Chapter 4   Summery and Conclusions

Manganese is the 12th most abundant element in the earth's crust and 4th most used metal following iron, aluminum, and copper. It has numerous applications which impact on our daily lives as consumers, whether it is of objects made of steel, portable batteries, or aluminum beverage cans. In each case manganese plays a vital role in improving the properties of the alloys and compounds involved in each specific application. One vital feature of manganese is its role as an essential element in maintaining human health. The exact role of it is not fully understood, but complex cellular reactions involving metallo-enzymes, have been identified.

About 90% of all manganese consumed annually goes into steel as an alloying element. The next most important market for manganese in dioxide form is that of portable dry batteries. A stream of new processes and metallurgical/chemical applications as diverse as beverage cans, agricultural pesticides and fungicides and electronic circuitry used in consumer products have been developed for manganese with significant impact on markets in the 20th century.

Manganese occurs most commonly in nature as oxides (*pyrolusite, braunite, manganite* and *hausmannite*, sulphide (manganese blende and *hauerite*), carbonate (*rhodochrosite*) and silicate (*tephroite, knebelite* and *rhodamite*). It also occurs in most (50–350 g/Kg) iron ores.

Besides the large variety of metallurgical uses, the important non-metallurgical use of manganese are found in dry-cell batteries, pigments, paint driers, animal feed, trace element fertilizers, catalysts, potassium permanganate, manganese phosphate coating, manganese ferrite, Maneb, MMT, fireworks etc.

The most important Mn compounds exist in Mn^{2+}, Mn^{4+} or Mn^{7+} oxidation states. Some divalent manganese compounds are sulfate, halides, nitrate, hydroxide, oxides which are found in nature as *manganosite*, carbonate which occurs in nature as *rhodochrosite*, etc.

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Trivalent manganese ion called as manganic ion scarcely exists in aqueous solution. The sesquioxide, Mn_2O_3, exists in dimorphic forms. The α-Mn_2O_3 exists in nature as the mineral *bixbyite*. The γ-Mn_2O_3 form is unstable and thus does not occur in nature and it may be synthesized by the dehydration of the precipitated hydrated form at 250 °C in vacuum.

The mixed valent oxide Mn_3O_4 occurs in nature as the mineral *hasumannite*. The structure of this ferromagnetic material has been the subject of much dispute. Mn_3O_4 is most stable of the manganese oxides, and is formed when any of the other oxides or hydroxides are heated in air to 940-1000 °C. The oxidation of aqueous solutions of $Mn(OH)_2$ can also lead to the formation of Mn_3O_4.

The most significant Mn(IV) compound is its dioxide MnO_2. It is found in nature a black mineral called pyrolusite. Mn(IV) dioxide is more realistically represented by $MnO_{1.7-2.0}$, because it invariably contains varying percentages of lower valent manganese. It also exists in a number of different crystal forms, a various states of hydration and a variety of contents of foreign ions. The mineral pyrolusite is the primary example of β-MnO_2 (black to gray crystals), having the general formula MnO_x (x = 1.95-2.00). This mineral is characterized by a high degree of crystallinity and an almost perfect stoichiometric composition. The β group can be visualized as being composed of single chains of edge-shared MnO_6 octahedra, cross-linked to neighboring chains, through corner sharing of oxygen atoms. The crystal structure of *ramsdellite* is similar to that of β-MnO_2. *Ramsdellite* and *pyrolusite* are the only manganese dioxide phases where the composition approaches the stoichiometric MnO_2 formula. *Ramsdellite* transforms to pyrolusite on heating to 250 °C.

MnO_2 typically loses its adsorbed water between 25-105 °C. The complete removal of interlayer water, which results in collapse of the crystal lattice, requires temperatures as high as 150-250 °C. In the γ-MnO_2 phase the condensation of OH groups occurs in the temperature range of 105-500 °C, resulting in the release of this most tightly bound water and collapse of the crystal lattice. The various MnO_2 phases eventually transform into thermodynamically stable β-Mn_3O_4. The term γ-MnO_2 is applied to a series of hydrated MnO_2 of moderate crystallinity that are suitable for battery purposes. The gamma group

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can be visualized as being composed of irregular structural combinations of β-MnO_2 (single-chain) and *ramsdellite* (double-chain) components.

Typical minerals belonging to δ-MnO_2 group include *birnessite, ranceite, takanelite, toddorokite, woodruffite, chalcophanite* and *lithioporite*. This phase is often labeled as hydrated MnO_2 because it typically contains 5-40% of chemically bound water. These dioxides have x = 1.7-2.0 for the general formula MnO_x and often also contain Na^+, Ca^{2+}, or Ba^{2+}. The oxidation of divalent manganese, or the reduction of potassium permanganate, leads to the formation of δ-MnO_2. These manganites generally follow the composition $M_2O.4MnO_2$, (where M =alkali metal).

The microorganisms, *Pedomicrobium manganicum* or *Hyphomicrobium manganoxydans* accelerates the oxidation of Mn(II) to MnO_2 by O_2 in the pH range of 5.5-7.5 in contrast to the pH 8.5-10 normally required for its chemical oxidation by O_2. Water purification chemistry depends on the oxidation of Mn(II) by a suitable oxidant, e.g, O_2 at pH > 9, or at lower pH potassium permanganate or ozone resulting in the formation of hydrous manganese dioxide.

