Degradation of Dye in Wastewater by Synthesized Manganese (III) Oxide Nanoparticles

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Abstract

Manganese sulphate from Popa manganese ore (Pyrolusite) sample was prepared by hydrometallurgical method. 43.81% yield percent of $MnSO_4.H_2O$ was found. XRD data showed that obtained $MnSO_4.H_2O$ was well matched with standard JCPDS 35-0751 of $MnSO_4.H_2O$. Manganese (III) oxide nanoparticles was synthesized from manganese sulphate by chemical co-precipitation method. To obtain the manganese (III) oxide nanoparticles, the metal carbonate precursor was heated at 200^{o} to 700° C. The XRD diffractograms of prepared manganese (III) oxide were well matched with JCPDS-41-1442 of Mn_2O_3 and revealed the cubic structure. The prepared manganese (III) oxide sample after calcination at 500 °C was confirmed by FE-SEM micrograph to have the smallest particle size and the most porous nature of surface. According to EDXRF data, relative abundance 81.7% of manganese oxide and 11.4% of iron oxide were found in prepared manganese (III) oxide powder at calcination temperature 500° C. By using Debye Scherrer's equation, the average crystallite size was found to be 35.09 nm. Catalytic degradation properties of prepared manganese (III) oxide nanoparticles was applied by using wastewater sample, it was collected from textile workshop in Inn Lay, Southern Shan State. The applications were done in two successive processes. The percent degradation of green colour of textile wastewater sample was found to be 59%, in 1st cycle for 4 hours contact time. After 2nd cycle, percent degradation was found to be 71% for 30 minutes contact time. Therefore, this manganese (III) oxide nanoparticles can be used for the catalytic degradation of waste dye water for environmental management.

Keywords: Pyrolusite, Manganese (III) oxide nanoparticles, Scherrer's equation, decolorization, methylene blue, congo red

Introduction

Pyrolusite is manganese dioxide, MnO_2, Manganese 63.2 percent, oxygen 36.8 percent (Read, 1976). In Myanmar, manganese ores are occurred in Popa, Kyaukpadaung, and Tagaung Township (Mandalay Region) and Pawe Island Bokpyin Township, Tanintharyi Region.

The hydrometallurgical processing of lower grade material avoids high temperature, reduction roasting that is conventionally used in processing high grade material to render the manganese to be acid leachable using sulphuric acid (H_2SO_4) (Norman *et al.*, 2010). The importance of the prior work in the development of manganese extractive metallurgy was the discovery that four valence manganese is readily leachable with sulphurous acid, which is a reducing acid formed by dissolving sulphur dioxide (SO_2) in and as such vastly improves the potential for economic recovery of Mn from lower grade resources.

The important reactions occurring when Artillery Peak manganese resources are leached with aqueous SO_2 are shown in the following equation:

$$MnO_2 + SO_2 \rightarrow MnSO_4 \qquad \text{---} \ (1)$$

Nanotechnology

In scientific terms nano has been used to identify length scales that are one billionth of a unit. This is typically a meter and so it often refer to things that are nanometers in size. In

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terms of nanotechnology, it has been defined as anything that has a unique property or function resulting from the size of the artifact being in the nano region and that the size region is between 0.1 and 100 nm (Barron, 2008).

Nanoparticles

The nanoparticles have a large surface area compared with total volume. The surface area to volume ratio is interesting chemical reactions typically occur on surfaces, so nanoparticles that have a high surface to energy ratio can be used in many interesting ways, such as in catalysis. The fabrication of nanomaterials with strict control over size, shape and crystalline structure has inspired the application of nanochemistry to numerous field including catalysis, medicine and electronics.

The most widespread route to fabrication of metal oxide nanoparticles involves the “bottom-up” approach involving the precipitation from aqueous solution from metal salts. Hydroxide, oxyhydroxide or hydrated **o**xide solid phases obtained via precipitation are made of particles whose average size may range from a few nanometers to a few microns. Particle morphology may vary depending on synthesis condition. Moreover, aging in aqueous solution may bring about significant dimensional, morphological and structural changes.

Manganese oxides are among these nanometric materials with a wide variety of application. These oxides have been used in electrode manufacturing and selective catalytic oxidation applications such as nitrogen and carbon oxide elimination in exhaust gas, as well as in the preparation of magnetic materials (David *et al.,* 2006). Manganese oxides are well known by their catalytic properties in different selective oxidation processes such as H_2O_2 decomposition. Therefore, in the study this research was selected as a reaction model to study decolourization effect.

