} \times 100\% \tag{1}$$

3. Results and discussion

3.1. Effect of banana peel amount

From an experimental viewpoint, manganese cannot be directly leached from manganese ore with H_2SO_4 without a suitable reducing agent. Therefore, the effect of the concentration of glucose present in the banana peels on the leaching efficiency of LGMO was investigated by varying the amount of banana peels (1, 2, 4, and 6 g) at an initial H_2SO_4 concentration of 5vol% at 80°C for 2 h. Fig. 1 shows the relevant results. The leaching efficiency of manganese gradually increased with an increase in the amount of banana peels. The yield reached a maximum value of ~87% when the banana peel amount was 4 g, following which it decreased.

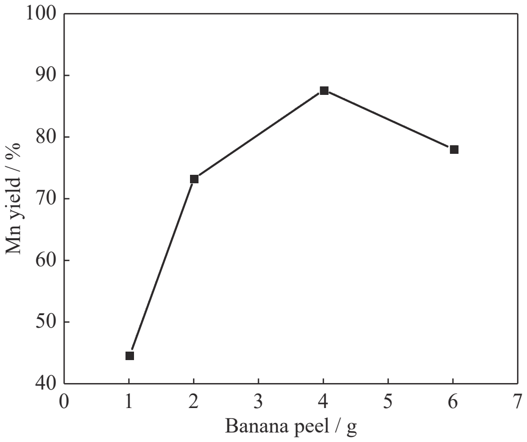

Fig. 1. Effect of banana peel on the yield of manganese leaching.

The XRF results listed in Table 1 point to a manganese decomposition of ~18wt%, probably because of the release of Mn^{2+} from LGMO into the aqueous solution at a banana peel amount of 4 g [17]; however, this dramatic increase in the leaching efficiency was not remarkable when the banana peel amount was 6 g, in which case the efficiency decreased abruptly to ~78%. Approximately 6wt% of manganese (Table 1) remained in the leached residue, indicating that manganese could not be recovered completely from the multiphase complex manganese ore, where some phases of manganese are difficult to leach in an acidic solution [18–19]. Similarly, the presence of a high silica content (~42wt%) in the residue implies that the leaching is restricted due to the encapsulation of manganese in the gangue.

Table 1. XRF chemical analyses of LGMO before and after leaching wt%

Chemical composition of as-mined LGMO before leaching

SiO_2	MnO	CaO	Fe_2O_3	Al_2O_3	TiO_2	NiO	V_2O_5	ZnO	SrO	ZrO_2
31.96	24.17	17.80	15.12	7.191	0.196	0.038	0.033	0.031	0.011	0.008

Chemical composition of LGMO after leaching with banana peel under optimum parameters

SiO_2	MnO	CaO	Fe_2O_3	SO_3	TiO_2	NiO	BaO	K_2O	SrO	ZrO_2
41.60	6.13	0.39	21.06	29.39	0.29	0.01	0.64	0.33	0.02	0.006

3.2. Effect of temperature

Several experiments were performed to determine the optimum temperature for leaching manganese from LGMO in dilute sulfuric acid (5vol%). All the experimental conditions were kept constant except for the temperature, which was varied from 60 to 120°C at 20°C intervals. The concentration of manganese in the pregnant leach solution obtained at varying temperatures was measured using AAS. Fig. 2 shows the results, indicating a high manganese leaching efficiency at a leaching temperature of 120°C. The yield of manganese increases from ~28% to 98% as the temperature is gradually increased from 60 to 120°C. The reduction of MnO_2 mainly depends on the hydrolysis of cellulose (polysaccharides) or lactose (disaccharides) into monosaccharaide compounds. For example, glucose is responsible for the reduction process and the hydrolysis process is directly proportional to the temperature, which increases the hydrolysis rate [20]. This can be attributed to the decrease in the solution viscosity with increasing temperature. Further increasing the temperature above 100°C did not show any significant increase in the yield of manganese (it only slightly increased from 97% to 98%); therefore, from an economic perspective, the most favorable temperature is 100°C.

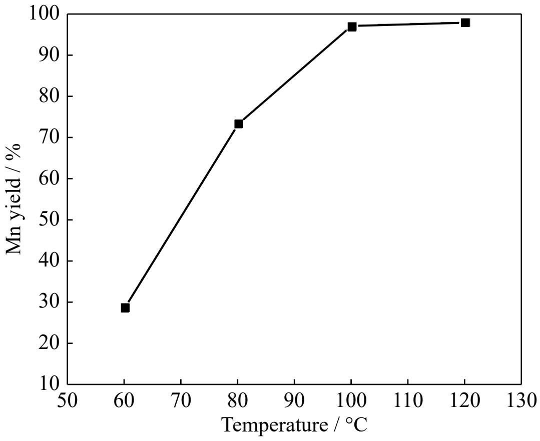

Fig. 2. Influence of temperature on the yield of manganese leaching from its ore.