Manganese dioxide (CMD) can be prepared by various chemical methods including the thermal decomposition of Mn salts such as $MnCO_3$ or $Mn(NO_3)_2$ under oxidizing conditions. CMD also results by the reduction of higher valent Mn compounds such as MnO_4^- salts.

Commercial process for the recovery of high purity MnO_2 is based on thermal decomposition of $Mn(NO_3)_2$, which results in a well-defined crystalline MnO_2 having purity greater than 99.5%. In another commercial process, CMD is produced from finely ground MnO_2 ore wherein the ore is reduced to Mn(II) oxide using H_2/CO and then leached with sulfuric acid followed by precipitation as carbonate using $(NH_4)_2CO_3$. The $MnCO_3$ is heated in air at 450 °C resulting in 80% conversion to MnO_2. The MnO_2 and $MnCO_3$ mixture is further leached with sulfuric acid and oxidized with $NaClO_3$. Following washing and drying, the product is found to have 60% Mn and 90% MnO_2.

The native ore is activated to a higher quality MnO_2 ore by chemically removing the top layer and create a new highly porous and active surface. In this purpose, the MnO_2 ore is first reduced to Mn_2O_3 either thermally, by heating it to 600-800 °C in air, or at

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300 °C in the presence of a reducing agent. The reduced mass is then treated with hot sulfuric acid and the Mn_2O_3 disproportionate to a highly active γ-MnO_2 and $MnSO_4$.

A hydrated MnO_2 is generated in the oxidation of o-toluenesulfonamide to sulfonbenzimide (saccharin) with $KMnO_4$ in alkaline medium. The co-product MnO_2 (CMD) produces a product containing approximately 79% MnO_2, 5-18% water, and alkali contents of 4-12% as KOH after washing and careful drying. The MnO_2 powder, thus obtained called *Permanox* is a poorly crystalline form of γ-MnO_2.

Anodic oxidation of Mn(II) salts is developed to obtain MnO_2 called as electrolytic manganese dioxide or EMD. EMD obtained by this way is strictly a nonstoichiometric MnO_2 containing 2-5% lower valent manganese oxides and 3-5% chemically bound water. EMD is prepared from the electrolyses of acidified manganese sulfate solutions. The MnO_2 formed by this method is generally considered to be of the γ-MnO_2, but at low acid concentration, some β-MnO_2 may be co-produced, and conversely, at high acid concentration, the formation of the α-MnO_2 phase is favored. More recently EMD was suggested to contain predominantly the $\propto$-phase instead of γ-MnO_2. The ore *rhodochrosite* consisting on weight basis 58-68% $MnCO_3$; 30-35% Mn; 15-20% SiO_2; 2-3% Fe; 0.1-0.2% Pb; 0.2-0.3% Zn; 0.1% Ni and 0.01% Co, is primarily used in Japan for the production of EMD. EMD is also prepared from MnO_2 ore containing a minimum of 75% MnO_2.

The current efficiency in the electrolyses step is 90-95%, making the energy requirements on the order of 0.45 kWh/Kg of EMD. Oxygen is generated at the anode as the principal by-product. This can become significant in electrolytes having high sulfuric acid concentration. At the cathode, a mole of hydrogen is generated for each mole of EMD produced. The main disadvantages of this method producing EMD in the form of a solid deposit on the anode are that i) *the process must be interrupted to remove the anodes from the cells* and ii) *stripping the MnO$_2$ is a labor-intensive operation.*

Newer technology called the suspension-bath process allows small MnO_2 particles to adsorb on the electrode surface, thus allowing for higher current densities to be used during electrolysis. The resulting MnO_2 has a macro porous structure, even though some of the micropore area (BET surface area = 10-25 m^2/g) is lost.

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Very recently, an Ag^+ ion catalysed preparation of EMD has recently discribed. This is a homogeneous electrocatalysis and allows MnO_2 to be prepared in a convenient process. It uses Ag^+ ions to catalyze the anodic oxidation of Mn^{2+} ions wherein Ag^+ ion is oxidized easily on an anode to form Ag^{2+} ions which in turn, oxidizes easily Mn^{2+} ions to MnO_2.

Pentavalent Mn(V) exists only as MnO_4^{3-} called hypomanganate. In water, it instantly disproportionate to Mn(VI) and MnO_2. The most important Mn(V) compound is K_3MnO_4, a key intermediate in the manufacture of $KMnO_4$.

The hexavalent manganese compounds are known as sodium, potassium, rubidium, cesium, barium, and strontium salts. They are prepared by heating an aqueous solution of alkali metal permanganate in the presence of an excess of strong alkali, excluding carbon dioxide.

Permanganic acid $HMnO_4$ having Mn in +7 state is conveniently prepared in the laboratory from barium permanganate and sulfuric acid, or by anodic oxidation of ferromanganese in a divided cell using H_2SO_4 as the electrolyte. The acidity of $HMnO_4$ is comparable to that of HNO_3. The anhydrous form of it is called as manganese heptoxide (Mn_2O_7). It is prepared by titrating solid potassium permanganate with concentrated sulfuric acid at 25-35 °C. Manganese heptoxide is hygroscopic and forms $HMnO_4$ with water.

