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TECHNICAL PAPER

Preparation of Industrial Manganese Compound from a Low-Grade Spessartine Ore by Hydrometallurgical Process

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Abstract The increasing global demands for pure manganese in steel production and manganese compound as dietary additives, fertilizer, pigment, cells and fine chemicals production cannot be over-emphasized. Thus, continuous efforts in developing low cost and eco-friendly route for purifying the manganese ore to meet some defined industrial demands become paramount. Therefore, this study focused on reductive leaching and solvent extraction techniques for the purification of a Nigerian manganese ore containing admixture of *spessartine* ($O_{96.00}Mn_{24.00}Al_{16.00}Si_{24\cdot00}$) and *quartz* ($Si_{3.00}O_{6.00}$). During leaching, parameters such as leachant concentration and reaction temperature on the extent of ore dissolution were examined accordingly for the establishment of extraction conditions. At optimal leaching conditions (1.5 mol/L H_2SO_4 + 0.2 g spent tea, 75 °C), 80.2% of the initial 10 g/L ore reacted within 120 min. The derived dissolution activation energy (Ea) of 35.5 kJ/mol supported the diffusion reaction mechanism. Thus, the leachate at optimal leaching was appropriately treated by alkaline precipitation and solvent extraction techniques using sodium hydroxide and (di-2-ethylhexyl) phosphoric acid (D2EHPA) respectively, to obtain pure manganese solution. The purified solution was further beneficiated to obtain manganese sulphate monohydrate ($MnSO_4.H_2O$, melting point = 692.4 °C: 47-304-7403) of high industrial value. The unleached residue ($\sim$ 19.8%) analyzed by XRD consisted of siliceous impurities (SiO_2) which could serve as an important by-product for some defined industries.

Keywords Spessartine ore · Nigeria · Manganese · Manganese compound · Reductive leaching · Solvent extraction · D2EHPA

1 Introduction

To date, manganese is an important nonferrous element with wide arrays of applications in steel production, preparation of dietary additives, fertilizers, pigments, cells and fine chemicals. To meet the ever increasing industrial demand for manganese, coupled with the gradual depletion of high grade manganese ore, many efforts have been made to recover this metal from low grade ores [1, 2]. However, with the extensive exploitation and consumption of high grade manganese ore (total Mn $> 35\%$), considerable attention is focused on the development and utilization of the low grade manganese ore (total Mn $< 35\%$), which has a low business value [3]. Pyrolusite (MnO_2) and most importantly spessartine ($Mn_3Al_2(SiO_4)_3$), are examples of industrial manganese ores that can be processed in meeting the aforementioned demands.

The conventional pyro-metallurgical processes for utilizing manganese ores are often characterized by high energy consumption and production cost coupled with low productivity and environmental pollution [4]. Conversely,

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hydrometallurgical treatment of low grade manganese ores has attracted great attention in recent years, as many efforts have been applied in the development of efficient and economical processes to recover manganese from its ores for industrial utilizations [5].

Africa is known to have vast abundance of manganese ore varieties (over 80%), predominantly in countries like South Africa, Gabon, Cote d'Ivoire, Nigeria, Burkina Faso and Ghana [6]. In Nigeria, deposit of these ores as proven reserves in the form of meta sedimentary rocks are much pronounced in north-western Nigeria (Zaria, Kebbi) and south-southern part (Calabar) [7]. Thus, the abundance and the increasing global industrial demands for purified manganese and its compound prompt continuous interest in the purification of low grade source of manganese ore for additional industrial value. During the ore treatment, various leachants and reductants such as sulphuric, hydrochloric, nitric, oxalic and citric acids, methanol, hydrogen peroxide etc. are used in the leaching process. However, leaching with sulphuric acid seems to be the most common approach [8]. Although, a greener approach for the reduction of manganese ore using agricultural biomass is more effective, accessible, renewable, economical and highly reactive under mild acidic conditions [9–15]. For example, sawdust [9], waste tea [10], bagasse [11], cane molasses [12], dried leave [13], corn stalk [14], wheat stalk [15] contains one or more of reducing components such as lignin, hemicelluloses, cellulose, polyphenol and polysaccharides. However, the hydrolysis of this biomass often promotes the release of glucose for possible reduction of tetravalent manganese prior to its beneficiation [9–15].

As the upstream or front end of every hydrometallurgical operation through leaching is to generate leach-liquor or pregnant solution, the downstream operation is to successfully treat the leach liquor by some defined separation process, leading to recovery of metal of interest [16]. Thus, in recovering manganese from the leach-liquor, alkaline precipitation and liquid–liquid extraction has been the most adopted techniques owing to differential solubility of individual metals under defined conditions using specific extracting agents. Organo-phosphorus and carboxylic acid cation exchange reagents are mostly used in manganese extraction [17], some pertinent one includes: PC 88A-phosphonic acid, Tributyl phosphoric acid (TBP), di-2-ethylhexyl phosphoric acid (D2EHPA), Versatic-10,4-pyridine carboxylic acid, bis-2,4,4-trimethylpentyl phosphinic acid (Cyanex 272), PIA-8-Phosphinic acid. From the aforementioned extractants, D2EHPA is the most widely used owing to its low-cost, high selectivity and complexing ability to extract manganese from other impurities [17, 18]. Roberto et al. [19] supported this claim as compared to cyanex 272 during the treatment of pyrolusite ore. According to these authors, larger change in pH of leach liquor after appropriate purification lead to higher distribution coefficient, thereby yielding an extraction efficiency of 95%. Valentina and Francesco [20] also reported D2EHPA to be a good candidate for the separation of manganese from nickel-metal hydride (NiMH) spent battery, yielding efficiency of 95% in two extraction stages.

After liquid–liquid separation, the final operation is to beneficiate the recovered metal to meet its aforementioned demands. This technique is basically through chemical separation process, to produce a compound that can serve as a valuable product for some defined industries [21]. Therefore, considering the excellent efficiency of D2EHPA, the present work is designed to investigate the potential of the D2EHPA extractant in the treatment of a Nigeria spessartine ore generated by sulphuric acid leachant-cum-spent tea reductant at optimized conditions for the purification, extraction and beneficiation to obtain high grade manganese sulphate monohydrate ($MnSO_4.H_2O$) of industrial value. Data in this area of study is practically limited in Nigeria hydrometallurgical research community [22].