Catalytic Degradation of Dye

About 15% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents. The release of those colored waste waters in the ecosystem are a dramatic source of non-aesthetic pollution, eutrophication and perturbation in the aquatic life. The wide spread of dye industries, which amounts is more than one million tons annually, combined with potential carcinogenic risk, cause severe environmental pollution. Several methods are available for color removal from waste water such as membrane separation, aerobic and anaerobic degradation using various microorganisms, chemical oxidation, coagulation and adsorption using different kind of adsorbents and reverse osmosis. Significant attentions have been focused on the use of hydrogen peroxide as the active oxidant for several commercial and industrial processes. The destructive oxidation of organic dye with H_2O_2 and catalyst manganese oxide has been studied (Kannan *et al*., 2011).

Materials and Method

Popa manganese ore sample and Pawe manganese ore sample were collected from Department of Geology, University of Yangon and Department of Geological Survey and mineral Exploration Ministry of Mines (DGSE) respectively. Manganese dioxide percent in above collected ore samples were determined by redox titration. By doing this, Manganese II oxide from Popa sample generated higher percent that of Pawe sample. So, Popa sample as selected for synthesis of manganese sulphate. Pyrolusite ores was also characterized by EDXRF and XRD analysis.

Manganese sulphate from ore was extracted by hydrometallurgical method. It was characterized by XRD. Manganese III oxide from manganese sulphate was synthesized by chemical co-precipitation method. In this research, it was prepared from the reaction between manganese sulphate tetrahydrate, sodium carbonate and disodium salt of ethylene diaminetetracetic acid. To prepar Manganese III oxide nanoparticles, the precursor was calcined at different temperatures according to 200, 400, 500, 600 and 700° C for 4 hours.

The obtained nanoparticles was characterized by XRD, EDXRF and SEM. Maximum wavelength of wastewater sample was determined by UV-visible spectrophometer (PD-303). Effect of catalytic decolourization of textile wastewater sample was determined by using prepared manganese (III) oxide nanoparticles.

Results and Discussion

In the present research, two manganese ore samples from different localities were analysed. These samples were collected from Popa Mount in Mandalay Region and Pawe Island near Bokpyin Township in Tanintharyi Region. In this research, percent of manganese dioxide in table (1) Popa and Pawe ore samples were found to be 67.02% and 59.84%, respectively. XRD measurements were carried on manganese ore samples. XRD diffractogram of Popa ore sample was shown in figure (1). According to EDXRF data in figure (2) and table (2), Popa manganese ore sample showed the highest content of MnO_2 (pyrolusite).

Table (1) Moisture and Manganese Dioxide in Manganese Ore Samples.

Name of sample	Moisture* (%)	Manganese dioxide** (%)
A	0.523	67.02
B	0.609	59.84

A = Popa manganese ore sample * Oven dry Method
B = Pawe manganese ore sample ** Redox titration

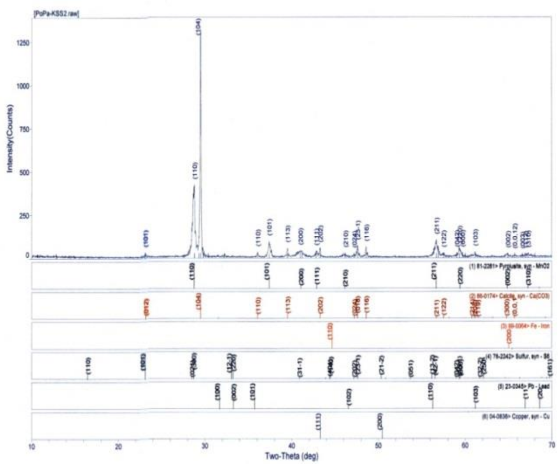

Figure (1) XRD diffractogram of the Popa manganese ore sample.

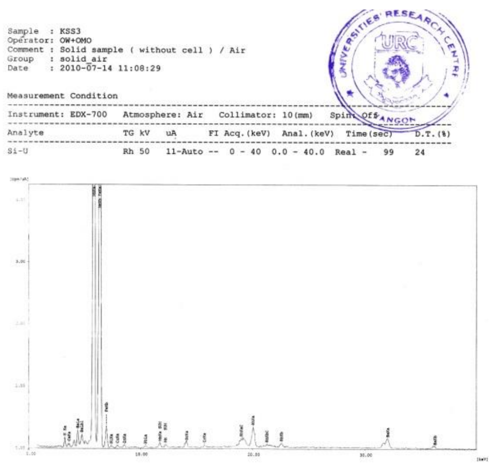

Figure (2) EDXRF spectrum of Popa manganese ore sample.