Manganese is also an essential micronutrient for good health and growth in plants, animals and humans. Symptoms of manganese toxicity and deficiency are found in plants. Manganese deficiencies are more common when the soil pH is low. Concentrations greater than about 500-1,000 ppm of manganese have been reported to be toxic for plants. Highly concentrations of manganese in soil can cause swelling of cell walls, withering of leafs and brown spots on leaves. Deficiencies can also cause these effects. Manganese ions are transported to the leaves after uptake from soil. When too little manganese can be absorbed from the soil this causes disturbances in plant mechanisms. For instance disturbance of the division of water to hydrogen and oxygen, in which manganese plays an important role.

For animals, manganese is found over thirty-six enzymes that are used for the carbohydrate, protein and fat metabolism. Manganese deficiency in animals includes

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impaired growth, skeletal abnormalities and altered metabolism of carbohydrates and lipids.

Although there is no direct evidence for manganese requirement for humans, the recommended dietary allowance for adults is fixed to be 2.5-5.0 mg of manganese per day. This means, manganese is not only necessary for humans to survive, but also toxic when present in too high concentrations. The shortages of manganese cause health effects with respect to fatness, glucose intolerance, blood clotting, skin problems, lowered cholesterol levels, skeleton disorders, birth defects, changes of hair color, neurological symptoms. Chronic manganese poisoning may result from prolonged inhalation of dust and fume. A high incidence of pneumonia and other upper respiratory infections have been found in workers exposed to dust or fume of manganese compounds. Manganese effects mainly in the respiratory tract and in the brain, and cause parkinson, lung embolism and bronchitis. Constant exposure for a longer period of time is even reported men to become impotent.

Inhalation of particulate Mn compounds such as MnO_2 leads to an inflammatory response in lungs of both humans and animals. However, the dermal absorption of inorganic Mn compounds is considered to be toxicologically insignificant. The primary exposure of the general population to Mn compounds is through diet.

Concentrations of manganese in groundwater are generally preferred to be <100 μg/L, although values ≥ 1,000 μg/L are common. According to World Health Organization (WHO), the recommended safe limit of the manganese is 1 ppm in drinking water and 5 ppm in irrigation water. Most of the Indian rivers are being highly polluted with this metal by the industries that use salts of this metal in a variety of reactions. The main reasons for this are due to lack of availability of competent technologies or information for the recovery of these costly materials from the effluents and converting them into their reusable form. The industries that discharge such effluents include mining, dry batteries, dyes and pigment industries. The untreated effluents from industries are expected to contain manganese of about 1,000 to 3,000 ppm, which are at much higher side than their corresponding permissible limits.

More or less, manganese is an aesthetically undesirable metallic element that is difficult to remove from acidic to neutral pH mine drainage. In spite of the

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thermodynamic prediction that oxygen should oxidize dissolved manganese (Mn^{2+}) to an oxide or a hydroxide, this does not happen. Mn recovery from Ozone technology has been suggested in mine water treatment. The pilot-scale ozonation system at the Little Toby Creek Treatment Plant in Elk County, PA operated by the Pennsylvania Department of Environmental Protection, is installed to treat limestone-based acid mine drainage water. It generates 8 pounds of ozone per day and treats a flow of 30 gallons per minute.

Other conventional methods for removing manganese ions from effluent include chemical reduction, electrochemical treatment, ion exchange and evaporative recovery. Most of these methods of manganese removal are highly expensive and inconsistent and may generate toxic sludge that requires very careful disposal. There is no single method, which may commonly be adapted to recover manganese and simultaneously convert into its reusable form from the effluents. The recovery methods, in general, vary from effluent to effluent depending on the constituents, physico-chemical characteristics and the desired form in which the metal is to be recovered.

In the present study it was attempted to study the feasibility of recovering Mn(II) as MnO_2 from acid effluent from one of the leading dye manufacturing industry in Gujarat, by various oxidative physicochemical methods. Further, the study was expected to asses the adoptability each method in terms of simplicity, purity, %recovery and economic viability of recovering toxic manganese from effluent waste in its reusable form by involving various reducing/oxidizing agents under variable experimental parameters like pH, temperature, time etc.

According to the proposed objectives, manganese was recovered as water insoluble $MnCO_3$ ppt and then oxidized to its oxide form with maximum dioxide by *viz.* fusion in absence and in the presence of various amounts of fusion media. Further, different chemical and electrochemical methods have been tested for the oxidative recovery of manganese directly from the industrial acid effluent or involving the isolated $MnCO_3$ to obtain the oxides with maximum MnO_2 composition for reusability. The adoptability of these methods in terms of simplicity, purity, %recovery and economic viability has been assessed. In fusion methods, Na_2CO_3, $NaOH$, $CaCO_3$, $MgCO_3$ have been used as cheap fusion medium; while chemical oxidation methods, various oxidizing agents under

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variable experimental parameters like pH, temperature, time etc have been employed. The main objective of the present work was to explore the possibility of recycling manganese to infinite times in the mainstream reaction process thereby stopping further dumping of industrial effluent and its associated waste causing environmental pollution. The chemical methods employed here involve the potentially strong oxidizing agents such as molecular oxygen under fusion conditions, bromate as sodium salt, permanganate as potassium salt, hydrogen peroxide, chlorine/hypochlorite/chlorite, nitrate, ozone and perchlorate under predetermined experimental conditions. Galvanostatic conditions were used for the electrochemical recovery of manganese in a batch process. The best method adoptable economically and procedurally to the industry, among all the procedures tested, was identified.