2 Materials and Methods

2.1 Materials

The Spessartine sample used in this study was sourced from Kaoje (11° 11′ 00″ North, 4° 7° 0″ East), Kebbi State, north-western part of Nigeria. The ore was crushed and pulverized into fine particles with the aid of laboratory crusher and mill; sieved into four different particle sizes: < 75 µm, 75, 90 and 112 µm using the ASTM standard sieves. Spent tea (Lipton brand, NAFDAC Reg. No. 01-0132) used as reductant was sourced from a Mallam Yakubu (Tea seller) at Tipper Garage area, Tanke, Ilorin, Kwara State, Nigeria. The spent tea was rinsed thoroughly using de-ionized water, dried and pulverized into < 75 µm fine particle size using acetone rinsed mortar and pestle. All reagents used in the entire experimental works were of analytical grade and were prepared according to standard measures using purified aqueous solvent. Also, the kerosene diluent was obtained at TOTAL Filling Station, Taiwo Road, Ilorin, Kwara State, Nigeria. It was doubly distilled prior to use in the preparation of different D2EHPA extractant concentrations.

2.2 Methods

2.2.1 *Leaching Studies*

The leaching experiments were carried out in a 250 ml Pyrex glass reactor equipped with a mechanical stirrer, kept over a ceramic hot plate. The reactor was filled with H_2SO_4 leachant (0.1–2.0 mol/L) and heated to the desired temperature [13, 22]. For each experimental run, the solution mixture was freshly prepared by dissolving 10 g/L of spessartine ore at 55 °C with moderate stirring. After each experiment, the slurry was filtered and the residue was thoroughly washed with de-ionized water. The fraction of the ore reacted was evaluated from the difference between the mass of the reacted and unreacted ore at various leaching time intervals up to 120 min after drying at 60 °C for 1 h in each case. The concentration that gave the maximum ore reaction was subsequently used for the optimization of other leaching parameters such as temperature, influence of reducing agent and particle size variation. The residue at optimal conditions (75 °C, 1.5 mol/L $H_2SO_4 + 0.2$ g spent tea, $< 75 \mu m$) during 120 min was analyzed by scanning electron micrography and X-ray diffraction respectively [23]. Appropriate kinetic plots were executed for better understanding of the dissolution mechanism, to establish favourable extraction conditions for appropriate beneficiation studies.

2.2.2 *Solvent Extraction Studies*

The quantity of manganese extracted from the ore was spectrophotometrically determined. The organic and aqueous phases were kept at a ratio of 1:1. A 25 mL of leach liquor (aqueous) and organic phase (D2EHPA dissolved in kerosene) were mixed in a stoppered bottle and agitated for 25 min. After phase separation, the metal concentration in the aqueous phase was analyzed by Buck scientific ACCUYS 211 atomic absorption spectrophotometer and the concentration in the organic phase was determined by mass balance. Experiments were also carried out to determine: (1) effect of D2EHPA on manganese extraction (2) effect of pH at constant A/O volume ratio to the extent of manganese ion extraction and (3) the appropriate plots from (1) and (2) to determine the extraction mechanism at optimal condition and were accordingly examined and characterized [24].

3 Results and Discussion

3.1 Ore Characterization

The chemical composition of the raw spessartine ore examined by EDXRF gave 16.61% Mn, 18.37% Fe, 17.05% Si, 1.15% Al, 0.69% S, 0.14% W and 0.55% Sn by weight. Also, the EDS spectrum (Fig. 1) was in support of EDXRF revealing MnO (9.91%), Fe_2O_3 (6.44%), SiO_2 (30.32%) and Al_2O_3 (0.59%) as major constituents present in the ore.

The mineralogical purity as defined by X-ray diffractometer (XRD) analysis indicate that the ore is comprised of mainly admixture of spessartine ($O_{96.00}Mn_{24.00}Al_{16.00}Si_{24}$: 96-900-2700) and quartz ($Si_{3.00}O_{6.00}$: 96-900-9667) (Fig. 2).

From the SEM result (Fig. 3a), a distinct light grey region **(A)** and dark grey region **(B)** denote the presence of manganese and ferrosilicate compound [25] as examined at 50,000 × magnification. Also, as studied under micrography at 40 × magnification (Fig. 3b), the raw ore indicate distinctive textural features. The yellowish to orange region **(A)** is attributed to spessartine ($Mn_3Al_2(SiO_4)_3$), complimented with the large black region **(B)** which is attributed to thermally stable manganese oxide, indicating bixbyite (Mn_2O_3). Also, admixture of iron and other trace impurities in the form of haematite (Fe_2O_3) is present in the brownish region marked as **(C)** while the predominant associated guages are identified as silicious compound (SiO_2) marked as **(D)** [26, 27].

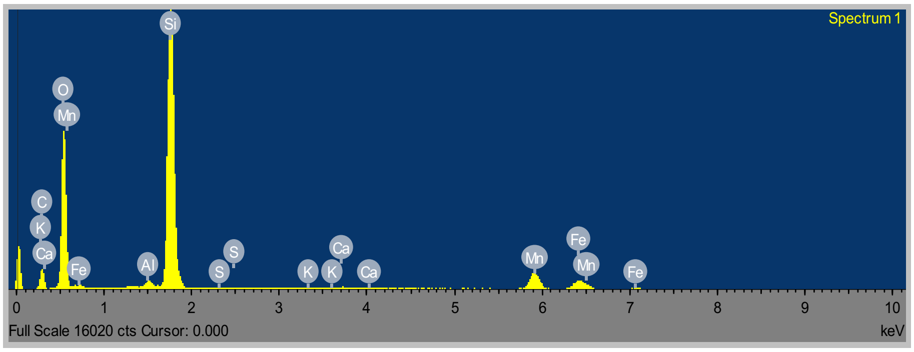
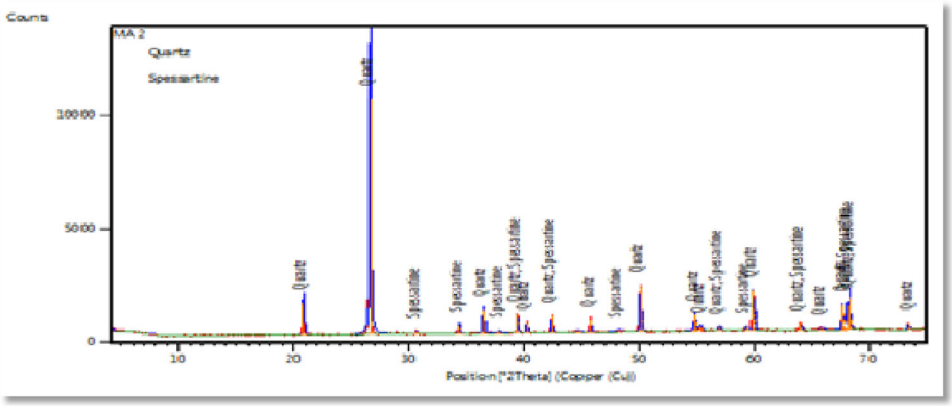


