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Synthesis of manganese oxide from manganese ore of bajaur agency khyber Pakhtunkhwa (KPK), Pakistan

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ABSTRACT

In the present work manganese sulphate developed from the Bajaur (KPK, Pakistan) manganese ore was utilized successfully for the synthesized Manganese Oxide chemically by an alkali-oxidation of manganese sulphate using the co-precipitation method. The advantages of this eco-friendly co-precipitation method include quick and easy preparation, simple control of particle size, and cost-effective composition using local ore. Because of the readily available raw materials and the controlled reaction conditions, this method is widely used in industry. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the synthetic manganese oxide. Fourier transforms infrared spectroscopy (FTIR) Infrared reveals that the O-Mn-O vibrational mode occurs in pure manganese oxide at wavelengths between 600 and 500 cm^{-1}. The chemical composition was obtained by EDX analysis and confirmed the presence of Mn and O in the sample. Experimental optimization was done for the manganese oxide precipitation conditions. The findings show that a variety of parameters have an impact on the product yield; the precursor ratio and reaction temperature are the most important variables, and the reaction time and pH value have the greatest impact on the quality of crystallization.

Keywords: Manganese Oxide; alkali-Oxidation; $MnSO_4$

Introduction

Over 300 different minerals contain manganese, which is the twelfth most common metal in the earth's crust (JCPDS, 1979). Pyrolusite, hausmannite romanechite, rhodochrosite and manganite are found to date as the main minerals and source of manganese (Craig and Vaughan, 1994; Roberts *et al.* 1990). In 2021, 49.5 million metric tons of manganese was produced globally. According to Riaz *et al.* (2010) industrial users prefer rich deposits with manganese concentrations above 35%.

Fig. 1. displays the amount of manganese ore consumed globally. These specific facts necessitate the development of viable beneficiation techniques for local manganese ores that can economically process their minerals. Pyrometallurgy, hydrometallurgy, and biometallurgy are popular techniques for processing manganese ore. Pyrometallurgical processes are widespread but have some disadvantages, including high costs, energy consumption, low productivity, and significant pollution (Zhang *et al.* 2013). Using microorganism activity, the process of biometallurgy removes metal from ore. Since each type of metal requires a different adaptation, the biometallurgical method has sadly not yet been commercialized (Lee *et al.* 2001). Hydrometallurgy is an additional method of processing manganese ore. Leaching with an acid or base solution, the target element is separated from the other elements (gangue elements) in this process. According to (Gosh and Ray 1991), the advantages of hydrometallurgy include its suitability for lean, low-grade, and complex ore, ease of control over each processing step, ability to reduce environmental pollution, and viability on both a small- and large-scales. Numerous studies on the manganese ore leaching process have been published. Sulphuric acid and oxalic acid were used in the hydrometallurgy method for manganese ore, and much of the manganese was successfully leached (Sahoo *et al.* 2001) as manganese sulphate.

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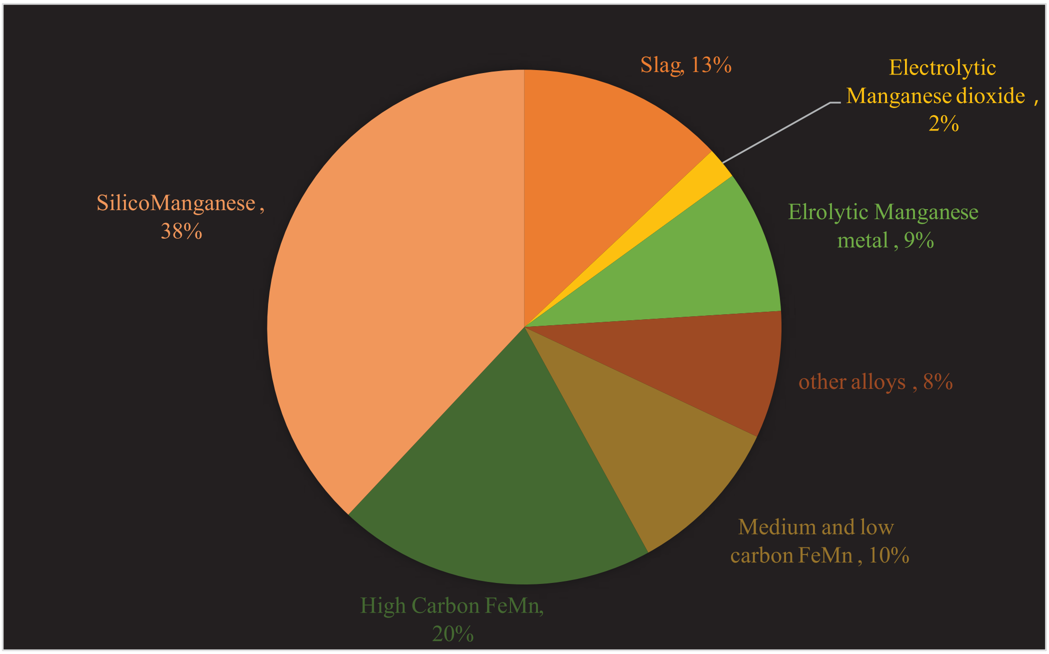