First of all, the dark brown acid effluent discharge from the reactor after the specific oxidation reaction in the preparation of reactive azo dye intermediate by M/s Atul Industries Ltd., Atul, Valsad was characterized. The amount of commercial sodium bromate ($NaBrO_3$) as well as potassium permanganate each required for the complete conversion of Mn(II) to Mn(IV) state (MnO_2) in 100 ml of effluent was determined. Further, the sample (Pyrolusite ore) which was the source for Mn(II) in the effluent, commercially procured and regularly used by M/s Atul Ltd., was also studied. It possessed 85% Mn(IV) as MnO_2 and 3.07% interlayer water/most tightly bound water releasable and/or dehydroxylation between 160-480 °C and 7.08% oxygen releasable between 480-630 °C. The sample showed characteristic diffraction peaks at 28.62°, 37.33°, 41°, 42.83°, 46.4°, 56.56°, 59.30°, 64.84°, 67°, 72.36° (2θ) of Pyrolusite (β-MnO_2)[163] together with peaks at 22.22°, 33.14°, 35.5°, 36.5° 42°, 42°, 57°, 67° (2θ) characteristic for γ-MnO_2[163c] indicating that the sample contains β-MnO_2 mixed with some γ-MnO_2 phase as an impurity.

4.1. Manganese extraction as MnCO$_3$

In this method, the major quantity of sulfuric acid was first neutralized with cheaply available calcium carbonate to the safe pH 1, where the complication metal hydrolysis be concealed and filtration of pure calcium sulfate be handled safely. The manganese was then precipitated by adding sodium carbonate after neutralizing the sulfuric acid. This

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method works to be simple and better as the manganese recovery is close to about 100%. Additionally, the economics for the recovery of manganese particularly from dilute solutions, as carbonate, is an easy and attractive method. On the basis of the market prices (Table 4.1) as provided by the concerned industry for all the inputs, the cost calculations for the production of one kg of $MnCO_3$ is calculated and depicted in Table 4.2 and it comes to be an attractive price of about Rs. 22.19

Table 4.1. The prices as provided by M/s Atul Ltd. Valsad as of various chemicals employed in the manganese recovery are as below.

Name	Unit Price (Rs)	Name	Price (Rs)
$CaCO_3$:	1.00 per kg;	$NaClO_3$:;	31.00 per kg
$KMnO_4$:	60.00 per kg;	$NaBrO_3$	145.00 per kg
Na_2CO_3:;	10.50 per kg	NaOH:	21.00 per kg
Cl_2 gas:;	10.00 per kg	Electricity	6.50 per unit
H_2SO_4:	1.75 per kg	H_2O_2:;	24.00 per kg
	3.22 per Lit.		7.20 per lit (30% w/v)

Table 4.2. Approximate cost calculations for the preparation of one kg $MnCO_3$ from ME.

Raw material	Quantity required	Rate per kg	Cost in Rs.
Effluent	25.974 lit (@ 38.5 g per lit)	---	---
$CaCO_3$	4.155 kgs (160 g per lit)	1.00	4.16
Na_2CO_3	1.560 kgs (@ 60 g per lit)	10.50	16.38
Electricity	0.25 Units (filtration)	6.50	1.65
	Preparation cost of 1 kg $MnCO_3$		**22.19**

4.2. Oxidative extraction by fusion

Oxidative recovery of manganese from its acid effluent was carried out by separating it as manganese carbonate first followed by heating in aerial oxygen to below 500 °C to get manganese oxides *via* MnO, Mn_2O_3 etc with maximum $\%MnO_2$ composition. The fusion was carried out in the presence and in the absence of fusion media such as Na_2CO_3, NaOH, $CaCO_3$ and $MgCO_3$.

Fusion with none. In this method, $MnCO_3$ was fused between 200-800 °C for a period of 2-10 h under air circulation. The MnO_2 composition (Table 3.2) in these samples was found to vary between 20-64% depending on the temperature and fusion time. The data revealed that at a given fusion time say 4 h, the $\%$ MnO_2 increased

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gradually with the increase in temperature (20.64% at 200 °C to 64.1% in 5 h 500 °C) and it decreased thereafter due to decomposition of high valent manganese oxides Mn_2O_3 or of higher order. It is also noticed from fusion data that the $MnCO_3$ on heating in aerial conditions for 2 h at temperatures between 450–500 °C, gives the oxide close to the formula that of Mn_2O_3, which on heating further tends to oxidize to give MnO_2 in the range between 3-10%. On the contrary, if it is heated to temperatures lower than 400 °C or higher than 500 °C, $MnCO_3$ gives oxides close to the formula that of Mn_3O_4 with 38-42% manganese in high valent state.

Thermogravimetric analyses (TGA) of these untreated fused samples at 450 °C for 4 h and 6 h, showed two endothermic weight losses. The sample heated to 4 h (Figure3.3(a)) showed more (6 and 11 %) weight loss than (4 and 6%) that heated for 6 h (Figure3.3(b)). This in other words, indicated that carrying fusion for longer times at temperatures between 300 and 450 °C is preferred to short durations to have sample with more MnO_2-content and less inter-layer/tightly bound water. X-ray diffraction (Figure 3.4(a,b)) patterns of these samples revealed the formation of δ-MnO_2[175,176] instead of β-MnO_2. The present study further revealed that the acid treatment (suspending overnight in 6 N HCl) to the fused $MnCO_3$ sample could help in enhancing the MnO_2 composition to 80% with the change in morphological structure from δ-MnO_2 to ε-MnO_2[177,178] .