Fig. 1 EDS spectrum of raw spessartine ore

Fig. 2 X-ray diffraction pattern of raw spessartine ore showing the identified compounds



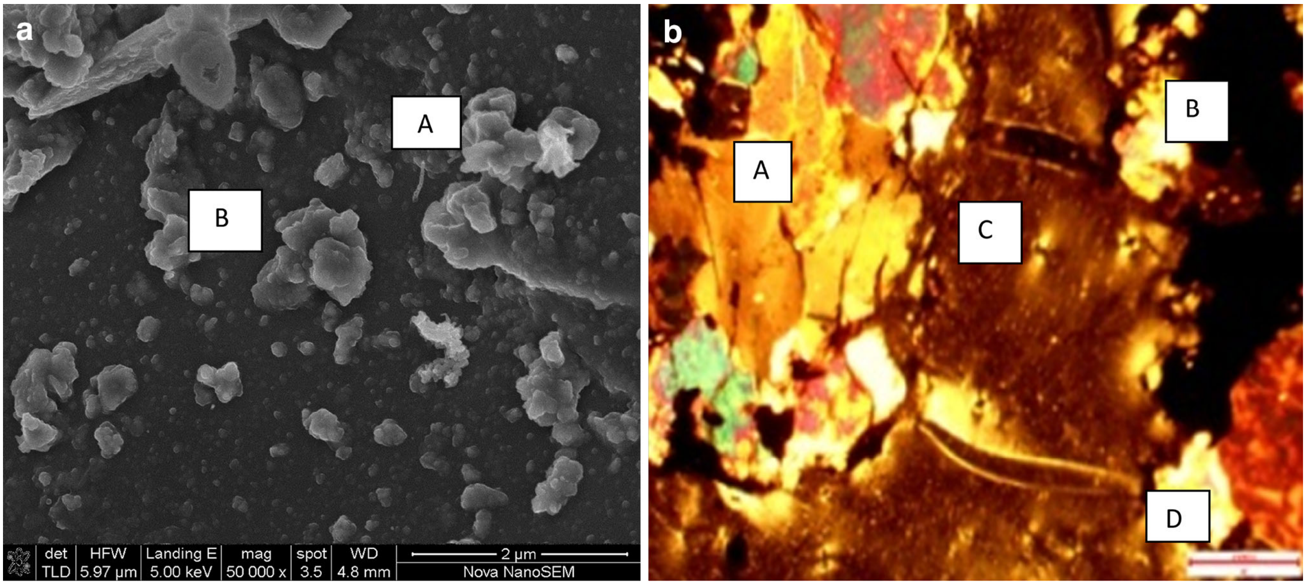


Fig. 3 **a** SEM micrographs of raw spessartine ore, **b** The photomicrography of raw spessartine ore, scale bar 2/100(In) at 40 × magnification

3.2 Effect of Sulphuric Acid Concentration

The effect of sulphuric acid concentration (0.1–2.0 mol/L) on the dissolution of spessartine ore has been investigated, while keeping other experimental conditions constant. The result indicates that leaching efficiency increases as H_2SO_4 concentration increases from 0.1–1.5 mol/L and decreases moderately with further increase in concentration to 2.0 mol/L (Fig. 4).

Experimental conditions: Temperature = 55 °C, Particle Size < 75 µm, Solid to liquid ratio = 10 g/L, Leachant concentration = 0.1–2.0 mol/L H_2SO_4 with moderate stirring.

For example, the extent of dissolution reach 48.4 and 45.0% by 1.5 and 2.0 mol/L H_2SO_4 solution respectively within 120 min. With these data, it is evident that the optimum concentration for influencing sulphuric acid leachant is 1.5 mol/L and this is maintained to optimize other leaching parameters in the study. The reason for the drastic decrease in the dissolution yield can among others

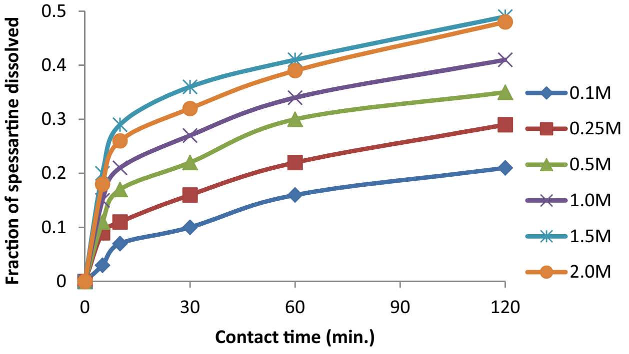


Fig. 4 The effect of sulphuric acid concentration on spessartine ore dissolution

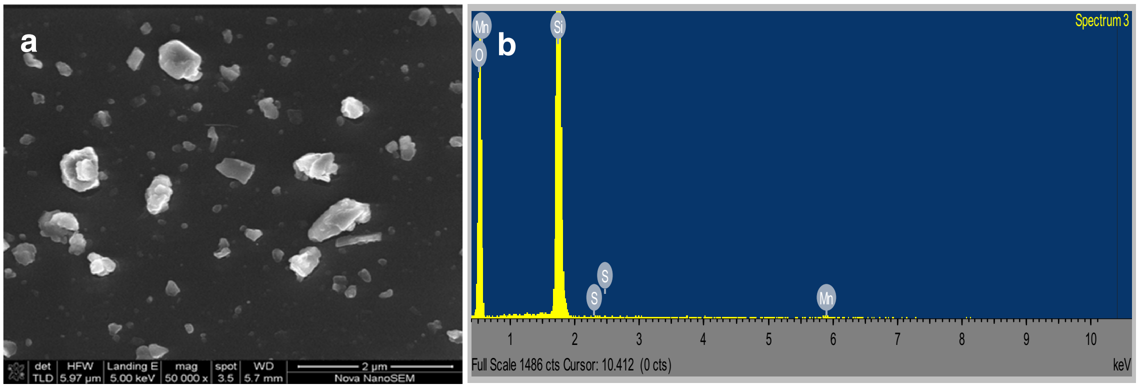


Fig. 5 **a** SEM image of sulphuric acid. **b** EDS image of sulphuric acid leached residue of spessartine ore at optimal conditions

be due to precipitation phenomena and the nature of tetravalent manganese (MnO_2) produced [22] as summarized in Eq. (1):

$$\underset{\text{(Spessartine)}}{Mn_3Al_2(SiO_4)_3} + 2H_2SO_4 \rightarrow Mn_2(SO_4)_3 + MnO_2 + 2Al(OH_2) + 3SiO_2 \quad (1)$$