3.3. Effect of leaching time

The influence of leaching time on the yield of Mn leaching was studied in the 2–5 h time window. Fig. 3 shows the results in graphical form. The observations made can be attributed to the fact that manganese reduces from its ore due to the available fixed amount of banana peel that hydrolyzed its constituent hemicellulose in sulfuric acid. Since no additional hemicellulos is available, further increasing the time does not influence the manganese leaching efficiency.

Previous studies also reported that at low concentrations of banana peel, all the available hemicellulose in the banana peels (25.5wt%) was utilized for manganese reduction [16,21]. The time–yield plot (Fig. 3) shows an anomalous behavior. The leaching efficiency is the highest at a leaching time of 2 h. The leaching efficiency abruptly decreases up to 3 h, then increases in the 3–4 h window, and ultimately decreases after 5 h. The abrupt decrease in the leaching efficiency at a leaching time of 3 h may be attributed to the fact that all the available hemicellulose in banana peels was utilized for manganese reduction during this time. The decrease in the leaching rate for 3 h may also indicate a low leaching activity in hydrometallurgical processes. The optimum leaching time was, therefore, set to 2 h at which the manganese leaching efficiency was maximum (~73%). The dissolution of manganese from LGMO by plant powders containing glucose is known to occur in at least four steps (in series): (1) hydrolyzation of monosaccharaides, (2) diffuses of the reductant from liquid to Mn-grains via the boundary layer, (3) nucleation and hydration of the products at the active sites, and (4) diffusion into the solution. Thus involved reactions are strictly time-dependent [22].

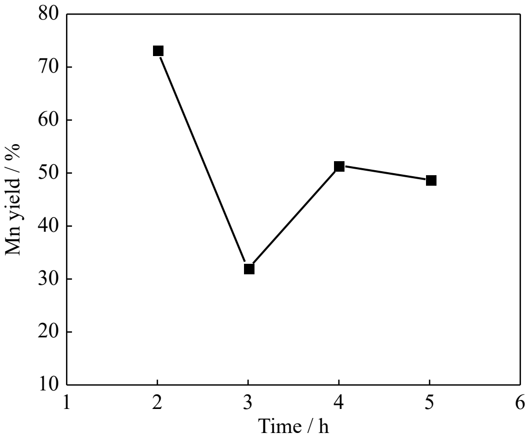

Fig. 3. Effect of time on the yield of manganese leached from LGMO.

3.4. Effect of H_2SO_4 concentration

The influence of H_2SO_4 concentration on the dissolution of manganese from LGMO was examined by varying the concentration from 5vol% to 20vol% at intervals of 5vol% while keeping the other parameters constant, i.e., leaching time of 2 h, manganese ore amount of 5 g, banana peel amount of 2 g, temperature of 80°C, and agitation rate of 300 r/min. Fig. 4 shows the results. The leaching efficiency was ~73% at a concentration of 5vol% and increased up to ~98% at 15vol%. This demonstrates that the hydrolyzing degree of polysaccharide and cellulose significantly improved at an H_2SO_4 concentration of 15vol% and accelerated the leaching of manganese from LGMO by obtaining hydrogen ions more easily [18]. The decomposition rate of MnO_2 was higher at 15vol% H_2SO_4, further verifying the encapsulation of manganese in the gangue minerals, because the presence of more concentrated H_2SO_4 allowed more dissolution and relieved more manganese ions to the solution. However, a further increase in the H_2SO_4 concentration up to 20vol% caused an abrupt decrease in the manganese leaching efficiency up to ~72%, demonstrating that the leaching activity of Mn from LGMO in hydrometallurgical processes is relatively low at higher H_2SO_4 concentrations [20]. Consequently, from an economic perspective, an H_2SO_4 concentration of 15vol% seems to be adequate for Mn leaching; any additional consumption of H_2SO_4 should be avoided.