Fusion with Na_2CO_3. (a) At low weight ratio. This is carried out at low (0.2-1.0) and high (1.3-5.3) weight Na_2CO_3 to $MnCO_3$ ratio. In this method, the $MnCO_3$ ppt was mixed in wet condition with Na_2CO_3 and then fused at the temperatures between 300-500 °C for a period of 2-5 h to give 51-76% MnO_2 after leaching of the unreacted Mn(II) by giving acid treatment. The data in Tables 3.2 and 3.3 showed that the fusion of $MnCO_3$ in the presence of Na_2CO_3 favored 9-12% more MnO_2 formation in 2-5 h fusion. The data has further proved that in the presence of 1:3 – 1:4 (w/w) Na_2CO_3 to $MnCO_3$ ratio, the %MnO_2 increased with the increase in temperature and obtained maximum of 70-73 % in 2-3 h fusion at temperature 500 °C. But, the %MnO_2 decreased with the increase of both Na_2CO_3 weight and fusion temperature.

Thermogravimetric (TGA) data (Figure 3.5) of fused samples with Na_2CO_3 showed two endothermic weight losses due to strongly bound water and/or dehydroxylation and

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the conversion of Mn(IV)O$_x$ (MnO$_2$) to Mn(II,IV)O$_x$ or Mn(III)O$_x$ (Mn$_2$O$_3$) with the loss of oxygen at high temperature. It is surprisingly noted that the weight loss due to strongly bound water and/or dehydroxylation or total weight loss between 160-780 °C decreased (13.97 and 9.42 % weight loss with 1 g; 8.53 and 7.52% with 1.93 g; and 6.65 and 5.63% with 3.87 g NaCO$_3$ as seen in Figure3.5a-c) regularly with increase in Na$_2$CO$_3$ to MnCO$_3$ weight ratio. The X-ray diffraction (Figure 3.6) patterns of the fused MnCO$_3$ sample along with (1, 1.93 and 3.87 g) Na$_2$CO$_3$ showed nearly identical diffraction peaks which are close to those of α-MnO$_2$ sample[173,174,176,179-185].

(b)At high weight ratio. MnCO$_3$ ppt was fused with 5,10, and 15 g (1.30-3.92) Na$_2$CO$_3$, at 450 °C for a period of 2.5 h under air circulation and treated overnight with 10-50 ml of 6 N HCl to get 71-93% pure MnO$_2$. The data in Tables 3.2 – 3.4 showed that the fused MnCO$_3$ in Na$_2$CO$_3$ gave high yields and more (81.5, 91.9, 93.7%) purity of MnO$_2$ than that in low Na$_2$CO$_3$:MnCO$_3$ weight ratio. Thermogravimetric (TGA) data showed two weight loss at the temperature range 160-450 °C and 460-700 °C. The magnitude of first (4-7%) and second (6.5-7%) endothermic jumps are relatively less due to their high purity on account of less tightly bound water/hydroxyl groups. The samples showed nearly identical diffraction peaks (9.37, 12.83, 23.15, 25.35, 36.81, ~42, ~47, 53-58, 6~1, ~66.5 and 78.76° in case of 5 g and 9.21, 12.83, 28.33, 29.58, 37.06, ~42, ~47, 53-58 and 66.41° in case of 10 g; and 8.94, 12.61, 18.27, ~25, 36.73, ~42, ~47-58, 65.94 and ~78° in case of 15 g Na$_2$CO$_3$) which are close to those of α-MnO$_2$ sample[173,174,176,179-185].

Contrastingly, the fused sample with 20 g Na$_2$CO$_3$ was less (71.5% MnO$_2$) pure and exhibited a different peak at 31.76° along with small peaks at 9.32, 12.77, 25.78, 27.40, 31.76, 37.02, 41.27, 45.49, 56.47, 66.25 and 75.31° which are close to the structural pattern of Mn$_2$O$_3$[173-187].

The economics of manganese recovery as α-MnO$_2$ (93.7% pure) particularly from dilute solutions *via* MnCO$_3$ fusion in Na$_2$CO$_3$ medium is also an attractive method. On the basis of the market prices (Table 4.1) as provided by the concerned industry for all the inputs, the cost calculations for the production of one kg of α-MnO$_2$ is calculated and

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depicted in Table 4.3 and it comes to be an attractive price of about Rs. 33.54 after the assumption that the Na_2CO_3 used in the fusion process recovered totally.

Table 4.3. Approximate cost calculations for the preparation of one kg α-MnO_2 by fusion with 3.95 times Na_2CO_3.