However, to enhance the dissolution efficiency, a reducing agent is needed to bring manganese dissolution to a more stable and soluble state [28, 29]. The SEM–EDS analysis of the undissolved residue (– 51.2%) at optimal conditions (1.5 M H_2SO_4; 55 °C; 120 min) depicted in Fig. 5a, b contain partly dispersed shinning patches, reflecting presence of un-reacted manganese oxide (Fig. 5a). The compositions of this residue is 22.86% Mn, 28.43% Si, 0.08% S and 48.62% O (Fig. 5b).

3.3 Effect of Spent Tea Mass at Constant Sulphuric Acid Leachant

Following the results of the influence of sulphuric acid leachant yielding 48.4% during 120 min at optimal conditions, the variation of the spent tea mass from 0.05 to 0.2 g at constant 1.5 mol/L sulphuric acid solution has been investigated (Fig. 6).

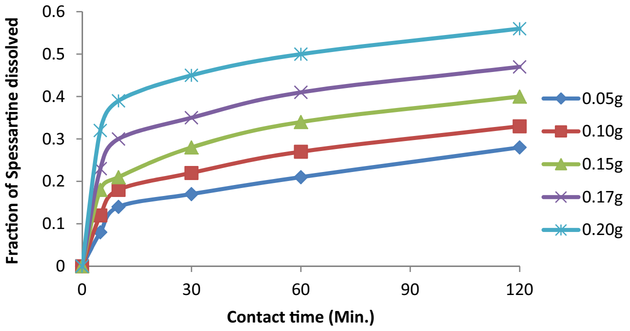


Fig. 6 The effect of various mass of spent tea on spessartine-ore dissolution

Experimental conditions Temperature = 55 °C, Particle Size < 75 µm, Solid to liquid ratio = 10 g/L, Leachant concentration = 1.5 mol/L H_2SO_4 + 0.05–0.2 g spent tea mass with moderate stirring.

As evident from the result in (Fig. 6), the addition of spent tea increases the dissolution efficiency to 59% as against 48.4% recorded at 55 °C in sulphuric acid media alone. This increase in dissolution efficiency is attributed to the increased amount of spent tea which causes an increase in the leaching of manganese due to excess availability of H^+ ion concentration [26]. It is important to note from our preliminary investigation that the weight of spent tea addition beyond 2.0 g has not been considered in this study to overcome possible rough surface envisaged in the residual analysis by SEM [9, 27].

3.4 Effect of Reaction Temperature

To investigate whether reaction temperature can be a retarding or improving factor on the influence of spent tea at constant sulphuric acid leachant concentration, temperature range of 25 to 75 °C have been investigated along other constant conditions as summarized in (Fig. 7).

Experimental conditions Temperature = 25–75 °C, Particle Size < 75 µm, Solid to liquid ratio = 10 g/L, Leachant concentration = 1.5 mol/L H_2SO_4 + 0.2 g spent tea mass with moderate stirring.

It is evident from (Fig. 7), that the hydrolysis of spent tea at constant sulphuric acid leachant concentration is proportional to temperature [9–15]. Conversely, the manganese leaching substantially improves from 35 to 80.2% for the temperature ranges of 25–75 °C within 120 min at moderate stirring. This is due to the fact that when reaction temperature increases, particle tends to collide more effectively thereby improving the dissolution process. Thus, the established optimized conditions promote favourable extraction of manganese, compared to results by

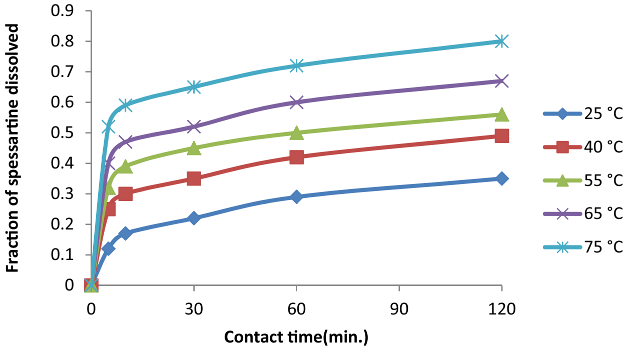


Fig. 7 Effect of reaction temperature on dissolution of spessartine ore

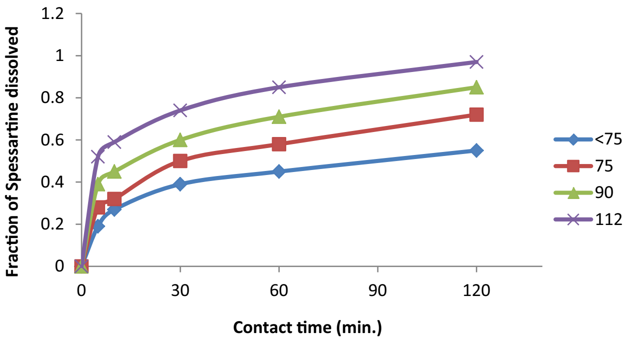


Fig. 8 Effect of particle size on dissolution of spessartine ore

Tang et al. [10] during the treatment of Gabonese manganese oxide ore. However, temperature above 75 °C has not been considered in this study to possibly prevent excessive acid loss through evaporation [30].

3.5 Effect of Particle Size

The effect of particle size has been studied by varying different size fractions of < 75, 75, 90 and 112 µm using 1.5 mol/L sulphuric acid + 0.20 g spent tea leachant at 75 °C with moderate stirring as depicted in (Fig. 8). The result shows that manganese dissolution decreases as particle size increases. At optimal conditions of 35.5, 53.5, 60 and 80.2% of the initial, 10 g/L ore has been found to react within 120 min with particle size of 112, 90, 75 and < 75 µm respectively.