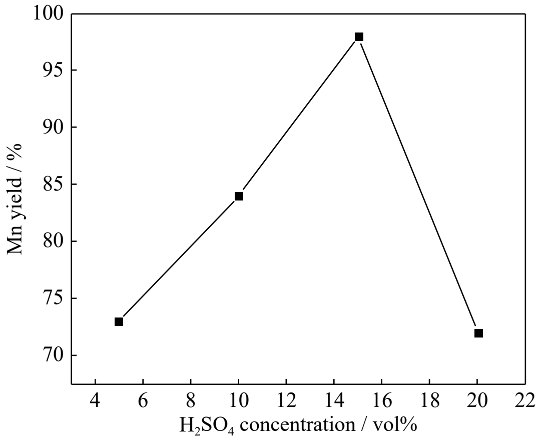

Fig. 4. Effect of sulfuric acid concentration on the yield of manganese leached from LGMO.

3.5. Characterization of leached residue using XRD, XRF and SEM−EDS

To investigate the hydrometallurgical reductive leaching of Mn from LGMO using banana peels, the phase(s), chemical composition, and microstructural analyses before and after leaching were carried out using XRD, XRF, and SEM−EDS, respectively. The XRD pattern of the LGMO sample revealed that the sample was mainly composed of pyrochroite (MnO_2), hausmannite (Mn_3O_4), spessartine ($Mn_3Al_2(SiO_4)_3$), pyrolusite ($Mn(OH)_2$), quartz (SiO_2), hematite (α-Fe_2O_3), and calcite ($CaCO_3$) [23]. The phase analysis after leaching revealed the disappearance of most of the phases leaving quartz as the residue and a single peak for pyrolusite (Fig. 5), where the inter-planner spacing (d-values) and relative intensities corresponding to the observed XRD peaks for the residue (after leaching) matched those of quartz (SiO_2) as the major phase along with a single peak at 2θ = 28.66° indicating the presence of pyrolusite as a secondary minor phase in the residue.

Table 1 lists the results of the chemical analyses of LGMO before and after leaching. It is further confirmed that most of the manganese in the LGMO was leached from the sample and that the manganese content decreased from 24.17wt% to 6.13wt% in the residue, i.e., after leaching.

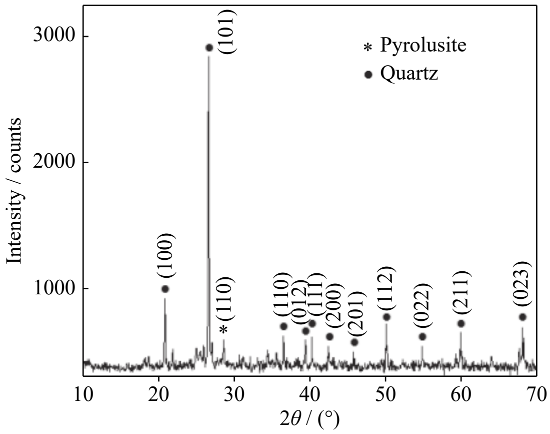

Fig. 5. XRD pattern of LGMO after leaching.

Figs. 6(a) and 6(b) show the morphological changes in the ore grains/particles before and after hydrometallurgical leaching observed by SEM, respectively. The SEM image, shown in Fig. 6(a), reveals highly compact manganese ore grains of varying sizes (~50 mm) before leaching [24−25]. The surface morphology of the investigated LGMO sample was changed to porous and small, thin needle-like micro-features after leaching (Fig. 6(b)).

3.6. Kinetic analysis of manganese leaching

The LGMO contains several phases of manganese oxide encapsulated in gangue grains, such as quartz and hematite, as confirmed by XRD and XRF analyses. Furthermore, the manganese particles appear to be dispersed within the host gangue mineral, making the structure even more complex. Moreover, the SEM analysis confirms that the morphology of the LGMO after leaching changes significantly from a

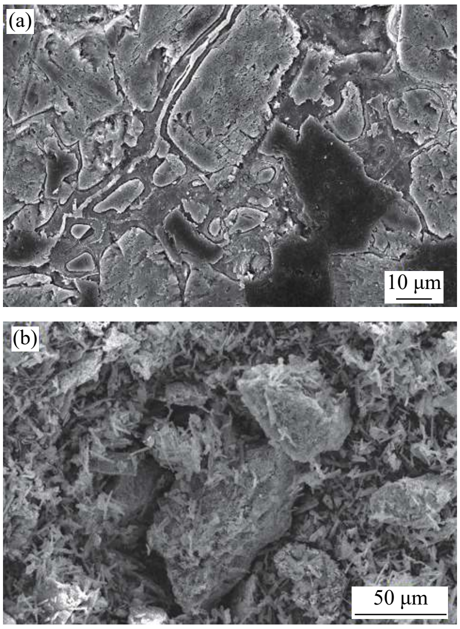

Fig. 6. Secondary electron SEM images of LGMO (a) before leaching and (b) after leaching.