Raw material	Quantity required	Rate per kg	Cost in Rs.
Effluent	40 lit (@ 25 g per lit)	---	---
$CaCO_3$	6.40 kgs (160 g per lit)	1.00	4.16
Na_2CO_3	2.40 kgs (@ 60 g per lit)	10.50	16.38
Electricity	2 Units (filtration & fusion)	6.50	13.00
	Preparation cost of 1 kg α-MnO_2		**33.54**

Fusion with $CaCO_3/MgCO_3$. $MnCO_3$ when fused with 2 g $CaCO_3$ at 450 °C for a period of 2.5 h gave 93% pure MnO_2 after acid treatment. However, the yield was relatively lower than that obtained in the fusion with 15 g Na_2CO_3. The X-ray diffraction peaks at ~9.3, ~22, 36.97, 42.24, 57 and 66.89° nearly resembles to the peak patterns of γ-MnO_2 [163c,181,183,188]. On the contrary, $MnCO_3$ when fused with 2 g $MgCO_3$ at 450 °C for a period of 2.5 h gave 85.8% pure MnO_2 after acid treatment. However, the X-ray diffraction pattern exhibited different pattern by showing peaks at 32.65, 36.97, 42.14, 56 and 67° along with a small peak at around 49° which resembles to that of the sample obtained with 20 g Na_2CO_3 (Figure 3.8d), and close to the structural pattern of Mn_2O_3 [173-187].

In addition to the solution of environmental contamination from industrial manganese effluents, the economics of manganese recovery as γ-MnO_2 (93% pure) particularly from dilute solutions *via* $MnCO_3$-fusion in $CaCO_3$ medium is also attractive. On the basis of the market prices (Table 4.1) as provided by the concerned industry for all the inputs, the cost calculations for the production of one kg of γ-MnO_2 is calculated and depicted in Table 4.4 and it comes to be an attractive price of about Rs. 43.00.

Fusion with NaOH. $MnCO_3$ when fused with 0.1-1.0 g of NaOH (0.02 – 0.2 w/w NaOH) at 100-500°C for a period of 2-6 h and acid wash gave 45-73% pure MnO_2. The data in Table 3.5 revealed that the MnO_2 composition in these samples increased gradually from 45 to 73% as the fusion temperature increases from 100-500 °C. Fusion with 0.1 g NaOH at 100 °C for 24 h or 200 °C for 3 h produced the manganese oxide having about 46% MnO_2 which resembles to the 8% oxidized form of Mn_3O_4. The content increased further as the fusion was continued. The data in Table 3.5 revealed that

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i) the 3-5 h fusion with 0.4 and 1.0 g NaOH at 300 and 450 °C could not improve appreciably the %MnO_2 content and ii) the fusion of $MnCO_3$ with 0.1 g NaOH gives manganese oxide with relatively (~7%) less %MnO_2 than that obtained with 1 g Na_2CO_3 at the same temperatures between 400 and 500 °C and time between 2-4 h.

Table 4.4. Approximate cost calculations for the preparation of one kg γ-MnO_2 by fusion with 3.95 times Na_2CO_3.

Raw material	Quantity required	Rate per kg	Cost in Rs.
Effluent	50.761 lit (@ 19.7 g per lit)	---	---
$CaCO_3$	6.40 kgs (160 g per lit)	1.00	4.16
Na_2CO_3	2.40 kgs (@ 60 g per lit)	10.50	16.38
$CaCO_3$ (for fusion)	1.015kgs (@ 20 g per lit)	1.00	1.02
HCl (Con.)	2.80 lit (55 ml per lit)	3.00	8.40
Electricity	2 Units (filtration & fusion)	6.50	13.00
	Preparation cost of 1 kg γ-MnO_2		**42.96**

Thermogravimetric (TGA) data of fused samples at 450 °C for 2, 4 and 6 h with 0.1 g NaOH and for 3 h with 1 g NaOH were studied. All of them exhibited two weight loss (Figure 3.8) at temperature range 150-450 and 460-770 °C. The sample heated with 0.1 g NaOH (Figure3.8(a-c)) showed about 6, 3 and 2.5% weight loss in the temperature range 150-450 °C and 6, 6 and 7% weight loss in the temperature range 460-770 °C in 2, 4, 6 h fusion, respectively. The sample heated with 1 g NaOH (Figure3.8(d)) showed 9.7% weight loss in the first temperature range (150-450 °C) and 4.34% weight loss in the second temperature range (460-770 °C) in 3 h fusion revealing that the strongly bound interlayer water/hydroxyl groups as well as the loss of oxygen in the conversion of Mn(IV)O_x (MnO_2) to Mn(II,IV)O_x or Mn(III)O_x (Mn_2O_3) are not much influenced by the amount of NaOH employed for fusion. All the samples showed nearly identical diffraction peaks (18.31, 31.77, 36.31, 56.41, 62.19 and 66.5° in case of 0.1 g NaOH for 2 h; 12.58, 25.19, 31.72, 36.75, 45.39, 54 and 67, 79° in case of 0.1 g NaOH for 4 h; and 12.5, 23, 31.72, 37.05, 42.24, ~53-57 and 67° in case of 1 g NaOH for 3 h fusion) which are close to the structural pattern of γ-MnO_2[163c,181,183,188].

