

Chapter 2

Experimental

2.1. Reagents

Laboratory reagent (LR) grade chemicals such as sodium hydroxide (98% NaOH), silver nitrate (AgNO_3) from Qualigens Fine Chemicals, India, anhydrous sodium carbonate (99.5% Na_2CO_3), nitric acid (69-72% HNO_3), sulphuric acid (98.07% H_2SO_4), analytical reagent (AR) grade chemicals, sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) from S.D. Fine-chem Limited, India, potassium permanganate (KMnO_4) and precipitated calcium carbonate (CaCO_3) from Ranbaxy Fine Chemicals Limited, India, were purchased and used.

A highly pure potassium iodate (KIO_3) from Qualigens Fine Chemicals Limited, potassium iodide (KI) from Ranbaxy Fine Chemicals Limited and starch powder from S.D. Fine Chemicals Limited all from India were obtained and employed as received in the present study. Highly pure cylindrical Cl_2 gas obtained from Alchemies Gasses & Chemicals Pvt. Ltd., India and AR grade sodium oxalate from Ranbaxy Fine Chemicals Limited were used in these studies.

All glassware were cleaned with detergent solution, rinsed with tap water, soaked in 2% (v/v) HNO_3 , followed by rinsing with water and drying in the oven at 120 °C. Doubly distilled water and RO (Reverse Osmosis) treated deionized water were employed to prepare all experimental solutions required in these studies.

2.2. Solutions preparation

A 10% (v/v) H_2SO_4 solution was prepared by diluting 10 ml of conc. H_2SO_4 to 100 ml with double distilled water, and used in the present studies.

2.2.1. Standard potassium iodate. Standard 0.01 M KIO_3 (Mol. Wt. 214) solution was prepared by dissolving 0.214 g of an oven dried KIO_3 at 100 °C in 100 ml double distilled water.

2.2.2. *Sodium thiosulphate.* A fresh solution of 0.01 M sodium thiosulphate (Hypo, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, Mol. Wt 248.19) solution was prepared by dissolving 1.240 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 500 ml double distilled water and estimated by iodometric method^{161a}.

2.2.3. *Potassium permanganate.* A quantity of 0.7902 g of AR grade potassium permanganate (KMnO_4) was weighed in a watch glass and dissolved in double distilled water and diluted to 250 ml in a volumetric flask to give 0.1 N KMnO_4 . It was further standardized by iodometric method^{161b} as given in the following section.

2.2.4. *Ferrous sulfate.* AR grade ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was oven dried at 120 °C for 2 h and allowed it to cool in a covered vessel in desiccator. 6.95 g of this preheated and cooled $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was weighed into a 250 ml volumetric flask and 200 ml of double distilled water was added to it along with 12.5 ml of concentrated sulphuric acid. The contents were cooled to 30 °C under constant stirring till all the FeSO_4 was dissolved and diluted to 250 ml in a standard flask to give 0.1 N FeSO_4 solution. The solution was further standardized for Fe(II) by permanganometry^{161c} as discussed in the following section.

2.2.5. *Silver nitrate.* A quantity of 4.246 g of AR grade silver nitrate (AgNO_3) was weighed, dissolved in double distilled water and diluted to 250 ml in a volumetric flask to give 0.1 M AgNO_3 . It was further standardized with standard sodium chloride solution^{161d} as given in the following section.

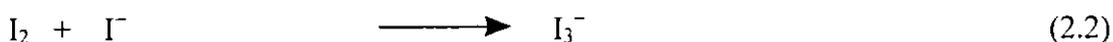
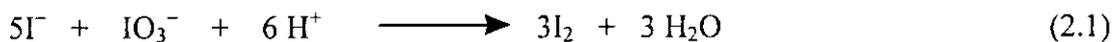
2.2.6. *Sodium carbonate.* AR grade sodium carbonate (Na_2CO_3) was oven dried at 120 °C and 5.3 g of the anhydrous sodium carbonate was dissolved in 250 ml distilled water to produce 0.1 N solution.