Experimental conditions Temperature = 75 °C, Particle Size < 75–112 µm, Solid to liquid ratio = 10 g/L, Leachant concentration = 1.5 mol/L H_2SO_4 + 0.2 g spent tea mass with moderate stirring.

The SEM–EDS analysis of the undissolved residue (− 19.8%) at optimal condition (1.5 M H_2SO_4 + 0.2 g spent tea, 75 °C, < 75 µm, 120 min) depicted in (Fig. 9a, b), shows scarcely dispersed small grain-sized dark patches suggesting silicilleous compound on the surface of the ore. This is attributed to high selective leaching ability of spent tea reductant in sulphuric acid media (Fig. 9a). The EDS analysis in Fig. 9b confirm to this claim as peaks corresponding to manganese is totally absent, indicating complete dissolution under the optimized conditions. The predominant components of the residue as examined by EDS include silica (39.38%) and oxygen (60.62%).

4 Discussions

4.1 Dissolution Kinetics Analysis

Many kinetic models have been described to yield comprehensive information regarding mineral dissolution mechanism for the determination of the rate limiting step

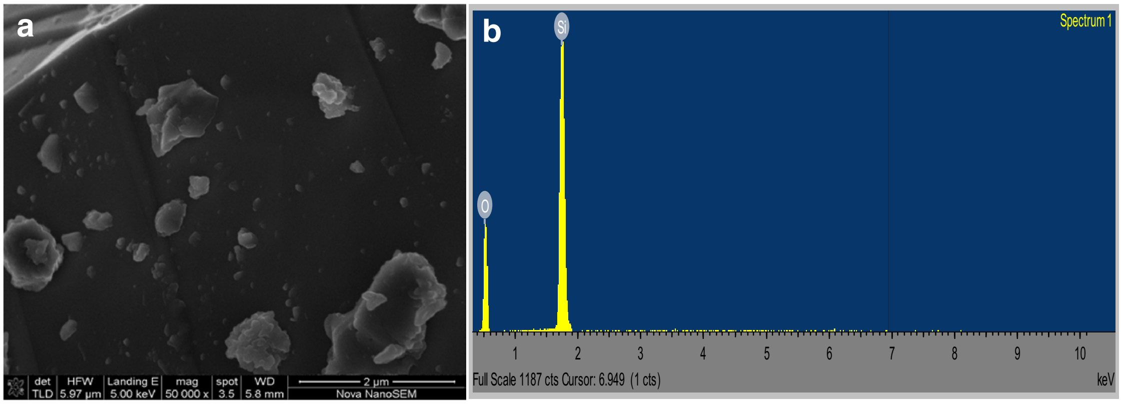


Fig. 9 **a** SEM image of the sulphuric, **b** EDS image of the sulphuric acid-cum-spent tea leached residue of spessartine ore at optimal conditions

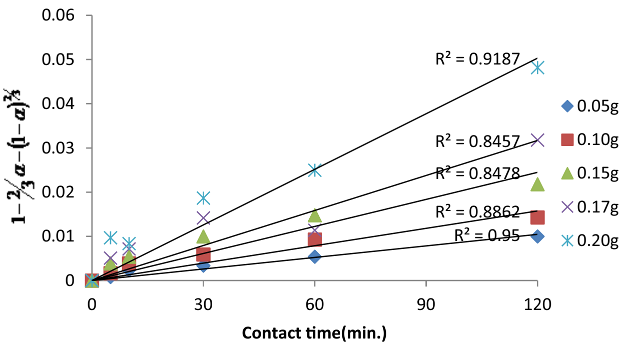


Fig. 10 $1 - {}^{2}\!/_{3}\alpha - (1 - \alpha)^{2/3}$ versus contact time (min.) at different spent tea mass at constant 1.5 M H_2SO_4 solution

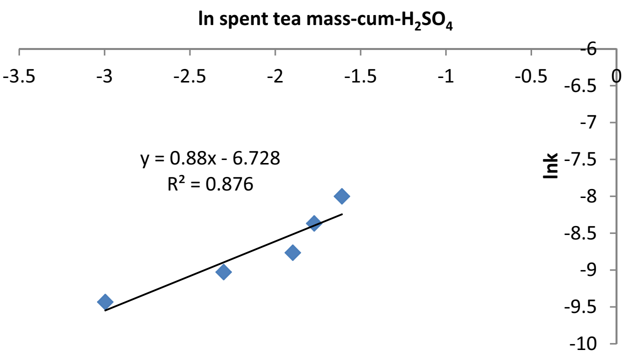


Fig. 11 Plot of lnk versus ln spent tea mass-cum-H_2SO_4

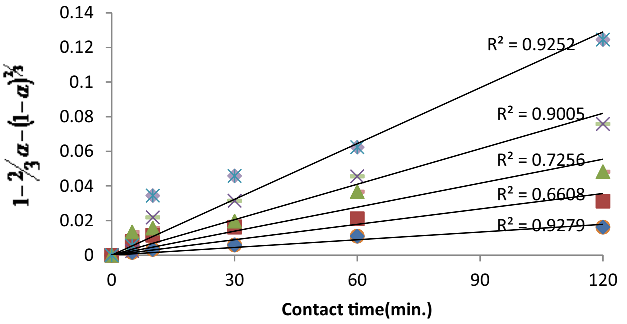


Fig. 12 $1 - {}^{2}\!/_{3}\alpha - (1 - \alpha)^{2/3}$ versus contact time (min) at different temperature ranges

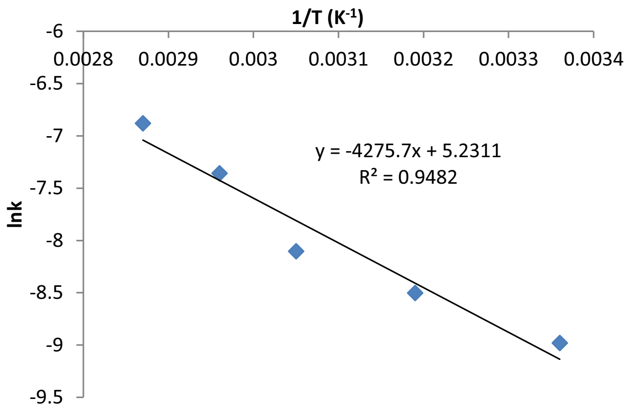


Fig. 13 Arrhenius plot of lnK versus 1/T (K^{-1})