4.3. Oxidative chemical extraction

Oxidation by chlorine gas. This work was proposed and executed on bench scale on the basis of thermodynamic data for standard Mn(II)-Cl_2 (Eq 3.9, $E°=+0.129$ V) and Mn(II)-HClO (Eq 3.10, $E°=+0.27$ V) cells in weakly acidic/neutral medium. Accordingly,

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the Mn(II)sulfate in the filtrate at pH around 2, was reacted with chlorine for 1 h in the presence of 92.5 g of (40%) lime. After completion of the reaction, the resulting brownish-black precipitate was filtered. The manganese oxide and lime was washed several times with hot water and treated with 130 ml of 30% HCl in 50 ml water and filtered to get 55.5% pure brownish black MnO_2 after drying at 120 °C for 2 h. The sample showed three weight losses in TGA 14% in 50-150 °C, 7% 160-440 °C and 12% in the range 460-770 °C. Further, the sample showed diffraction peaks at 12.5, 23, 31.40, 37.40, 42.5, 56.5 and 66.30° which are close to the peak pattern of γ-MnO_2 [163c,181,183,188].

Oxidation by bromate. This work was proposed and implemented on the basis of standard Mn(II)-BrO_3^- (Eq 3.16, E^o = +0.29 V) cell in strongly acidic medium and the standard Mn(II)-BrO_3^- (Eq 3.17, E^o = +0.22 V) cell in weakly acidic solutions. The former conditions are better than the latter as the separation of by-product as bromine is complete.

In strongly acidic solutions. Accordingly, Mn(II) was reacted with the required/ optimized quantity of $NaBrO_3$ at 80 °C for 15-20 min to get 88% pure MnO_2 and Br_2. The flask was cooled to room temperature and filtered through a sintered G-4 glass crucible. Thermogravimetric (TGA) data of MnO_2 sample showed four weight loss at the temperature range 50-260, 260-350, 350-410 and 410-580 °C. The first endothermic jump with a weight loss of 2.5% could be due to loss of hydrated water, while the second and third jumps with weight loss of 8.2 and 5.5%, respectively could be due to strongly bound interlayer water and/or dehydroxylation as known in the literature[163-165]. The fourth endothermic jump between 410-580 °C amounting to 8% weight loss is attributed to the conversion of Mn(IV)O_x (MnO_2) to Mn(II,IV)O_x or Mn(III)O_x (Mn_2O_3) with the loss of oxygen[163-168]. The sample showed major diffraction peak at 12.63, 17.97, 26, 27.91, 36, 37.51, 38, 39, 42, 46, 47, 49, 55.9, 60.14, 65.42, 66.75 and 72.93° which are close to those of α-MnO_2[173,174,176,179-185].

This method of manganese recovery appears to be advantageous as there are no secondary effluents generated, H_2SO_4 and Br_2 are side products. The most important observation made here is that the MnO_2 obtained has crystal structure close to that of α-MnO_2. In addition to the solution of environmental contamination from industrial

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manganese effluents, the economics of manganese recovery as α-MnO$_2$ (88% pure) is also attractive. On the basis of the market prices (Table 4.1) as provided by the concerned industry for all the inputs, the cost calculations for the production of one kg of 88% pure α-MnO$_2$ is calculated and depicted in Table 4.5 and it comes to be an attractive price of about Rs. 34.48

Table 4.5. Approximate cost calculations for the preparation of one kg α-MnO$_2$ by chemical oxidation with sodium bromate in strongly acidic solutions.

Raw material	Quantity required	Rate per kg	Cost in Rs.
Effluent	48.78 lit (@ 20.5 g per lit)	---	---
NaBrO$_3$ (Regeneration price)*	0.815 kg (@ 16.7 g per lit)	23.46	19.12
Operational losses of NaBrO$_3$ (2% over NaBrO$_3$ cost)	0.0163 kg (@ 0.2 g/100 ml)	145.00	2.36
Electricity	2 Units (heating & filtration)	6.50	13.00
	Preparation cost of 1 kg α-MnO$_2$		**34.48**

*See Annexure I for the regeneration of NaBrO$_3$

Oxidation by permanganate. This work was proposed and implemented on the basis of standard Mn(II)-MnO$_4^-$ (Eq 3.24, E^0 = +0.46 V) cell in moderately strong or weakly acidic solutions. The advantage of this method is that the potential (+0.46 V) of this cell indicates the spontaneous nature of the process while, the product and by-product of MnO$_4^-$ are MnO$_2$ which is insoluble and can easily be separated from the solution. Accordingly, the effluent was reacted with KMnO$_4$ for 24 h and the reaction products were allowed to stand for another 24 h for completion of the reaction to get 80% pure MnO$_2$. The sample showed three weight losses at the temperature range 200-520, 520-570 and 570-650 °C. The first and second endothermic jumps, collectively measures a weight loss of 8.5% could be due to loss of both strongly bound interlayer hydrated water and/or dehydroxylation[163-165]. The endothermic jump between 570-650 °C is attributed to the loss of oxygen during the conversion of Mn(IV)O$_x$ (MnO$_2$) to Mn(II,IV)O$_x$ or Mn(III)O$_x$ (Mn$_2$O$_3$) [163-168]. The sample depicted major diffraction peak at 12.74, 17.97, 28.86, 37.68, 42.04, 49.9, 55.98, 60.28, 65.57 and 66.75° which are close to the structural pattern of α-MnO$_2$ [173,174,176,179-185].