2.2.7. *Potassium chromate indicator.* 4.2 g potassium chromate (K_2CrO_4) and 0.7 g potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were mixed and dissolved in water and made up to 100 ml in volumetric flask to serve as potassium chromate indicator^{162 a}.

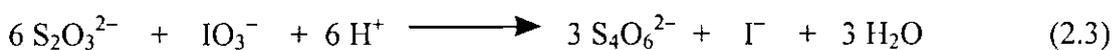
2.3. Standardization

2.3.1. *Sodium thiosulfate solution*^{161e}. To 5 ml of the standard 0.01 M KIO_3 , 10 ml of 10% KI solution and 5 drops of 2 N H_2SO_4 were added. Subsequently, a yellow color

solution was produced due to the formation of I₂ and KI₃ (Eqs 2.1 and 2.2) in the solution. The quantity of I₂ was estimated by titrating the solution against 0.01 M Na₂S₂O₃ using 1 or 2 drops 2% soluble starch solution. Starch was added at the stage when the color of the solution turned to a pale yellow, which in turn changed to blue. The titration was continued until the blue color disappears.



The concentration of sodium thiosulfate (M₁) was determined employing the overall redox reaction between thiosulfate and iodate as given in (Eq. 2.3) and the empirical equation Eq. 2.4.



$$[\text{Na}_2\text{S}_2\text{O}_3] = M_1 = \frac{V_2 M_2}{n_2} \times \frac{n_1}{V_1} \quad (2.4)$$

where V₁ = volume of Na₂S₂O₃ consumed, M₁ = molarity of Na₂S₂O₃; n₁ = 6; V₂ = volume of KIO₃ (5 ml) taken; n₂ = 1.

2.3 2. *Silver nitrate solution*^{161d}. To 25 ml of standard 0.1 M sodium chloride solution taken in a 250 ml conical flask resting on a white tile, 1 ml of the potassium chromate indicator was added. The solution was then titrated by slowly adding silver nitrate solution from a burette. The contents in the flask were constantly swirled until a red color was formed by the addition of each drop begins to disappear more slowly indicating that most of the chloride has been precipitated. The drop wise addition of silver nitrate was continued until a faint but distinct change in color occurred. The faint reddish brown color should persist after brisk shaking. (Note: If the end point is overstepped (production of a deep reddish brown color), more of the chloride solution was added and titrated again). The blank (indicator) reading was determined by adding 1 ml of the indicator solution to a volume (40 ml) of water equal to the final volume in the titration, and then 0.01 M silver nitrate was added until the color of the blank matches the color of the titrated solution. The indicator blank correction, which should not amount to more than 0.03 0.10 ml of silver nitrate, was deducted from the volume of silver nitrate used in the

titration. The above titration was repeated twice with 25 ml of sodium chloride solution. The concentration of silver nitrate (M_3) was then determined by employing the Eqs 2.5–2.7.



$$[\text{AgNO}_3] = M_3 = \frac{V_4 M_4}{V_3} \quad (2.7)$$

where V_3 is the volume of AgNO_3 consumed, M_4 is the molarity of NaCl ; V_4 is the volume of NaCl (25 ml) taken.

2.3.3. *Permanganate solution*^{161f}. AR grade sodium oxalate was dried at 120 °C for 2 h and allowed to cool in a desiccator. 0.3 g of the dry sodium oxalate was weighed accurately from a weighing bottle into a 600 ml beaker. To it, 240 ml of recently prepared distilled water and 12.5 ml of concentrated or 250 ml of 2 N sulphuric acid were added. The mixture was cooled to 30 °C and stirred until the oxalate was dissolved completely. 90% of the required quantity of permanganate solution from a burette was then added at a rate of 35 ml per minute while stirring slowly. The solution was once again heated to 60°C with the use of a thermometer as stirring rod, and continued the titration by adding permanganate solution until a faint pink colour persisted for 30 seconds. The last 1.0 ml was added drop wise, with particular care to allow each drop to become decolorized before the next was introduced. The above experiment was repeated with two other similar quantities of sodium oxalate. The normal (N) concentration of potassium permanganate solution was then calculated with the help of the following equations, Eqs 2.8 – 2.10.



$$[\text{KMnO}_4] = N = \frac{W_{\text{Ox}}}{67 \times V_5} \quad (2.10)$$

where V_5 = volume of KMnO_4 consumed, W_{Ox} = weight of sodium oxalate taken (0.3 g); 67 is the equivalent weight of sodium oxalate.