Table (2) Semi-quantitative Analysis of Popa Manganese Ore Samples.

Sr No	Element	Abundance(%)
1	Ca	18.507
2	Mn	81.334
3	Sr	0.159

Manganese Extraction from Medium Great Manganese ore Sample

Popa manganese ore sample was used for further research work due to the pyrolusite ore according to XRD data. Preparations of manganese sulphate as shown in figure (3) were carried by hydrometallurgical method. Manganese was extracted as manganese sulphate and its percent was observed in increasing after extraction than before (cf.Table. 3). The prepared manganese sulphate were characterized by XRD. In XRD data of the prepared $MnSO_4$ from ore are in agreement with standard JCPDS 35-0751 of $MnSO_4$ (cf. Figure 4).

Figure (3) Photograph of prepared $MnSO_4.H_2O$ from Popa manganese ore by hydrometallurgical method.

Table (3) Manganese and Iron Contents of the Popa Ore Sample Before and After Extraction.

Sr. No.	Element	Before extract	After extract
1	Manganese	42.35(%)	97.25(%)
2	Iron	33.01(ppm)	ND

ND = non detective

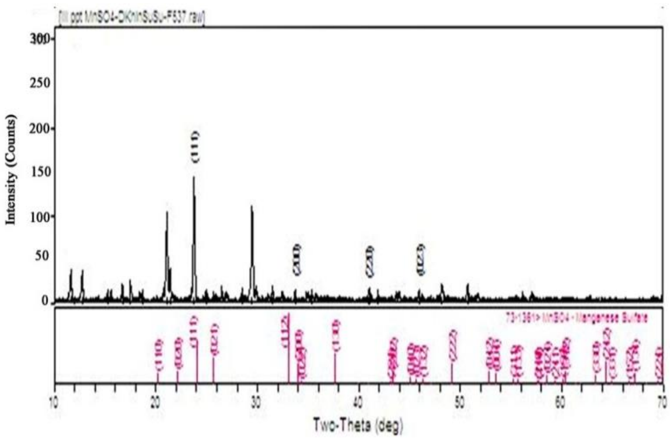

Figure (4) XRD diffractogram of $MnSO_4.H_2O$ obtained by hydrometallurgical method.

Preparation of Manganese (III) Oxide Nanoparticles

This research is carried out for low concentration, the quantity obtained will be very small; on the other hand high concentrations will increase the size of the nanoparticles (Tharayil *et al.*, 2008). Therefore, the samples were prepared from 0.5 M solution due to comprise between quantity and quality. The metal carbonate precipitate was filtered from the reaction mixture and washed several times with alcohol and distilled water to remove impurities, including the traces of EDTA and the original reactants if any.

In this research, the TG-DTA measurement of precursor was performed. The DTA profiles of prepared sample in figure (5) and table (4) indicated that the endothermic peak at about break temperature 127°C showed dehydration of hydrated water in precursor. The exothermic peaks at break temperature 371°C was also indicated due to the decomposition of organic species and further decomposition of organic residue and initial formation of manganese oxide, respectively.

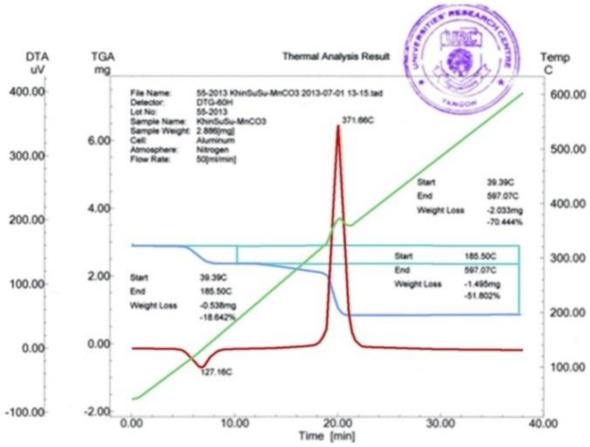

Figure (5) TG-DTA thermogram of precursor for Mn_2O_3 powder before calcinations.

Table (4) Thermal Analysis Data of Precursor for Manganese (III) Oxide Powder Before Calcinations.