smooth surface to a rough one with needle-like features. These results support the appropriateness of using the SCM to describe the kinetics of manganese leaching from LGMO. In general, the classical models provide three basic equations to interpret the surface chemical reaction controlled kinetic model (Eq. (2)), internal diffusion-controlled kinetic model (Eq. (3)), and mixed-controlled kinetic model (Eq. (4)) [26–28]:

$$1-(1-x)^{1/3}=kt \tag{2}$$

$$1-\frac{2}{3}x-(1-x)^{2/3}=kt \tag{3}$$

$$\left[(1-x)^{-1/3}-1\right]+\frac{1}{3}\ln(1-x)=kt \tag{4}$$

where x is the fraction of the manganese reacted; t is the leaching time, min; and k is the apparent reaction rate constant, min^{-1}.

The leaching efficiency of manganese leaching from LGMO in the time range of 10–60 min out of the range of 10–120 min at various temperatures (60–100°C (333–373 K)) describe the measurement of a sensible rate that is appropriate for studying the leaching mechanism (Fig. 7). The kinetic data for manganese extraction were evaluated using various kinetic models (Eqs. (2)–(4)) to judge the reaction mechanism. The results are shown in Figs. 8(a)–8(c), which demonstrates the good fit of the SCM (Eq. (2)) with the highest correlation coefficient values (R^2). This indicates that the extraction of Mn is controlled by a surface chemical reaction mechanism.

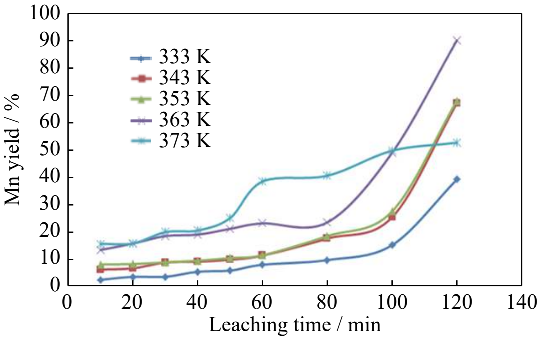

Fig. 7. Effect of reaction temperature on the yield of manganese from LGMO at various time durations.