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2.4. Effluent characterization

For experimental convenience, 10 ml of original manganese effluent (ME) was diluted to 100 ml in a volumetric flask with distilled water to give a ten-time diluted solution labeled as ME₁₀. 10 ml of ME₁₀ effluent solution was further diluted to 100 ml to give a 100 time diluted effluent labeled as ME₁₀₀. The diluted effluents ME₁₀ and ME₁₀₀ were used in the original effluent characterization.

2.4.1. *Sulfate estimation*^{162 b}. To 10 ml of 100-time diluted effluent, ME₁₀₀ taken in a 400 ml beaker having a provision of stirring rod and clock glass cover, 0.6 ml of concentrated hydrochloric acid was added and then diluted to 250 ml with distilled water. The mixture was then heated to boil and to it excess (12 ml) of warm 5% BaCl₂ solution was added drop-wise from a pipette under stirring throughout the addition. The precipitate of BaSO₄ (Eq 2.11) was allowed to settle for a minute and then the supernatant liquid was tested for complete precipitation by adding few drops of BaCl₂ solution. Barium sulphate precipitate was filtered when no more precipitate was obtained through G-4 sintered glass crucible, washed with hot distilled water and dried at 120 °C in a air oven for 2 h. The BaSO₄ precipitate was cooled in a desiccator and weighed and determined the % (w/v) of sulfate present in the original effluent using Eq 2.11.



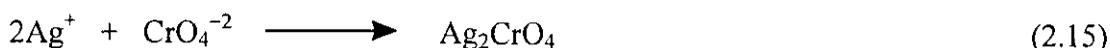
2.4.2. *Acid estimation*. To 10 ml of ME₁₀₀ solution in a 250 ml titration flask, 5 drops of methyl orange indicator was added and titrated against standard 0.1 N Na₂CO₃ solution under constant stirring till the solution turns to pink from the yellow. The same procedure was repeated with the phenolphthalein indicator wherein the phenolphthalein changes colorless to pink at the end point. The acidity of the solution in the original effluent was determined by the empirical formula shown in Eqs 2.12 and 2.13.



$$M_7 = \frac{V_8 M_8}{n_8} \times \frac{n_7}{V_7} \times 100 \quad (2.13)$$

Where V_7 is the volume of Na_2CO_3 consumed, M_7 is the molarity of Na_2CO_3 , n_7 is 1, V_8 is the volume of ME_{100} (10 ml) taken and n_8 is 2.

2.4.3. *Chloride estimation*^{161a}. To 25 ml of ME_{100} (100-time diluted effluent) solution in a 250 ml conical flask resting on a white tile, 1 ml of the potassium chromate indicator solution was added. The mixture was titrated against silver nitrate solution by adding drop wise from a burette under constant stirring till the red colour formed by the addition of each drop begins to disappear more slowly with an indication that most of the chloride has been precipitated. The drop wise addition of silver nitrate was continued until a faint but distinct change in color occurred. This faint reddish brown color should persist after brisk shaking. (Note: when a deep reddish brown color produced due to overstepping of end point, some more known amount of chloride solution was added and continued the titration again). The above experiment was repeated with the 1 ml of indicator blank solution and water to make the final volume in the titration flask wherein 0.01 M silver nitrate was added drop wise until the color of the blank matches with the color of the titrated solution with 25 ml of NaCl (ME_{100}) solution. The indicator blank correction, which should not amount to more than 0.03-0.10 ml of silver nitrate, was deducted from the volume of silver nitrate solution used in the titration of 25 ml of NaCl (ME_{100}) solution. The titration with 25 ml portions of sodium chloride solution was repeated at least twice which should agree within 0.1 ml. The concentration of chloride (M_9) in the original effluent was determined by employing the equations Eqs 2.14 – 2.16.



$$[\text{Cl}^-] = M_9 = \frac{V_{10} M_{10}}{V_9} \times 100 \quad (2.16)$$

where V_9 is the volume of effluent ME_{100} taken for analysis (25 ml); M_{10} is the molarity of AgNO_3 and V_{10} is the volume of AgNO_3 (burette reading) consumed.