Sr. No.	Temperature Range (°C)	Break temperature (°C)	Weight loss (%)	Remark
1	50-200	127 (endo peak)	18.64	Dehydration of hydrated water in precursor
2	200-600	371 (exo peak)	51.80	Decomposition and combustion of organic species which combined weakly with Mn_2O_3 precursor

Characterization of manganese (III) oxide nanoparticles

In this research, prepared manganese oxide nanoparticles were characterized by FE-SEM, EDXRF and XRD techniques. The FE-SEM micrographs indicated that the prepared manganese (III) oxide sample after calcined at 500° C was more porous nature of surface than calcined at 700° C as shown in figure (6). Therefore, dye can enter the porous of the prepared manganese (III) oxide powder sample (Day, 1991). Figure (7) showed the EDXRF spectrum of calcined powder sample in which manganese oxide 81.7%, iron oxide 11.4% were found (cf. Table 5). The crystalline nature of manganese (III) oxide was investigated by XRD technique. The XRD patterns of prepared manganese (III) oxide in figure (8) were well matched with JCPDS file and revealed the presence of cubic phase. The average crystallite sizes were determined from the XRD data using the Scherrer equation (Guillaume *et al*., 2012).

$$t = \frac{0.9\,\lambda}{B\cos\theta} \text{ -------------(2)}$$

According to calculate by Scherrer equation, the calcinations temperature increases with particle size increases in table (6). The XRD peaks were broadened to the nano crystalline nature of particles (Tharayil *et al.*, 2008). Manganese (III) oxide nanoparticles is cubic lattic structure. Crystalinity index was found to be ~0.49 (cf. Table 7). So manganese (III) oxide nanoparticles is single crystalline type.

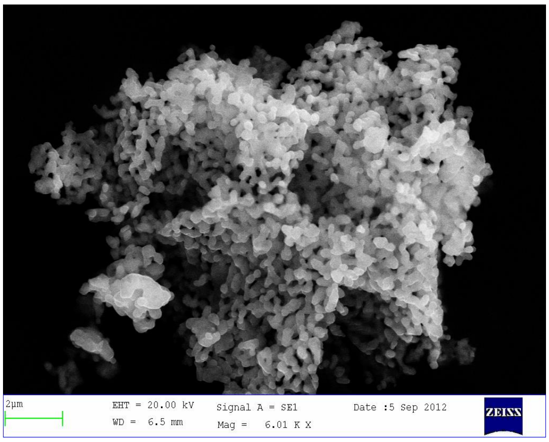

Figure (6) FE-SEM micrograph of the Mn_2O_3nanoparticles

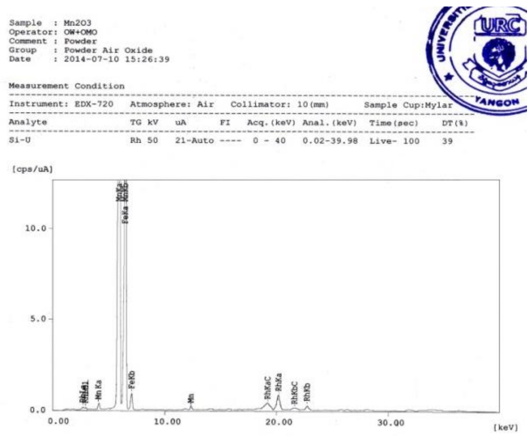

Figure (7) EDXRF spectrum of obtained Mn_2O_3 nanoparticles

Table (5) Semi-quantitative Analysis of the Prepared Manganese (III) Oxide After Calcination at 500°C by EDXRF Technique

No.	Element	Relative abundance (%)
1	MnO	81.71
2	Fe_2O_3	11.36

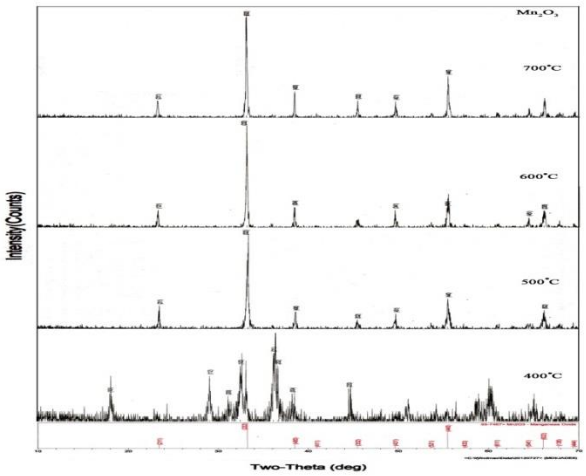

Figure (8) Comparison of XRD diffractograms of the Mn_2O_3 nanoparticles obtained at different calcination temperatures.