Fig. 1. Global consumption of manganese ore (Source: Waheed-Ur-Rehman, ISAM 2015)

Which is an antecedent compound for many reactions and a product of the leaching process with sulphuric acid, is used in a variety of industrial applications, including fertilizer, textiles, pigment, and pharmacy. In various chemical forms, manganese is a metal that is strategically significant as a raw material and for use in a variety of industrial processes. The highest demand for manganese alloys is in the steelmaking industry. Commercial significance also pertains to various manganese salts. To encourage plant growth, soil is amended with manganese sulphate ($MnSO_4$). It is an effective reducing agent and is especially helpful in the production of paint and varnish driers. Potassium permanganate ($KMnO_4$) is a deep purple compound with many applications, but its main ones are as antiseptics, disinfectants, and water purifiers. The use of manganese oxides, such as MnO, MnO_2 and Mn_3O_4, in significant industrial processes like waste water treatment, as a catalyst, a sensor, a supercapacitor, and as the cathode material in dry cell batteries, is well documented. Chemical manganese dioxide (CMD), electrolytic manganese dioxide (EMD), natural manganese dioxide (NMD), and active manganese dioxide (AMD) are some of the different types of manganese dioxide that are available (Jiangang *et al*. 2010). Manganese oxides with excellent properties can be produced using a variety of creative and efficient methods (Xiaodi *et al*. 2013). The thermal decomposition method, the oxidation method using a strong oxidant, the reduction of high-valence manganese salts, and the direct oxidation method are some of the current common ways to prepare manganese oxide (Lili *et al*. 2014). According to Shuijin *et al*. (2006), the thermal decomposition method is further divided into the thermal decomposition of nitrate and the thermal decomposition of carbonate salts. Many researchers have paid close attention in recent years, to the preparation of CMD and the study of its properties. Frequently it is employed in the synthesis of organic materials as a chemical oxidant (Wang *et al*. 2008). It is produced directly from the ore, although significant amounts are also synthesized primarily through the reductive roasting and leaching of manganese ores (which contain about 40% Mn), followed by hydrometallurgical processing (Darmane *et al*. 2008; and Wensheng and Chu, 2007). As in Pakistan, huge sums of valuable foreign currency are spent each year to import manganese alloys and other chemicals to satisfy the ever-increasing demand of the steel and chemicals industries. Locally produced manganese ores can be processed into manganese sulphate and manganese oxide to increase their economic value. There are very few known reserves of manganese ore in Pakistan. However, Pakistan's Khyber Pakhtunkhwa (KPK) and Balochistan provinces contain economically significant reserves of manganese ore. Bajaur and Mohmand Agencies in Pakistan's FATA (Federally Administered Tribal Area) have been found to contain manganese ore reserves (Fig. 2). The manganese ore at the Bajaur Agency is of a high grade, with an average weighted grade (manganese < 43%) along with substantial silica and iron as major composition constituents. It is also accessible, which is economically significant in terms of mining and beneficiation operations for the availability of raw materials for the domestic production of manganese-based products (Rubina *et al*. 2014). In this paper, the alkali-oxidation method for producing manganese oxide is explained in relation to the use of manganese sulphate, which was produced from the readily available Bajaur manganese ore. The objective is to use a readily available raw, high-grade manganese ore in a straight-forward operation with minimal waste.

Materials and methods

Preparation of the sample

Mineralogical examination of the Bajaur Agency manganese deposits revealed the presence of Mn oxide and Mn silicate minerals, which include Hausmannite and Braunite, respectively. The residual minerals are calcite and silicate (Fig. 4). The gangue minerals and the manganese minerals are interspersed with very fine-grained manganese minerals (Riaz *et al.* 2010). For the current study, a representative sample of the Bajaur manganese ore was taken (Fig. 3). The lumps of ore ranged in size from 50 to 150 mm. It was crushed in a laboratory jaw crusher to a size of 20 to 25 mm, and then it was put through a roll crusher to produce a product of 5 to 6 mm. While the remaining ore was used for mineralogical and processing studies, a head sample for chemical analysis and for X-ray diffraction was obtained by coning-quartering and riffling the crushed ore. Using disc pulverize (Denver, USA), the crushed sample was further ground down to 100% - 200 mesh (74µm).

Chemical analysis

The representative pulverized manganese ore sample was chemically analyzed using gravimetric, volumetric, and instrumental techniques. Gravimetric analysis was used to determine the amounts of silica and alumina, while titration was used to determine the amounts of Mn, iron, calcium, and magnesium. Flame photometer (PFP7, Jenway Limited, England) measurements of sodium and potassium were made. Fig. 4 and Table I provide the results of X-ray diffraction and the chemical analysis.