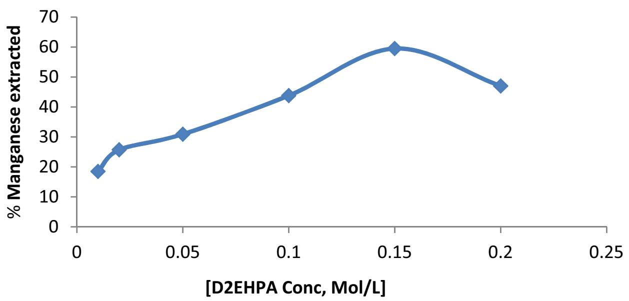


Fig. 14 Effect of D2EHPA concentration on manganese extraction

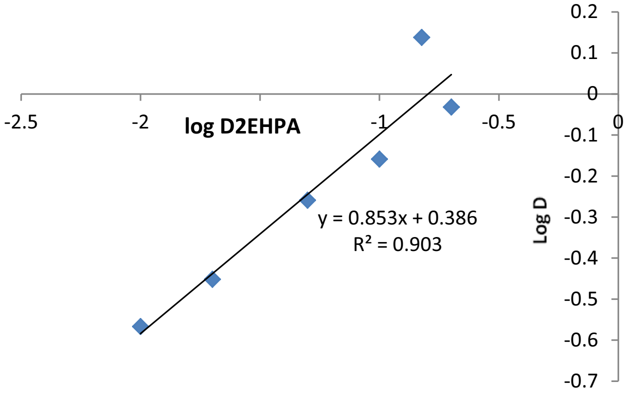


Fig. 15 The plot of log D as a function of log [D2EHPA]

involving heterogeneous process. According to shrinking core model (SCM) mechanism, the solid reactant is considered as non-porous particle and is initially surrounded by a fluid film through which mass transfer occurs between the solid particle and the bulk of the fluid [31]. The reaction between a solid and fluid can be represented as:

$$aA_{(\mathrm{fluid})} + bB_{(\mathrm{Solid})} \rightarrow \mathrm{Products}, \qquad (2)$$

a and *b* represent the stoichiometric coefficient and A, B denote the fluid reactants and the solid undergoing dissolution respectively [32]. In order to obtain the kinetic parameters and the rate controlling step for spessartine ore dissolution by sulphuric acid in the presence of spent tea, the experimental data in (Fig. 6) are correlated with the following diffusion and surface controlled kinetic equations:

$$1 - 2/3\alpha - (1 - \propto_B)^{2/3} = k_d t \quad (\text{Diffusion control}) \qquad (3)$$

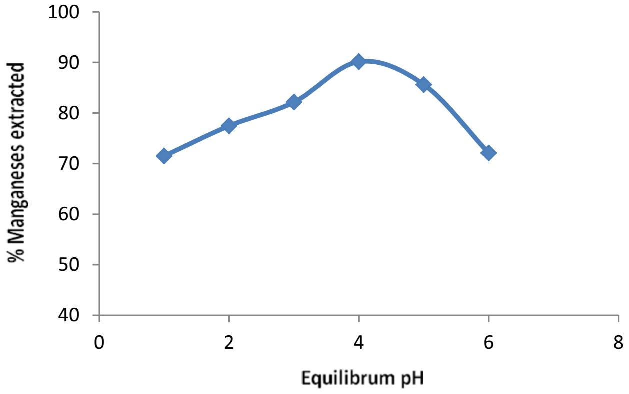


Fig. 16 Effect of equilibrium pH on manganese extraction in D2EHPA extractant

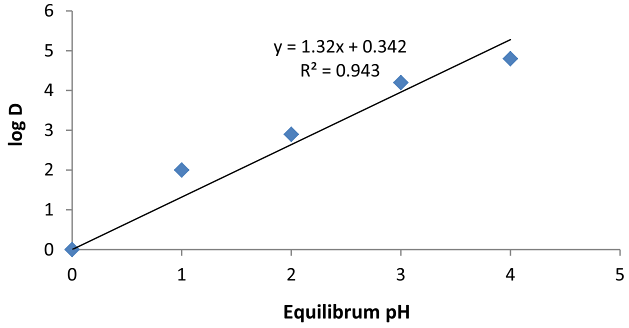


Fig. 17 The plot of log D as a function of equilibrium pH

$$1-(1-\alpha)^{1/3}=\frac{KMCo}{r\rho}=k_{r}t \quad \text{(Surface control)} \tag{4}$$

k_d and k_r denotes the rate constants for the ash/product layer diffusion and surface chemical reaction respectively, t is the contact time (min) and α is fraction of the reacted ore. However, evaluating the two Eqs. (3) and (4), the relation between $1-2/3\alpha-(1-\propto_{B})^{2/3}$ of Eq. (3) plotted against contact time at different spent tea mass in constant sulphuric acid leachant fit the data most as shown in (Fig. 10) with average correlation coefficient > 0.9, as compared to the results fitting Eq. (4) with average correlation of 0.43.

Experimental conditions Same as in Fig. 6.

From Fig. 10, it is concluded that the leaching of spessartine is controlled by the diffusion process. The experimental rate constant k are determined from slopes of Fig. 10 and is used to construct the plot of ln k versus ln spent tea mass-cum-sulphuric acid solution giving a reaction order of 0.88, approximated as one which indicates a first order reaction at defined leachant concentration (Fig. 11).

For the estimation of dissolution activation energy, the reaction between the overall rate constant and reaction temperature is expressed by Arrhenius Eqs. (5) and (6):

$$k=A\exp(-Ea/RT) \tag{5}$$

$$\ln k=\ln A-\frac{Ea}{RT} \tag{6}$$

A is frequency factor, Ea is apparent dissolution activation energy and R is universal gas constant. Thus, dissolution data at different temperatures (Fig. 7) has been linearized with Eq. (3) and the results obtained at different leaching times are summarized in (Fig. 12).

Experimental conditions Same as in Fig. 7.

The apparent activation energy (Ea) determined from the Arrhenius plot in Fig. 13, is found to be 35.5 kJ/mol thereby supporting the diffusion control mechanism [30].