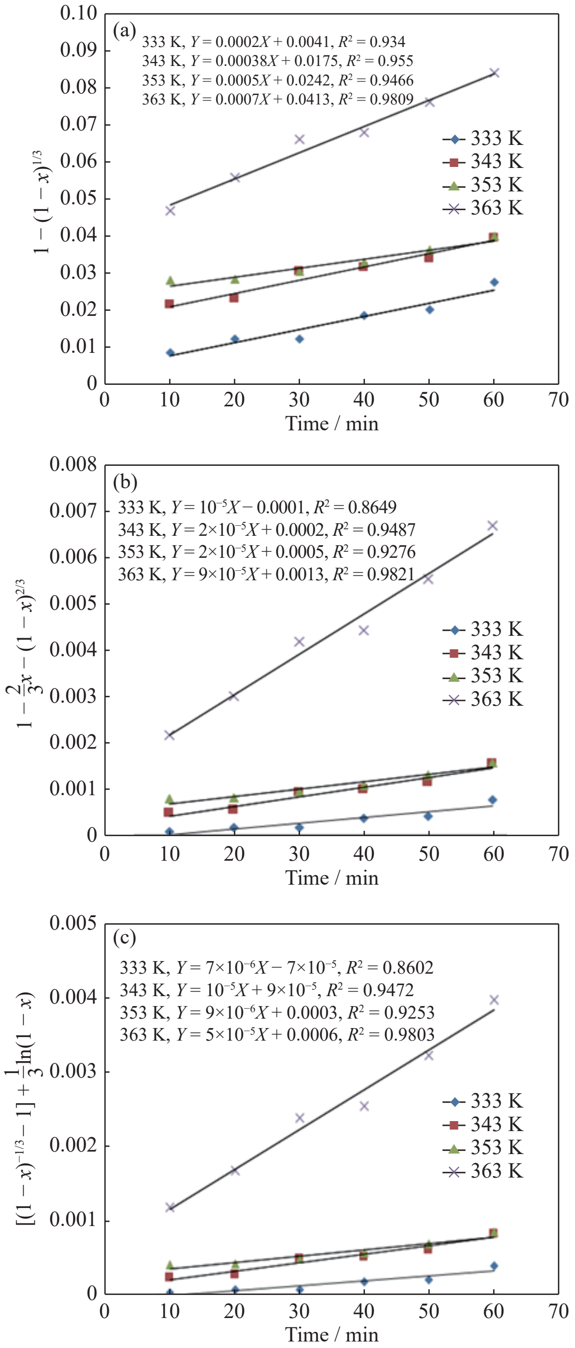

Fig. 8. Plots of various kinetic model equations versus time at different temperatures for leaching manganese from LGMO: (a) $1-(1-x)^{1/3}=kt$; (b) $1-(2/3)x-(1-x)^{2/3}=kt$; (c) $[(1-x)^{-1/3}-1]+(1/3)\ln(1-x)=kt$.

Table 2 lists the values of the shrinking core rate constant obtained at different temperatures. With the rate constant values, the apparent activation energy (E_a) was determined using the well-known Arrhenius equation:

$$\ln k=\ln A-\frac{E_a}{RT} \tag{5}$$

where k is the reaction rate constant, and $\ln A$ is the Arrhenius factor, E_a is the apparent activation energy ($\text{kJ}\cdot\text{mol}^{-1}$), R is the gas constant (R = 8.315 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), and T is the absolute temperature. Fig. 9 shows that the plot of $\ln k$ versus $1/T$ is linear, demonstrating a good fit of the Arrhenius model with a slope $E_a/(RT)$ and intercept $\ln A$. The desired value of the activation energy (Table 2) was determined from the slope of the linear plot, which agreed well with those reported in literature [15,26].

The thermodynamic parameters, such as the activation, enthalpy change ($\Delta H^{\neq}$), and entropy change ($\Delta S^{\neq}$), were determined using the well-known Eyring equation (Eq. (6)).

Table 2. Kinetic and thermodynamic parameters for manganese leaching from LGMO.

Temperature / K	Rate constant / (10^{-3} min^{-1})	$\Delta G^{\neq}$ / (kJ·mol^{-1})	E_a / (kJ·mol^{-1})	$\Delta H^{\neq}$ / (kJ·mol^{-1})	$\Delta S^{\neq}$ / (J·K^{-1}·mol^{-1})
333	2	105.152	40.19	37.31	−203.72
343	4	107.189			
353	5	109.226			
363	7	111.263			

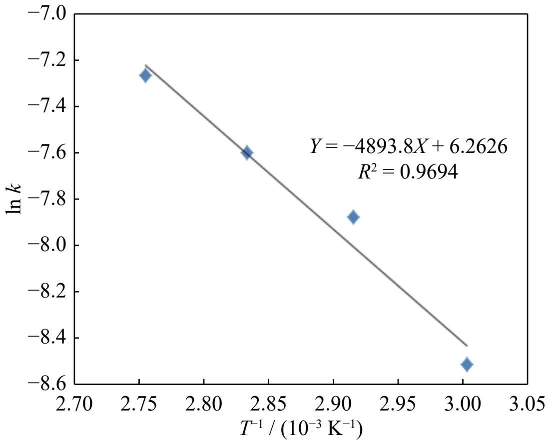

Fig. 9. Plot of ln *k* versus the reciprocal of temperature for leaching manganese from LGMO.

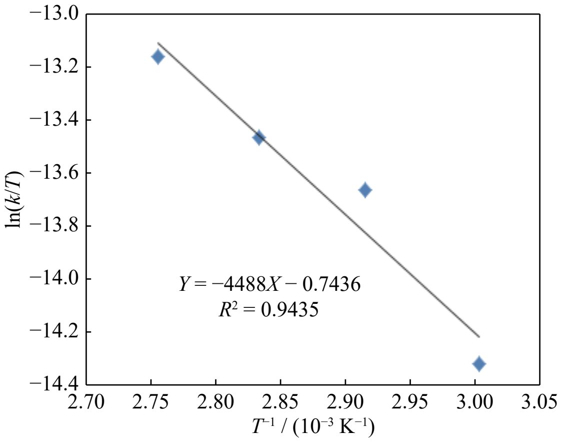

Fig. 10. Plot of ln(*k*/*T*) versus the reciprocal of temperature for leaching manganese from LGMO.