Table I. Chemical composition of the Bajaur Agency manganese ore

Elements	% Composition
Loss on ignition (LOI)	8.95
Calcium Oxide (CaO)	3.32
Magnesium Oxide (MgO)	0.440
Aluminum Oxide (Al_2O_3)	7.11
Iron Oxide (Fe_2O_3)	4.95
Silica (SiO_2)	26.52
Potassium Oxide (K_2O)	0.021
Sodium Oxide (Na_2O)	0.193
Manganese Oxide (MnO_2)	48.19

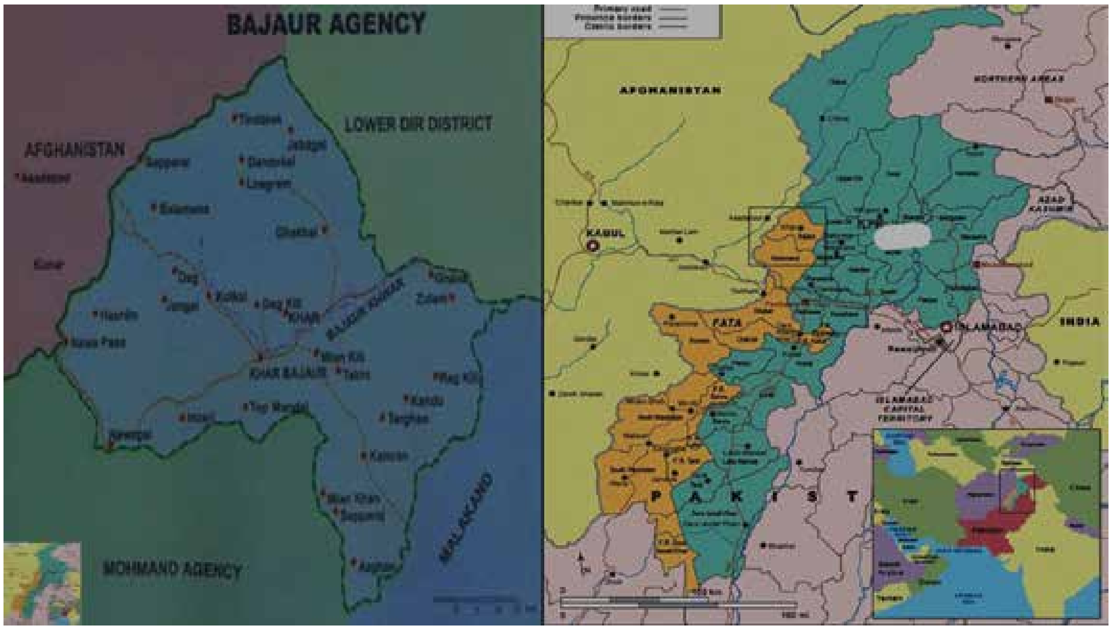


Fig. 2. Map of Pakistan showing the location of Bajaur Agency (Source: Rubina *et al.* 2014)

Manganese oxide powder synthesis

All chemicals used were analytical grade. Manganese Oxide precipitates were synthesized by experimentally optimized Co-precipitation method by using Manganese Sulphate effect of pH, temperature, reaction time and agitation rate were studied for maximum conversion as manganese oxide. Apparatus included: a super constant temperature bath (LCTW-A10, Labtron Equipment Ltd. UK); an electronic constant speed stirrer (ATAGO NO. 53127, ATAGO Co. Ltd. Japan); a pH meter (HI 98199 HANNA I instrument Co. UK.); an electric oven (GN 0127 Geotechnical Testing Equipment UK Ltd.)

Fig. 3. Representative sample of Manganese ore of Bajaur Agency area, KPK, Pakistan