4.2 Solvent Extraction Studies

The chemical composition of the leach liquor used in the solvent extraction investigation contains 2588.1 mg/L Mn^{2+}, 178.7 mg/L Al^{3+}, 1352.4 mg/L Fe^{3+} and 40.8 mg/L Ca^{2+}. However, prior to total manganese extraction, iron and aluminium which constitute the major impurities along with manganese are initially separated by alkaline precipitation at different pH. A white precipitate of aluminium (III) hydroxide is observed at pH of 3.0 and iron is precipitated as iron(III) hydroxide at pH of 3.5 as summarized in Eqs. (7) and (8) respectively [33].

$$Al^{3+}_{(aq)}+3OH^{-}_{(aq)} = Al(OH)_{3(S)}\downarrow \tag{7}$$

$$Fe^{3+}_{(aq)}+3OH^{-}_{(aq)} = Fe(OH)_{3(S)}\downarrow \tag{8}$$

After proper precipitation and seperations, the purified leach liquor used for total manganese extraction consists of 2514.4 mg/L Mn^{2+}, 11.2 mg/L Fe^{3+} and 0.2 mg/L Al^{3+}. Other detected ions such as Ca^{2+}, Mg^{2+} are present in low to trace levels ($<$ 0.01 mg/L).

4.3 Effect of D2EHPA Concentration

The effect of D2EHPA concentrations in kerosene diluent on the extraction of manganese has been investigated in the range of 0.01–0.20 mol/L along other constant conditions (Fig. 14).

Experimental conditions [D2EHPA] = 0.01–0.20 mol/L, Manganese concentration = 2588.1 mg/L, Phase ratio = 1:1, Contact time = 25 min, Equilibration time = 2 min.

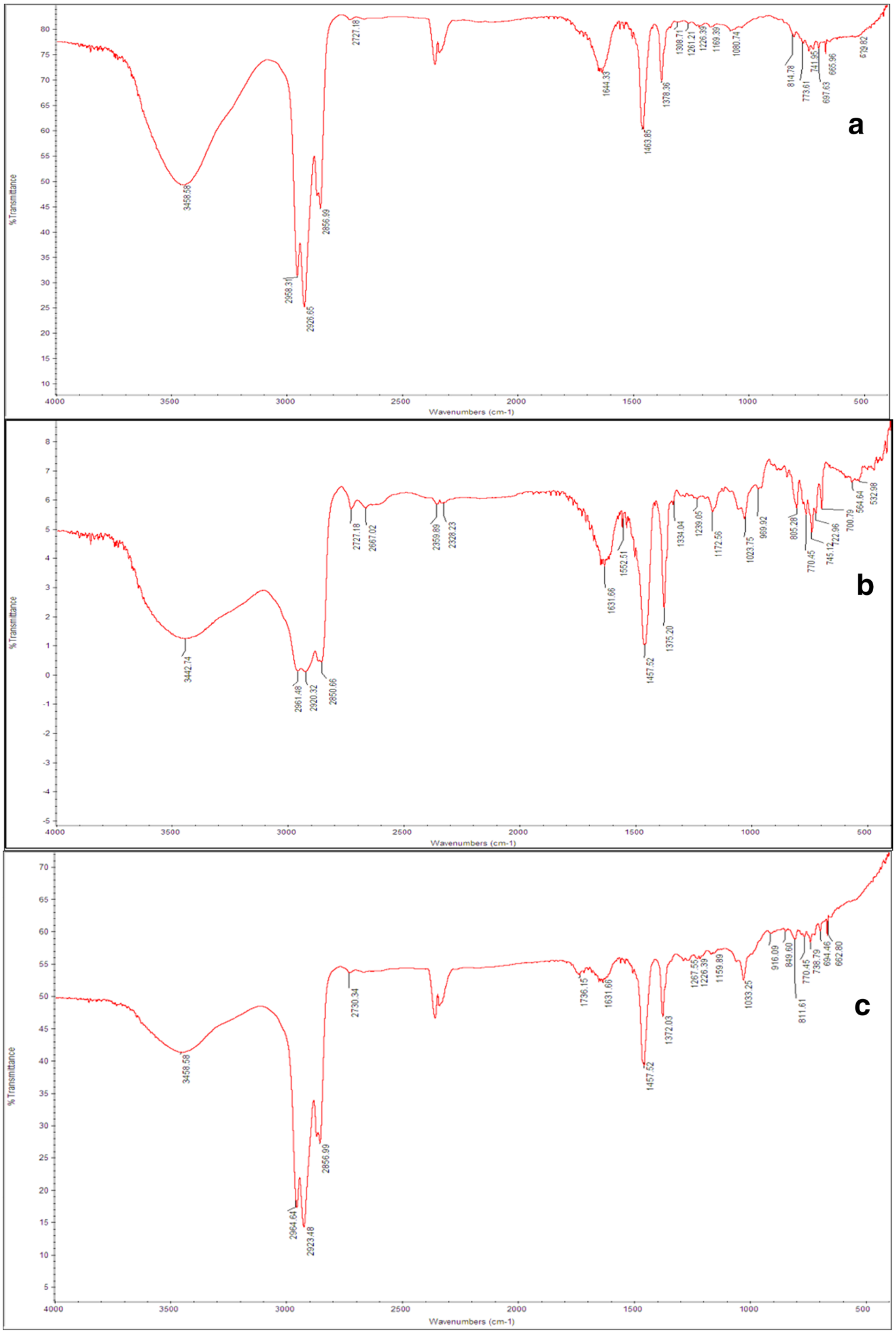


Fig. 18 FT-IR of the extractant (0.15 mol/L D2EHPA) (**a**); The Manganese loaded spectrum in D2EHPA (**b**); The FT-IR spectrum after stripping with 0.1 mol/L H_2SO_4 in D2EHPA (**c**)

From the experimental data, it can be noted that extraction of manganese increases from 18.5 to 59.5% as extractant concentration increases in the concentration range of 0.01–0.15 mol/L. Further increase in D2EHPA concentration to 0.20 mol/L lead to a decrease in percentage of manganese extracted. Hence, 0.152 mol/L has been chosen as the optimum concentration for further experimental studies.

The plot of log distribution ratio (D) versus log [D2EHPA] for manganese ion extraction in Fig. 15 produce a slope of 0.853, approximately one indicating that a mole of the extractant is exchanged for a mole of manganese ion during the extraction process.

4.4 Effect of pH on Mn^{2+} Extraction Using D2EHPA

The effect of pH on manganese extraction has been investigated using 0.15 mol/L D2EHPA by varying its pH in the range of 1–6. The appropriate plot is shown in Fig. 16.