2.5. Manganese extraction as MnCO_3

Procedure. To 100 ml effluent in a 500 ml beaker, 16 g of CaCO_3 was added in duration of 10 min with constant stirring. The solution was constantly stirred with the

help of a glass rod until the formation of carbon dioxide was ceased. The resulting semi-solid paste was filtered through sintered G-4 glass crucible. The white CaSO_4 ppt was thoroughly washed thrice each time with 25 ml of hot water. To the filtrate at pH 2, 6 g of Na_2CO_3 was added to precipitate MnCO_3 and allowed the ppt to settle. The completion of the reaction was ascertained by checking pH of the clear supernatant liquid to be between 9 or no further ppt formation by adding some more sodium carbonate to the clear supernatant liquid. The clear supernatant liquid was then filtered through sintered G-4 glass crucible. The ppt was washed with minimum 25 ml of hot water followed by drying at 120°C for 2 h to weigh 3.9 g. The by-product CaSO_4 was dried at 120°C and weighed to be 22 g.

2.6. Oxidative extraction by fusion from MnCO_3

2.6.1. *Fusion with none.* The MnCO_3 ppt obtained from 100 ml of the original effluent (ME) by the above procedure outlined under the section 2.5 was dried at 120°C for 2 h to weigh 3.9 g. It was transferred into a reddish clay pan and then fused in muffle furnace at the temperature range $200\text{-}800^\circ\text{C}$ for a period of 2-10 h under air circulation. The residue weighing 3.4 g was cooled to room temperature and studied further with or without treating overnight with HCl solution followed by filtration, washing with hot water and drying at 120°C . Brownish black powder having (20-81% MnO_2) was characterized by thermogravimetric analysis (TGA) and powder X-ray diffraction (XRD), while its % of MnO_2 purity was verified by volumetric method^{161c} using $\text{FeSO}_4\text{-KMnO}_4$ redox titration.

2.6.2. *Fusion with Na_2CO_3 .* The MnCO_3 ppt obtained from 100 ml of the original effluent (ME) by the above procedure outlined under the section 2.5 was dried at 120°C for 2 h to weigh 3.9 g and mixed thoroughly with 1-20 g (0.2 – 5.1 w/w Na_2CO_3 to MnCO_3 ratio) of Na_2CO_3 along with 5 ml of deionized water, dried, powdered and then fused in a reddish clay pan in a muffle furnace between $300\text{-}500^\circ\text{C}$ for a period of 2-5 h under air circulation. The residue was cooled to room temperature and washed with 50 ml hot water or alternatively treated overnight with 20-65 ml of 6 N HCl, filtered, washed with hot water and dried at 120°C . The filtrate was stored for reuse. The residue was treated with 3.0 ml of 6 N HCl (pH 1), filtered, washed with hot water and dried at 120°C . The brownish black powder having 51-93% MnO_2 was cooled, weighed between

1.83-3.06 g and characterized by thermogravimetric analysis (TGA) and powder X-ray diffraction (XRD), while its % of MnO_2 purity was verified by volumetric method^{161c} using FeSO_4 - KMnO_4 redox titration.

2.6.3. *Fusion with $\text{CaCO}_3/\text{MgCO}_3$.* The MnCO_3 ppt obtained from 100 ml of the original effluent (ME) by the above procedure outlined under the section 2.5 was dried at 120 °C for 2 h to weigh 3.9 g and mixed thoroughly with 2 g of $\text{CaCO}_3/\text{MgCO}_3$ along with 5 ml of deionized water, dried, powdered and then fused in a reddish clay pan in a muffle furnace at 450 °C for a period of 2½ h under air circulation. The residue was cooled, treated overnight with 12 ml of 6 N HCl, filtered, washed with hot water and dried at 120 °C. The brownish black powder was cooled, weighed and characterized by thermogravimetric analysis (TGA), powder X-ray diffraction (XRD) and IR, while its % of MnO_2 purity was verified by volumetric method^{161c} using FeSO_4 - KMnO_4 redox titration.