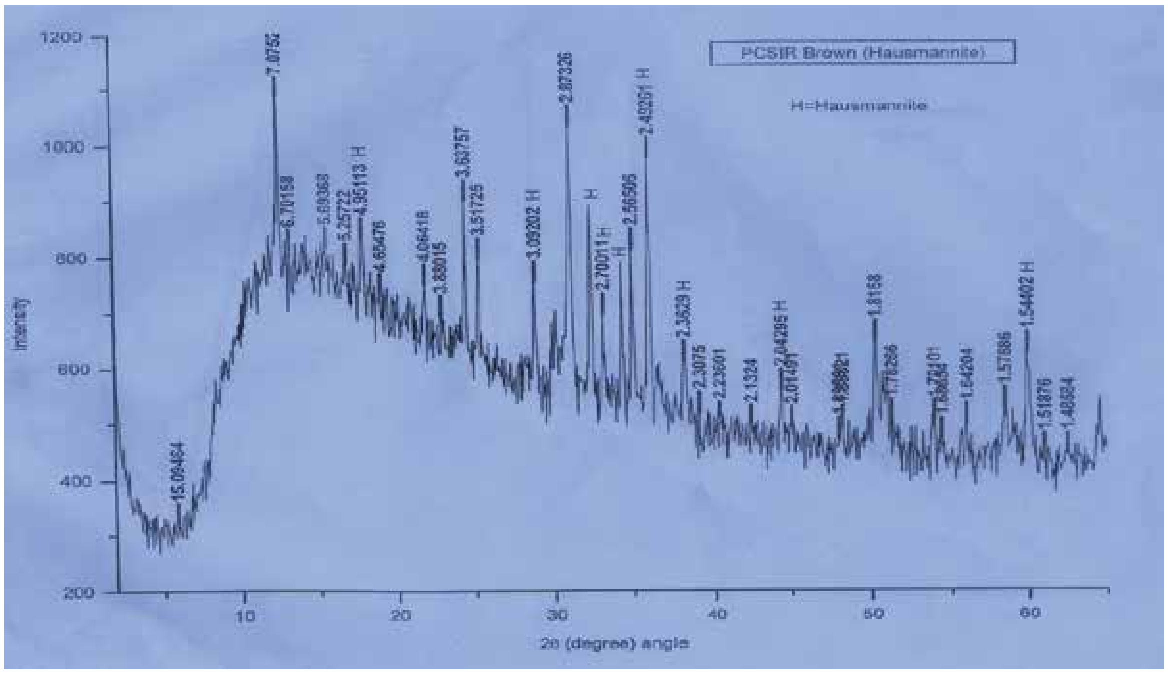


Fig. 4. X ray diffraction pattern of representative sample of manganese ore (Brown Hausmannite)

The Method is described below along with the flow chart (Fig.5)

A super-constant temperature bath was used to regulate the temperature. An electronic constant speed stirrer was used to stir the reaction mixture. In 2 litres of double-distilled water, 0.5 M manganese sulphate aqueous solution was made by continuously stirring at a constant temperature of 80°C. When the pH of the solution reached 11–12, sodium hydroxide solution was added while manganese sulfate and sodium hydroxide solutions were being stirred into the reaction vessel in the appropriate amounts. A constant temperature of 80°C was maintained during the stirring for two hours. Brown precipitates developed and was aged for 72 hours. At 110°C an electric oven was used to dry the product after filtering and washing with ethanol. Following drying, grinding, and sieving. In order to examine the powder's microstructure and elemental composition and the phase that was created was examined using a scanning electron microscope (SEM) equipped with energy dispersive x-ray microanalyzer (EDX; S3700N Hitachi, Japan). The O-Mn-O vibrational mode was detected using a Fourier transforms infrared (FTIR) spectrometer from Bruker, United States. Using the accepted procedure, ASTM E465-11(2017), the manganese oxide concentration was calculated.

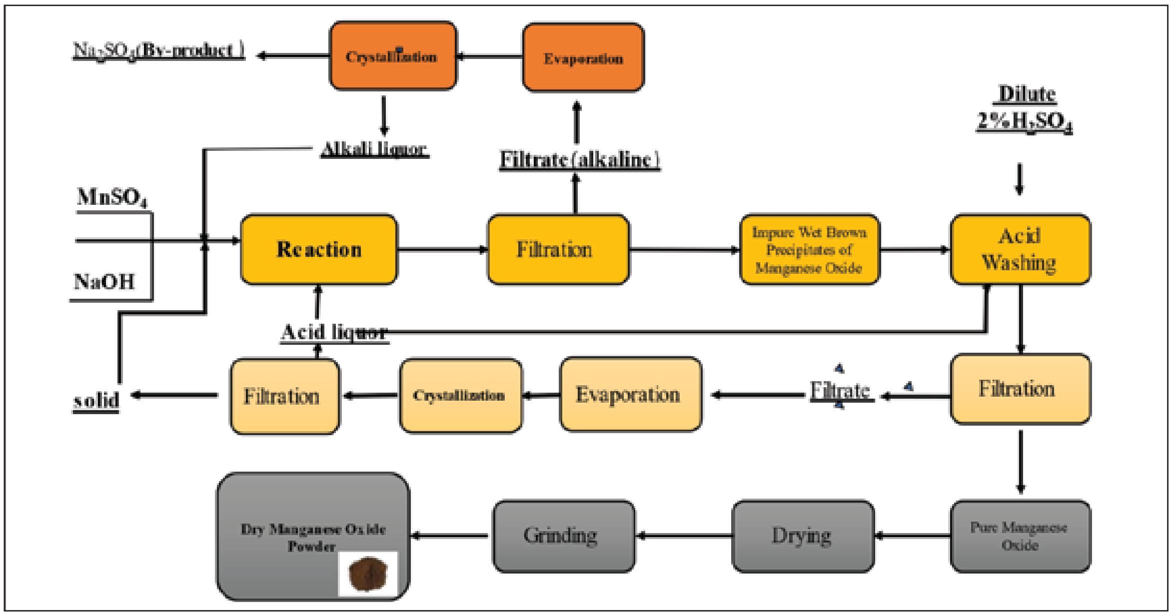


Fig. 5. Process for Preparing manganese oxide from $MnSO_4$ by alkali oxidation

Results and discussion

pH/alkali impact on conversion

100 ml of 17% $MnSO_4.H_2O$ aqueous solution at 75°C temperature were added to the reactor having 700 rpm stirring speed. The pH was adjusted with saturated sodium hydroxide solution, and the reaction time was 120 minutes. As the established concentration of Manganese Sulphate solution presents a strong acidity therefore in this experiment, we studied the effect of alkali on the conversion of acidic Manganese sulfate solution, to obtain manganese oxide at alkaline pH. Figure 7 shows that solution pH has a significant effect on conversion following pourbaix diagram (Fig. 6), which is presenting that the potential difference between Mn^{2+} and MnO_2 is high in acidic conditions. On the other hand, it is easy to oxidize $Mn(OH)_2$ to MnO_2 in alkaline conditions (Wenhao *et al.* 2019). Whole reaction is presented in equation form by (Jiangang *et al.* 2010), as

$$Mn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow Mn(OH)_2 \xrightarrow{AIR} MnO_{2(S)}$$