The linear form of the Eyring equation is given as

$$\frac{k}{T} = \frac{\Delta H^{\neq}}{RT} + \frac{\ln K_{\mathrm{B}}}{h} + \frac{\Delta S^{\neq}}{R} \tag{6}$$

where k and T represent the core diffusion rate constant and absolute temperature, respectively, R is the general gas constant, K_{B} is the Boltzmann constant, and h is the Planck's constant. Fig. 10 shows the thermodynamic Eyring plot, which exhibits a straight line with the slope and intercept equal to $\Delta H^{\neq}/R$ and $(\ln K_{\mathrm{B}})/h + \Delta S^{\neq}/R$, respectively. Eq. (7) was used to calculate the Gibbs free energy of activation ($\Delta G^{\neq}$):

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{7}$$

Table 2 lists the values of $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$. Clearly, the $\Delta G^{\neq}$ value increases with an increase in the temperature, demonstrating the spontaneity and feasibility of the reaction.

The higher positive values of $\Delta G^{\neq}$ at all the temperatures indicate that a driving force from an external source is necessary for the formation of an activated complex during the extraction. The positive $\Delta H^{\neq}$ values point to an endothermic nature of the leaching process, while the negative values of $\Delta S^{\neq}$ suggest that the activated complex exhibits a more ordered structure [29]. The results obtained in the present study regarding the maximum leaching efficiency of manganese under optimum conditions were compared with previously reported values and are summarized in Table 3.

Table 3. Reductive leaching of manganese using agricultural/biomass wastes

Reductant	Ore	Conditions	Key results	Refs.
Glucose	Mn nodules	2.5 M NH_3, 0.37 M NH_4Cl, 0.2 g of glucose per gram of nodules, 85°C, 4 h	100% Cu, 90% Ni, 60% Co recovery	[30]
Sawdust ($C_6H_{10}O_5$)	Low Mn ore	Aqueous H_2SO_4	90%–95% Mn recovery (99.6% pure)	[31]
Sucrose ($C_{12}H_{24}O_{11}$)	Pyrolusite	50–90°C, 20 g/L of sucrose, 1 M H_2SO_4, leaching time of 30 min	94%–95% Mn recovery	[20,17]
Lactose ($C_{12}H_{22}O_{11}$)	Low Mn ore	100 mesh Mn ore, 2 h, 90°C, 20% H_2SO_4	90%–92% Mn recovery	[32]
	Mn–Ag ore	Two stage leaching with H_2SO_4 and then thiourea	97% Mn, 98% Ag and Au recovery	[32]
Glycerine	Mn ore	Aqueous H_2SO_4	Increased Mn recovery	[33]
Triethanolamine and thiosulfate	MnO_2	1 M H_2SO_4, 200 mesh Mn ore, 2 M thiosulfate	Maximum Mn recovery	[30]
Oxalic acid (OX)	Low Mn ore	30.6 g/L OX, 0.5 M H_2SO_4, 85°C, 105 min	98.4% Mn recovery	[34]
Carboxylic acid (15%) HF (9%)	Ferro columbite	HF + tartaric (TR), citric, formic, oxalic (OX) acids	86% Fe, 90% Mn recovery	[35]

4. Conclusions

Reductive leaching of LGMO was successfully carried out using banana peel as the reductant in a dilute sulfuric acid medium. The present study demonstrated that the leaching efficiency of manganese can be significantly improved up to ~98% by appropriately selecting the weight of the banana peels used (4 g); the other optimum conditions are a leaching time of 2 h, leaching temperature of 120°C, a manganese ore amount of 5 g, and a sulfuric acid concentration 15vol%. The chemical and morphological investigations of the LGMO before and after leaching confirmed that a high amount of manganese was successfully leached into the pregnant leach solution, with the residue obtained containing only traces of manganese. The findings of the present study can be applied to the recovery of manganese from LGMOs at an industrial scale owing to the good reactivity, efficiency, availability, and economic feasibility of banana peels. Furthermore, the SCM can be used to describe the leaching process, where the leaching rate is controlled by a surface chemical reaction mechanism. The apparent activation energy (40.19 $kJ\cdot mol^{-1}$) and positive values of $\Delta G^{\neq}$ (105.152, 107.189, 109.226, and 111.263 $kJ\cdot mol^{-1}$) at various temperatures (333, 343, 353, and 363 K) demonstrate the requirement of an energy barrier for the successful extraction of manganese. The thermodynamic parameters ($\Delta H^{\neq}$ = 37.31 $kJ\cdot mol^{-1}$, $\Delta S^{\neq}$ = −203.72 $J\cdot K^{-1}\cdot mol^{-1}$) associated with the activation indicated that the extraction of manganese follows as entropy-driven extraction mechanism.

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