2.6.4. *Fusion with NaOH.* The MnCO_3 ppt obtained from 100 ml of the original effluent (ME) by the above procedure outlined under the section 2.5 was dried at 120 °C for 2 h to weigh 3.9 g and mixed thoroughly with 0.1-1.0 g of NaOH (0.02 – 0.2 w/w NaOH to MnCO_3 ratio) along with 5 ml of deionized water, dried, powdered and then fused in a reddish clay pan in a muffle furnace between 100-500 °C for a period of 2-6 h under air circulation. The residue was cooled to room temperature and washed with 50 ml hot water. The filtrate was stored for reuse. The residue was treated with 4 ml of 6 N HCl (pH 1), filtered, washed with hot water and dried at 120 °C. The brownish black MnO_2 was cooled and characterized by thermogravimetric analysis (TGA) and powder X-ray diffraction (XRD), while its % of MnO_2 purity was verified by volumetric method^{161c} using FeSO_4 - KMnO_4 redox titration.

2.7. Oxidative chemical extraction

2.7.1. *Oxidation by chlorine gas.* 500 ml of brown colored manganese effluent was transferred into a 1,000 ml beaker and to it 80 g CaCO_3 and 50 g CaCl_2 (fused) was added sequentially under stirring for 30 min and then filtered through G-4 sintered glass crucible. The CaSO_4 precipitate was washed with hot water to turn white. To the filtrate

whose pH was measured to be 2, 92.5 g 40% lime was added and the whole mixture was then transferred into two-necked round bottom flask for purging Cl_2 gas and an outlet to take out the unreacted chlorine gas through a long glass column containing NaOH solution. Chlorine was passed through the solution for 1 h with the flow rate of 0.5 g/min. After completion of the reaction, the resulting brownish-black precipitate was filtered through G-4 sintered glass crucible and the precipitate of manganese oxide and lime was washed several times with hot water. The ppt was treated with 130 ml of 30% HCl in 50 ml water and again filtered through G-4 sintered glass crucible. The brownish black ppt was the washed thoroughly with hot water, dried at 120 °C for 2 h and characterized.

2.7.2. *Oxidation by bromate. (a) Optimization study.* 10 ml of manganese effluent (ME) was transferred into a 100 ml beaker. To it, variable amounts, starting from 0.3-3 ml, of 10% NaBrO_3 solution was added, in different sets and heated for 20 min to maintain 80 °C internal temperature on a hot water bath. After completion of the reaction, the solution was cooled to room temperature and filtered over a Qualigens filter paper (640de) and washed the ppt with 40 ml hot water for 2 times. The filter paper is transferred into 250 ml conical flask and estimated the quantity of MnO_2 obtained by the oxidation of manganese(II) by sodium bromate by volumetric method^{161c} using FeSO_4 - KMnO_4 redox titration. The quantity of MnO_2 obtained with 10 ml effluent in mg was plotted against the weight of sodium bromate reacted and used to optimize weight required to extract the manganese completely from its effluent.

(b) *From effluent as such.* To 100 ml of ME effluent taken into three necked 250 ml round bottom flask, 1.67 g (the optimized quantity determined by the procedure given below) of NaBrO_3 was dissolved and heated to 80 °C for 20 h on a water bath. The liberated brownish bromine vapors collected above the solution in the flask was evacuated by purging N_2 gas and collected them in a tower containing 7.5 ml in 6.67% w/w NaOH solution. The heating of the reaction mixture was stopped when the liberation of bromine vapors are ceased while the purging was continued till the solution became colorless. The flask was cooled to room temperature and filtered through a sintered G-4 glass crucible. The black MnO_2 ppt was washed with hot water and dried at 120 °C, weighed and characterized.