Consequently, Mn^{2+} can be reduced more readily and the reaction rate increases as alkali concentration rises. When the pH is 11, the conversion is greatest. At pH 13 to 14, the amount of synthetic manganese dioxide produced decreases as a result of an increase in the absorption of low-valent manganese ions thus, 11 is considered to be the ideal pH (Fig. 7).

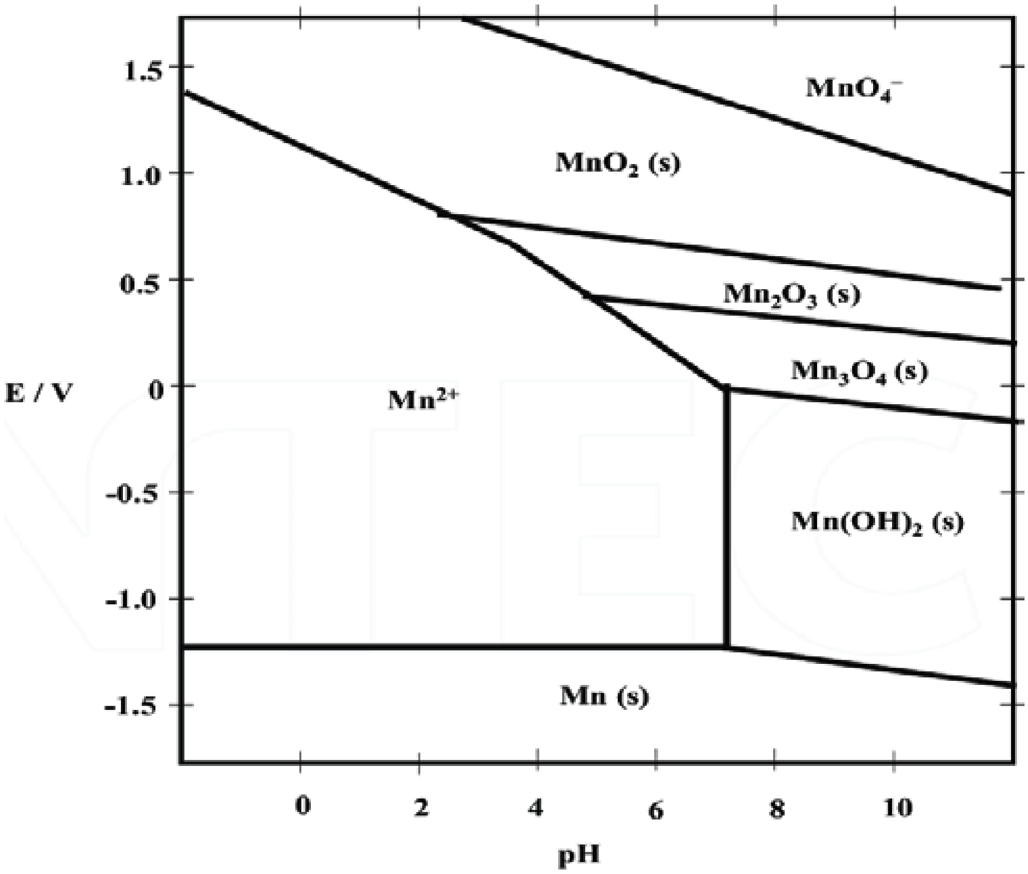


Fig. 6. Pourbaix diagram for manganese oxide

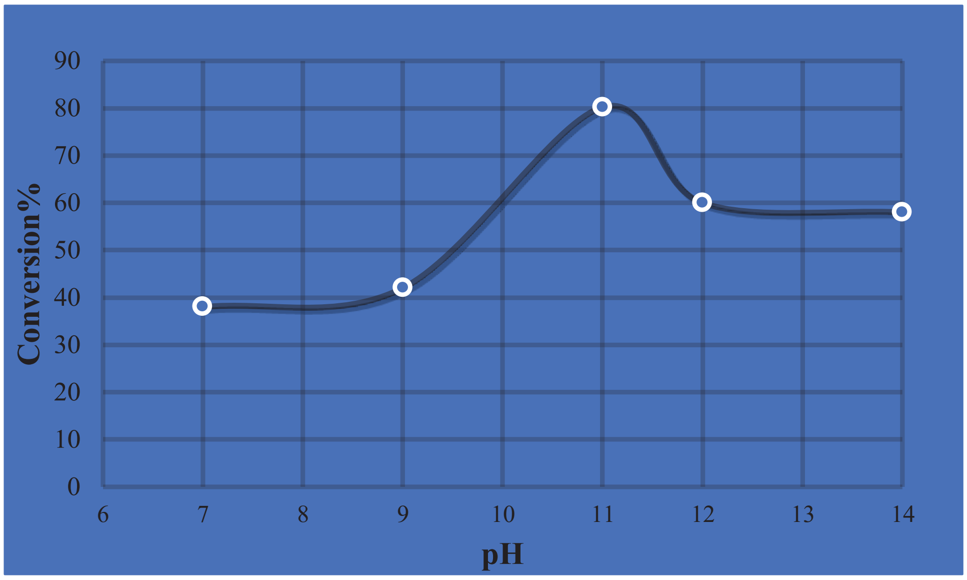


Fig. 7. Effect of pH on conversion at T=75^{O}C, R=700R/min, t=120min, CMnSO$_4$=0.5M