This method of manganese recovery appears to be advantageous as there are no secondary effluents generated. Instead, H$_2$SO$_4$ and extra MnO$_2$ are useful side products generated. The most important observation made here is that the MnO$_2$ obtained has

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crystal structure close to that of α-MnO$_2$. In addition to the solution of environmental contamination from industrial manganese effluents, the economics of manganese recovery as α-MnO$_2$ (80% pure) is also attractive. On the basis of the market prices (Table 4.1) as provided by the concerned industry for all the inputs, the cost calculations for the production of one kg of 88% pure α-MnO$_2$ is calculated and depicted in Table 4.6 and it comes to be an attractive price of about Rs. 40.60.

Table 4.6. Approximate cost calculations for the preparation of one kg α-MnO$_2$ by chemical oxidation with KMnO$_4$ in moderately strongly acidic solutions.

Raw material	Quantity required	Rate per kg	Cost in Rs.
Effluent	28.57 lit (@ 35 g per lit)	---	---
KMnO$_4$	0.742 kg (@ 26 g per lit)	23.46	19.12
Electricity	1 Units (Stirring & filtration)	6.50	6.50
	Preparation cost of 1 kg α-MnO$_2$		25.62

4.4. Oxidative chemical treatment on fused MnCO$_3$

Chlorate treatment. The fused MnCO$_3$ ppt having around 50% MnO$_2$ was made to react with 1.16 – 3.30 g (0.3 – 0.87 w/w ratio) of KClO$_3$ for 2 h at room temperature. The purity of MnO$_2$ samples was found to be enhanced to 72.14%. The sample showed two weight loss at the temperature range 200-470, and 480-650 °C. The first endothermic jump with a weight loss of about 6.5% was due to loss of dehydroxylation as known in the literature,[163-165] while the endothermic jump between 480-650 °C amounting to 4.4% weight loss is attributed to the conversion of Mn(IV)O$_x$ (MnO$_2$) to Mn(II,IV)O$_x$ or Mn(III)O$_x$ (Mn$_2$O$_3$) with the loss of oxygen[163-168]. Further, the sample showed major diffraction peak at 12.34, 18, 28.81, 31.5, 37.28, 42, 49, 56, 60, 62.52, 66.04, 67 which are close to the structural pattern of α-MnO$_2$ [173,174,176,179-185].

HNO$_3$ treatment. The fused MnCO$_3$ ppt having around 50% MnO$_2$ was mixed thoroughly with 50% HNO$_3$ in two/three necked round bottom flask and heated slowly to 220-240 °C over a sand bath for 2-3 h to give 80% pure MnO$_2$. The sample showed three weight losses at the temperature range 200-375, 375-500 and 500-650 °C. The first endothermic jump with a weight loss of about 3.5% and the second jump with a loss of about 2.8% are attributed to the loss of strongly bound interlayer water and/or dehydroxylation,[163-165] while the third endothermic jump amounting to 4.3% weight loss

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is attributed to the conversion of $Mn(IV)O_x$ (MnO_2) to $Mn(II,IV)O_x$ or $Mn(III)O_x$ (Mn_2O_3) with the loss of oxygen[163-168]. The sample showed major diffraction peaks at 18.59, 19.12, 22.5, 29.5, 37.24, 38, 42.72, 57, 65.41, 67 which are close to the structural pattern of the product obtained with Cl_2 gas assigned to be γ-MnO_2[163c,181,183,188].

Ozone treatment. The fused $MnCO_3$ ppt having around 50% MnO_2 was mixed thoroughly in 20 ml solution of 10% (v/v) H_2SO_4 in 30 ml of distilled water. The pH of the resulting mixture was noted to be around 1. Through it, electrically produced ozone gas was purged for 2-6 h, filtered through G-4 crucible and washed with hot water to give 70-74% pure MnO_2 free from acid. The sample showed three weight loss at the temperature range 200-430, 440-490 and 490-610 °C. The first endothermic jump with a weight loss of about 6% and the second with a loss of about 2% could be due to the loss of strongly bound interlayer water and/or dehydroxylation as known in the literature[163-165]. The endothermic jump between 490-610 °C amounting to 3.6% weight loss is attributed to the conversion of $Mn(IV)O_x$ (MnO_2) to $Mn(II,IV)O_x$ or $Mn(III)O_x$ (Mn_2O_3) with the loss of O_2[163-168]. The sample further, showed major diffraction peaks at 22, 28, 32, 36.66, 40.89, 41.83, 57, 60.15, 65.08 and 67° which are close to that of the product obtained with Cl_2/HNO_3 assigned to be γ-MnO_2[163c,181,183,188]. Thus, the present study indicates that the oxidative extraction of manganese by $MnCO_3$ fusion followed by strong oxidizing agents O_3 and HNO_3 in acidic conditions results in the morphological change from δ-MnO_2 give γ-MnO_2, while with ClO_3^- in acidic pH leads to the conversion of δ-MnO_2 to α-MnO_2.

4.5. Oxidative extraction by electro winning process

The present work was planed on the basis of thermodynamic data[173]. Accordingly, $Mn(II)$ was oxidized at pH 1 and in as such solution by applying 1 A against Pb anode and SS cathode plates for 2.36 h at a potential drop of 5-7 V. The electrochemically produced MnO_2 (about 0.26 g at pH 1 and 1.24 g in as such solution) was negligible against the expected yield (about 3.83 g) value. The poor yields of MnO_2 are accounted for the passivity of MnO_2 deposition over the anode surface.

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