(c) At pH 2. To 100 ml of ME effluent taken into a 500 ml beaker, 16 g of CaCO_3 was added in the duration of 10 min with constant stirring. The solution was constantly stirred with the help of a glass rod until the formation of carbon dioxide was ceased. The resulting semi-solid paste was filtered through sintered G-4 glass crucible. The white CaSO_4 ppt was thoroughly washed thrice with 25 ml of hot water each time. To the filtrate at pH 2, 1.3 g of NaBrO_3 was dissolved and heated to 80°C for 20 h on a water bath. The liberated vapors containing partially hydrobromic acid collected above the solution in the flask was evacuated by purging N_2 gas and collected them in a tower containing water/ NaOH solution. The flask was cooled to room temperature and filtered through a sintered G-4 glass crucible. The brownish black MnO_2 ppt was washed with hot water and dried at 120°C to get 2.05 g of MnO_2 . The purity of MnO_2 (88%) was checked by volumetric method^{161c} using FeSO_4 - KMnO_4 redox titration and thermogravimetric analysis (TGA) while the structural pattern by powder X-ray diffraction (XRD).

2.7.3. *Oxidation by permanganate.* To 100 ml of ME effluent into a 500 ml beaker, 2.60 g of KMnO_4 was added over a period of 1 h with constant stirring. Stirring was continued for 24 h and the reaction products were allowed to stand for another 24 h for completion of the reaction. The solution was filtered, and the MnO_2 ppt was washed thoroughly with water and dried at 120°C , weighed and characterized to get 3.7 g of MnO_2 powder. The purity of MnO_2 (80%) was checked by volumetric method^{161c} using FeSO_4 - KMnO_4 redox titration and thermogravimetric analysis (TGA) while the structural pattern by powder X-ray diffraction (XRD). The filtrate (4.65 N H_2SO_4) was collected for reuse in some other reactions or neutralized with lime to get white gypsum.

2.8. Oxidative chemical treatment on fused MnCO_3

2.8.1. *Chlorate treatment (a.)* The MnCO_3 ppt obtained from 100 ml of the original effluent (ME) by the above procedure outlined under the section 2.5. was dried at 120°C for 2 h to weigh 3.9 g. It was transferred into a reddish clay pan and then fused in muffle furnace at 400°C for a period of 2 h under air circulation. Brownish black ppt having around 50% MnO_2 weighing between 3 g was cooled and mixed thoroughly with 1.16 – 3.30 g (0.3 – 0.87 w/w ratio) of KClO_3 . To it, 20 ml of 10% (v/v) H_2SO_4 and 30 ml of

distilled water were added and stirred for 2 h at room temperature. The pH of the resulting mixture was noted to be 1. The MnO_2 ppt was filtered through the sintered G-4 glass crucible, dried to weigh 2.30 g at 120 °C. The purity of MnO_2 was checked (72%) by volumetric method^{161c} using $\text{FeSO}_4\text{-KMnO}_4$ redox titration and thermogravimetric analysis (TGA) while the structural pattern by powder X-ray diffraction (XRD).

(b) The MnCO_3 ppt obtained from 100 ml of the original effluent (ME) by the above procedure outlined under the section 2.5. was dried at 120 °C for 2 h to weigh 3 g. It was transferred into a reddish clay pan and then fused in muffle furnace at 400 °C for a period of 2 h under air circulation. Brownish black ppt having around 50% MnO_2 weighing between 2.4 g was cooled and mixed thoroughly with 0.7–2 g (0.3 – 0.87 w/w ratio) of KClO_3 , 13 ml of 10% (v/v) H_2SO_4 and 30 ml of distilled water and allowed to react at room temperature under stirring for 2 h. The pH of the resulting mixture was noted to be 1. The MnO_2 ppt was filtered through the sintered G-4 glass crucible, dried to weigh 1-2.14 g at 120 °C. The purity of MnO_2 was checked (78%) by volumetric method^{161c} using $\text{FeSO}_4\text{-KMnO}_4$ redox titration and thermogravimetric analysis (TGA) while the structural pattern by powder X-ray diffraction (XRD).