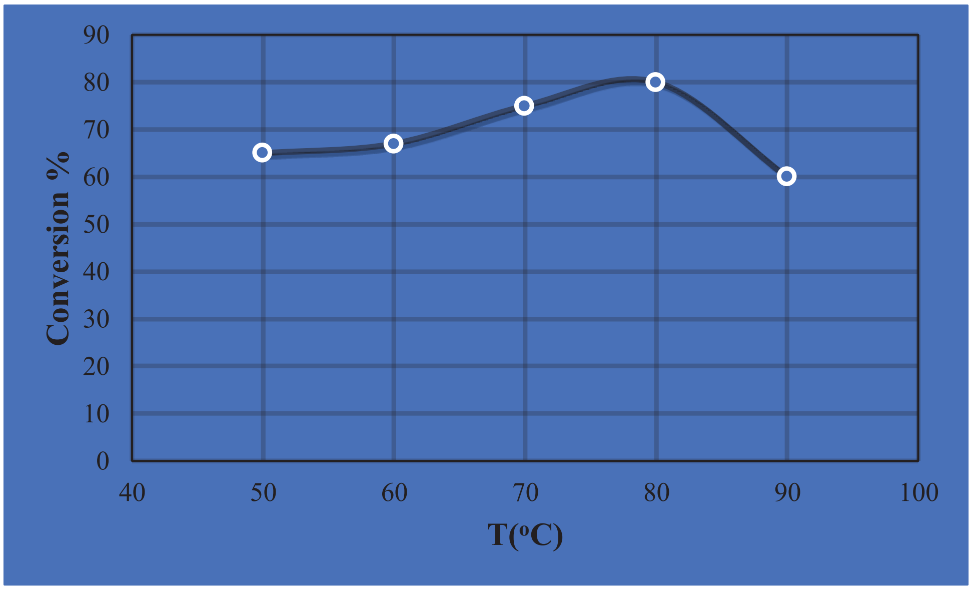


Fig. 8. Effect of temperature (T^{O}C) on Conversion at pH=11, R=700R/min, t=120min, CMnSO$_4$=0.5M

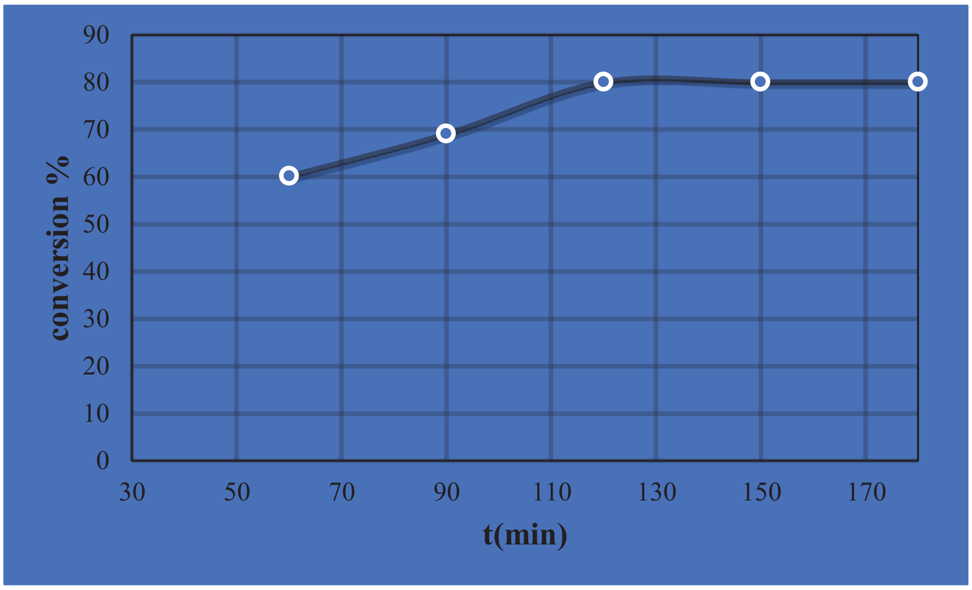


Fig. 9. Effect of time (t) on conversion at pH=11, T=75^{O}C. R=700R/min, CMnSO$_4$=0.5M

Temperature's impact on conversion

The conversion of MnSO$_4$ increases as the temperature rises from 50 to 80°C (Fig. 8); it reaches its maximum (82 %) at 80°C. The rate of the reaction and the conversion both increase as the temperature rises because it improves mass transfer and strengthens molecular collisions. As the temperature rises further, the percent conversion begins to fall. This is so because the oxidation of Mn^{2+} is a non-homogeneous reaction involving the solid, liquid, and gas phases. The reaction is hampered by the decrease in gas concentration caused by the solubility of air in the liquid phase, which decreases with increasing temperature. It follows that 80°C is the ideal reaction temperature as determined by experiment.