Experimental conditions Manganese concentration = 2588.1 mg/L, [D2EHPA] = 0.20 mol/L, Phase ratio: 1:1, pH = 1–6, Contact time = 25 min, Equilibration = 2 min.

Figure 16 illustrate the effect of pH on manganese extraction using D2EHPA in kerosene diluent with a varied pH range of 1–6. It is observed that manganese extraction increases from initial pH of 1–4, yielding extraction efficiency of 72.5, 77, 82.6 and 90% respectively. However, manganese recovery drastically decreases as solution pH increases from 5–6, thereby decreasing extraction efficiency from 85 to 72%. Hence, pH of 4 has been selected for subsequent optimization studies. The plot of log D versus equilibrium pH depicted in (Fig. 17), shows a linearity nature with a slope of 1.32, indicating that 1 mol of extractant is exchanged for a mole of manganese ion during the extraction process.

4.5 Extraction Mechanism

Considering the results of the extraction plots of Fig. 15 and 17, the extraction mechanism in this study follows the following stoichiometry [20]:

$$Mn^{2+}_{(aq)} + H_2A_{2(org)} \leftrightarrow MnA_{2(org)} + 2H^{+}_{(aq)}, \qquad (9)$$

H_2A_2 represents the D2EHPA extractant, MnA_2 is the complex in the organic phase, K_{ex} represents the equilibrium constant, while (aq) and (org) denotes the aqueous and organic phases, respectively.

$$K = [MnA_2][H^+]^2/[Mn]^{2+}[HA]^2, \qquad (10)$$

$[HA]_2$ refers to the possible dimeric form of the extracting agent

$$K = D[H^+]^2/[HA]^2 \qquad (11)$$

$$\text{Distribution ratio, } D = [MnA_2]/[Mn]^{2+} \qquad (12)$$

From Eqs. (9–12), the manganese extraction mechanism by D2EHPA extractant, is therefore consistent with the expression:

$$\log D = \log K + \log[HA]_2 - 2\log[H^+] \qquad (13)$$

4.6 Extraction Purity Analysis by FTIR

The analysis of the chemical bonding of the extractant, manganese organic loaded and pure stripped solutions, which enables identification of compounds present have been studied using Fourier transform infrared spectroscopy (FT-IR) as summarized in Fig. 18a–c. The D2EHPA extractants, show a broad OH band around 3458.58 cm^{-1} and a medium intensity band around 1454.35 and 1378.36 cm^{-1} indicating P–C and P–O which suggest the extractant to be organophosphorus [34] (Fig. 18a). The spectrum for the manganese loaded phase in D2EHPA, given as (Fig. 18b), show the presence of a broad band at 3442.74 cm^{-1} which can be attributed to O–H bending vibrations. Also, an intense P–O band at 1375.20 cm^{-1} which moves towards the frequencies of 1334.04 cm^{-1} characterizes P–O–Mn. The manganese stripped solution in Fig. 18c, shows a series of IR band in the bending region which is less intense and less broad compared to the band in the bending region of (Fig. 18a), indicating the total stripping of metal ion from the extractant loaded phase.

4.7 Hydrometallurgical Process Flow-Chart

The flow chart summarizing the important analytical operations for the recovery, purification and beneficiation of a Nigerian origin spessartine ore to obtain high grade

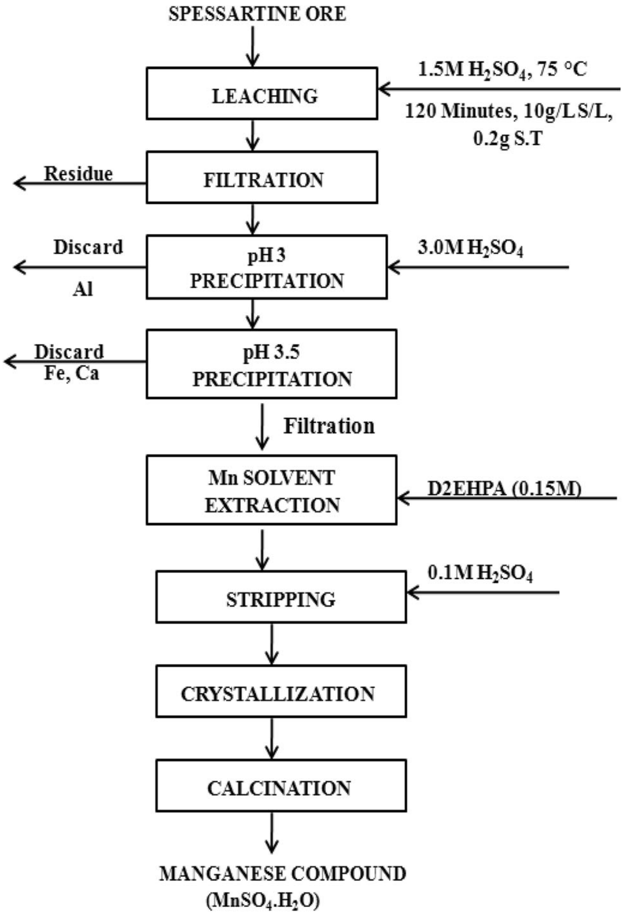


Fig. 19 A hydrometallurgical process flow-chart for purification and recovery of manganese compound from a Nigerian Spessartine ore [9]

manganese compound ($MnSO_4.H_2O$) of industrial value is depicted in (Fig. 19).

5 Conclusion

In this study, reductive leaching of a Nigerian spessartine ore by sulphuric acid-cum-spent tea leachant and solvent extraction techniques by di-2-ethylhexyl phosphoric acid (D2EHPA) in kerosene diluents for purification and beneficiation to obtain high grade manganese compound was examined. The extent of sulphuric acid dissolution reached 48.4%. However, with increasing reaction temperature and spent tea as reductant, manganese dissolution efficiency increased rapidly to 80.2%. The calculated apparent activation energy of 35.5 kJ/mol supported the diffusion reaction mechanism for the reductive-leaching process.

The leaching, precipitation and solvent extraction efficiencies in the treatment of the ore to obtain a high grade manganese sulphate monohydrate ($MnSO_4.H_2O$, melting point = 692.4 °C: 47-304-7403) through combinations of crystallisation and calcination of the product at optimal extraction conditions were found to be $> 90\%$. The results of this study could go a long way in helping the country in the present pursuit of economic diversification from the hard-earned foreign exchange through petroleum exploration.

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