2.8.2. *HNO₃ treatment.* The MnCO_3 ppt obtained from 100 ml of the original effluent (ME) by the above procedure outlined under the section 2.5. was dried at 120 °C for 2 h to weigh 3 g. It was transferred into a reddish clay pan and then fused in muffle furnace at 400 °C for a period of 2 h under air circulation. Brownish black ppt having around 50% MnO_2 weighing between 2.4 g was cooled and mixed thoroughly with 4 ml of 50% HNO_3 in three necked round bottom flask. The paste was heated slowly to 240 °C over a sand bath for 3 h. Nitrogen or air was steadily passed throughout the reaction through the flask to flush out the NO_2 gas which was produced during the decomposition of $\text{Mn}(\text{NO}_3)_2$ to give MnO_2 . The charred black product was powdered and transferred into a 250 ml beaker along with 50 ml hot water. The black precipitate was filtered through G-4 crucible and washed for 3 times with hot water and dried to weigh 1.45 g at 120 °C. The purity of MnO_2 was checked (85%) by volumetric method^{161c} using $\text{FeSO}_4\text{-KMnO}_4$ redox titration.

2.8.3. *Ozone treatment.* (a) The MnCO_3 ppt obtained from 100 ml of the original effluent (ME) by the above procedure outlined under the section 2.5 was dried at 120°C for 2 h to weigh 3 g. It was transferred into a reddish clay pan and then fused in muffle furnace at 400°C for a period of 2 h under air circulation. Brownish black ppt having around 50% MnO_2 weighing between 2.4 g was mixed thoroughly in 13 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 4 h, filtered through G-4 crucible and washed with hot water to free from acid. The ppt was dried to weigh 1.7 g at 120°C . The purity of MnO_2 was checked (80%) by volumetric method^{161c} using FeSO_4 - KMnO_4 redox titration.

(b) The MnCO_3 ppt obtained from 100 ml of the original effluent (ME) by the above procedure outlined under the section 2.5 was dried at 120°C for 2 h to weigh 3.9 g. It was transferred into a reddish clay pan and then fused in muffle furnace at 400°C for a period of 2 h under air circulation. Brownish black ppt having around 50% MnO_2 weighing between 3 g 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 free from acid. The ppt was dried to weigh 2.2 g at 120°C . The purity of MnO_2 was checked (71%) by volumetric method^{161c} using FeSO_4 - KMnO_4 redox titration.

2.9. Oxidative extraction by electro winning process

2.9.1. *At pH 1.* To 100 ml of effluent taken into a 500 ml beaker, 16 g of CaCO_3 was added in duration of 10 min with constant stirring with the help of a glass rod until carbon dioxide formation was ceased. The resulting semi-solid paste was filtered through sintered G-4 glass crucible. The white CaSO_4 ppt was thoroughly washed thrice with 25 ml of hot water each time. The filtrate was transferred into a 250 ml glass beaker and electrolyzed by applying 1 A current against Pb anode and SS cathode plates of size each 3 cm wide and 7 cm long for 2.36 h at a potential drop of 7 V using a DC galvanostatic power supply. The brown color MnO_2 ppt settled at the bottom and the scratched MnO_2 deposited on the anode was collected, filtered, washed with 25 ml hot water thrice

through sintered G-4 glass crucible. The MnO_2 ppt was dried at 120°C for 2 h to weigh 0.26 g. The purity of MnO_2 was checked by volumetric method^{161c} using $\text{FeSO}_4\text{-KMnO}_4$ redox titration

2.9.2. *From effluent as such.* 100 ml of ME was taken in a 500 ml glass beaker and electrolyzed for 2.36 h by applying 1 A current against 3 cm wide and 7 cm long Pb-plate anode and 3 cm wide and 7 cm long SS-plate cathode at a potential drop of 5 V using a DC galvanostatic power supply. The brown color MnO_2 ppt settled at the bottom and the scratched MnO_2 deposited on the anode were collected, filtered, washed with 25 ml hot water thrice through sintered G-4 glass crucible. The MnO_2 ppt was dried at 120°C for 2 h to weigh 1.24 g. The purity of MnO_2 was checked by volumetric method^{161c} using $\text{FeSO}_4\text{-KMnO}_4$ redox titration.