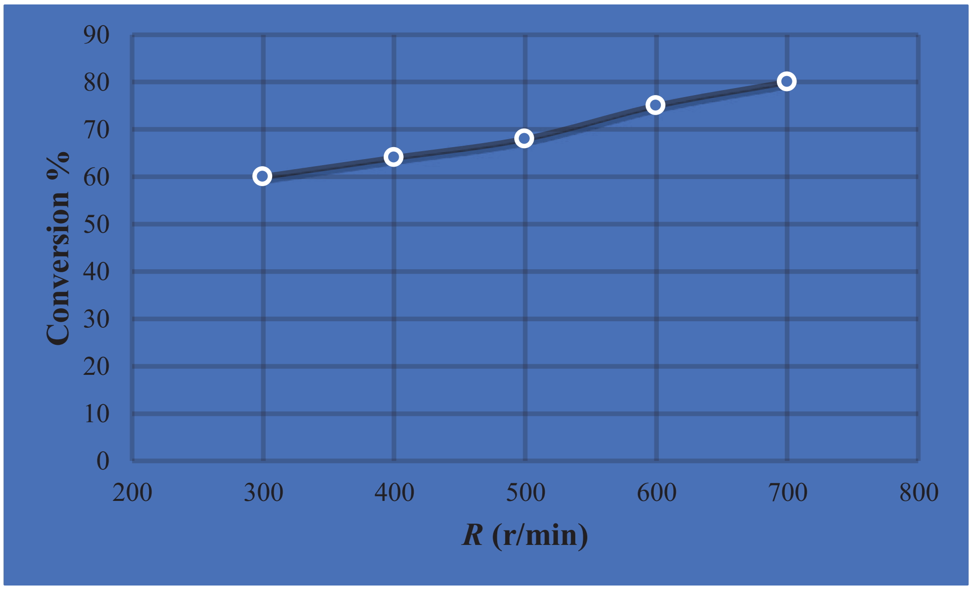


Fig. 10. Effect of rate of agitation(R) on conversion at T=75^{O}C, pH=11, CMnSO$_4$=0.5M

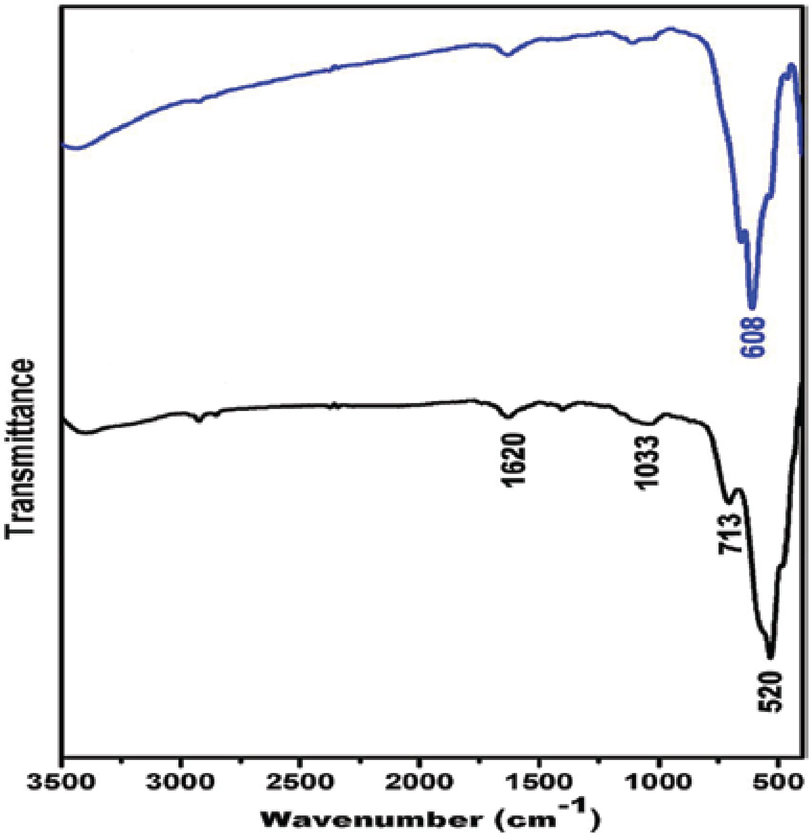


Fig. 11. FTIR patterns of manganese oxide in the wavelength range 500-3500 cm^{-1}