2.10. Product characterization

Determination of MnO_2 ^{161c}. (a) *Optimization studies.* 10 ml of manganese effluent (ME) was transferred into a 100 ml beaker. To it, variable amounts, starting from 0.3-3 ml, of 10% NaBrO_3 solution was added, in different sets and heated for 20 min to maintain 80°C internal temperature on a hot water bath. After completion of the reaction, the solution was cooled to room temperature and filtered over a Qualigens filter paper (640de) and washed the ppt with 40 ml hot water for 2 times. The filter paper is transferred into 250 ml conical flask. To it, 50 ml of standard 0.1 N FeSO_4 and 50 ml of 4 N sulphuric acid were added. The mixture was gently boiled until no black particles remain while placing a short funnel over the flask place to minimize the loss of water. The solution was then cooled and titrated the excess of ferrous sulfate present in the flask with standard 0.1 N potassium permanganate solution until the light pink color appeared and the burette reading was recorded as Y. The experiment was repeated without the MnO_2 sample produced from the effluent and the burette reading was recorded as X. The quantity of MnO_2 produced by the oxidation of manganese(II) present in the effluent by sodium bromate added externally was calculated in grams from the difference of burette readings (X-Y) and the known data using the following equations Eqs .2.17-2.19.





$$\text{MnO}_2 \text{ (g)} = \frac{(X - Y) N_{\text{KMnO}_4}}{N_{\text{FeSO}_4}} \times \frac{N_{\text{FeSO}_4}}{2} \times \frac{1}{V_{\text{ME}}} \times \frac{87}{100} \quad (2.19)$$

where X and Y are the burette readings of the titrations of blank and with MnO₂ sample obtained from the effluent, N_{KMnO₄} = Normality of KMnO₄ = 0.096086 N, N_{FeSO₄} = Normality of FeSO₄ = 0.1 N, molecules of Fe²⁺ interacting with each MnO₂ = 2 (Eq 2.18), molecular weight of MnO₂ = 87, V_{ME} = volume of effluent taken (10 ml).

(b) %MnO₂ in extracted samples. 0.2 g of the finally powered MnO₂ product extracted from the original effluent was weighed accurately into a conical flask. To it, 50 ml of standard 0.1 N FeSO₄ and 50 ml of 4 N sulphuric acid were added. The mixture was gently boiled until no black particles remain while placing a short funnel over the flask place to minimize the loss of water. The solution was then cooled and titrated the excess of ferrous sulfate present in the flask with standard 0.1 N potassium permanganate solution until the light pink color appeared and the burette reading was recorded as Y. The experiment was repeated without the MnO₂ sample and the burette readings were recorded as X. The content of MnO₂ in the extracted sample was calculated in percentage from the difference of burette readings (X-Y) and the known data with the help of equations Eqs 2.17, 2.18 and 2.20.

$$\% \text{MnO}_2 = \frac{(X - Y) N_{\text{KMnO}_4}}{N_{\text{FeSO}_4}} \times \frac{N_{\text{FeSO}_4}}{2} \times \frac{87}{1000} \times \frac{100}{W_s} \quad (2.20)$$

since 1 ml of 0.1 N KMnO₄ = 1 ml 0.1 N FeSO₄ = 0.004346 g MnO₂

2.11. Instrumentation

2.11.1. *Thermogravimetric analyses.* All the samples of MnO₂ were analyzed by thermogravimetric analyses by using METTLER TOLEDO models TGA/SDTA85/C.

2.10.2. *Powder X-ray spectroscopy.* The X-ray diffraction scans were carried out on a ScintagXDS2000 or Siemens diffract meter using Cu K_α radiation and a scanning rate of 0.05° (2θ) per second. The samples were prepared by packing powders of MnO₂ into

aluminum holders covered by a glass slide, producing a dense agglomerate of powder with a macroscopically flat surface suitable for X-ray diffraction studies. All the samples of MnO₂ were analyzed by PHILIPS Powder X-ray diffraction by using X'parts MPD.

2.11.3. *Galvanostat.* A regulated AC to DC power supply of Aplab make, Model L 1288SR having a potential range from 0–128 V and a current range from 0-8 A was used to recover the manganese as MnO₂ from its effluent ME.