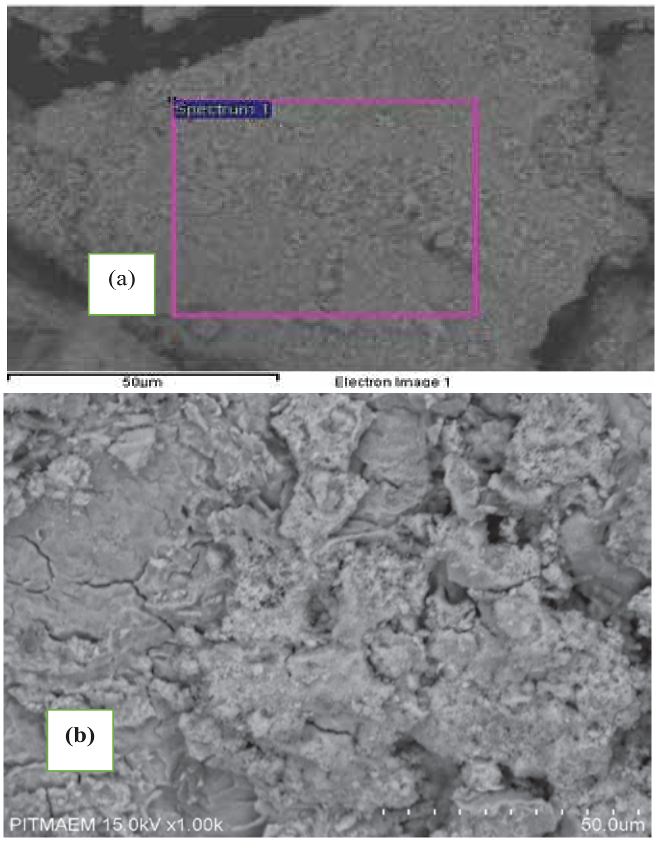


Fig. 12. SEM images of manganese oxide (a) honeycomb-like structure, (b) holes on honeycomb-like surface

Impact of reaction time

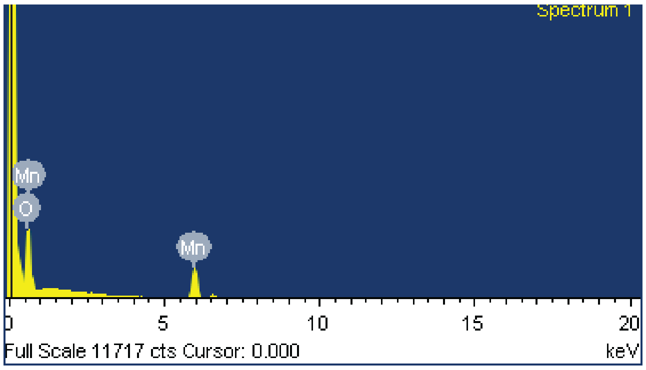
The effect of reaction time on conversion is shown in Figure 9. The findings suggest that conversion rises over time. At 120 minutes, the conversion is around 80%. Following this, not much changes. The ideal reaction time, as found through experiment, is two hours.

Impact of agitation on conversion

A stirring is helpful for mass transfer. Between the solid and liquid phases, agitation improves mass transfer. Fig. 10, which demonstrates how agitation speed significantly affects conversion. As the agitating speed picks up, conversion goes up. There was a 20% difference between the maximum and minimum conversion. The reaction is sped up by agitation because the intermediate, $Mn(OH)_2$, is a floc, which makes it easier to make solution contact with and transfer reactants between the three phases. However, excessive agitation could cause the solution to splash out; 700 rpm was determined to be the right speed.

Characterization methods

The characterization of synthetic manganese oxide powder was assessed using Fourier Transform Infrared (FTIR) spectroscopy in the 500–3500 cm^{-1} wavelength range (Fig. 11). Infrared (FT-IR) spectroscopy is renowned for its high sensitivity, particularly in identifying inorganic and organic species with low content. Particles of metal oxides and hydroxide most often give absorption spectra below 1000nm due to interatomic vibrations. Peaks between 500 and 600 cm^{-1} were attributed to the Mn-O stretching mode (Balamurugan *et al.* 2015). Therefore we infer from the above result that the synthesized substance is manganese oxide. The surface morphology of the particles is investigated using SEM analysis. SEM is used to define the morphology of the prepared sample. As can be seen in Fig. 12 (a, b), the prepared product is composed of manganese oxide having images of a honeycomb-like structure. A honeycomb-like structure with numerous holes is clearly visible on the product surface in the enlarged image of Fig. 12 (b). An Energy-Dispersive X-ray (EDX) spectroscope connected to the SEM was used to determine the average elemental composition of manganese oxide, as shown in (Fig. 13).



Element	Weight%	Atomic%
O	30.67	60.31
Mn	69.33	39.69
Totals	100.00	

Fig. 13. EDX analysis of manganese oxide showing the elemental composition

Conclusion

In conclusion, manganese oxide particles have been produced in a straightforward one-step solution phase method by alkali oxidizing manganese sulphate with sodium hydroxide at room temperature. The polycrystalline nature of the particles was discovered by SEM analysis. The industry has a great opportunity to scale-up the preparation of pure manganese oxide from local ores and adapt this low temperature synthetic route, which is based on a straight forward reaction without the use of catalysts or templates and considering no requirement of expensive and precise equipment.

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