Table (6) Average Crystallite Sizes of Prepared Manganese (III) Oxide Nanoparticles.

Sr. No.	**Calcined temperature (^{o}C)**	**Average crystallite size (nm)**
1	500	35.09
2	600	50.56
3	700	81.86

Crystal structure = cubic, (a = b= c , α = β = γ = 90°)

Table (7) Crystallinity Index for of Prepared Manganese (III) Oxide Nanoparticles.

Sample	**Dp (nm)**	**Dcry (nm)**	**I_{cry}(unitless)**	**Particle Type**
Mn_2O_3	40.33	81.86	~0.49	Single crystalline

Application of Catalytic Degradation Effect of Manganese (III) Oxide Nanoparticles on Dyeing Wastewater Samples

In this research, application of the prepared manganese (III) oxide nanoparticles was studied for the treatment of dye in wastewater. Wastewater samples were collected from textile workshops in Inn Lay, Southern Shan State. Before the testing, the absorption spectrum of wastewater was recorded by UV-visible spectrophotometer. Figure (9) shows the absorption spectrum of green colour of textile wastewater, the wavelength of maximum absorptions were found at 376 and 605 nm as shown in table (8). In the present research, the percent degradation of green colour of textile wastewater sample was measured. The percent degradation was found to be 57% in 1stcycle for 4 hours contact time (cf. Table 9). In 2nd cycle (using new nanoparticles) degradation percent were 71% for 30 mintue contact time. This nanoparticles is an effective catalyst for decolorizing and decomposing the dye. This is due to the intercalation of dyes into the Mn_2O_3 layer. So, catalytic decolorization properties of hydrogen peroxide were more effective due to the nanosized of Mn_2O_3.

Therefore, the prepared manganese (III) oxide nanoparticles are mild effective catalyst for the degradation of organic dye in wastewater sample. So the prepared manganese (III) oxide nanoparticles can be used for environmental conservation. Figure (10) indicated the Photograph of catalytic degradation of residual dye in wastewater sample by using manganese (III) oxide nanoparticles.

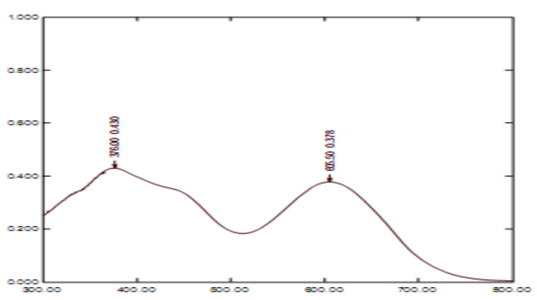

Figure (9) Maximum absorption spectrum of green colour of textile dye wastewater

Figure (10) Photograph of catalytic degradation of residual dye in wastewater by using Mn_2O_3 nanoparticles

Table (8) Absorption Data of Wastewater Sample.

Sr. No.	Color of wastewater	Wavelength (nm)	Absorbance
1	Green	376	0.430
		605	0.378

Table (9) Percent Catalytic Degradation of Green Colour of Textile Wastewater Sample.

No.	Absorbance at 605 nm	Decolourization degree (%)
Initial	0.527	0
After 1st cycle	0.224	57
After 2nd cycle	0.153	71

1st cycle for 4 h contact time
2nd cycle for 30 min contact time, Volume of wastewater 100 mL

Conclusion

In this research, the collected manganese ore samples were analysed by redox titration and modern instrumental analytical techniques. Popa manganese ore sample was pyrolusite (β-MnO_2) by XRD technique due to most of the peaks are well matched with library data of JCPDS-81-2261 of pyrolusite. The 67.02% of manganese dioxide was found in Popa manganese ore samples by titration. So Popa manganese ore sample was selected for further study. Manganese sulphate was prepared from Popa manganese ore sample by hydrometallurgical method. The prepared $MnSO_4.H_2O$ was characterized by XRD and FT IR techniques. The XRD data of the prepared $MnSO_4.H_2O$from ore are well matched library data.

Manganese (III) oxide nanoparticles was synthesized by chemical co-precipitation method in which precursor was firstly investigated by TG-DTA to obtain the decomposition temperature of precursor. It was calcined at different temperatures 400 to 700° C for 4hours. Prepared manganese (III) oxide nanoparticles was characterized by FE-SEM, EDXRF and XRD techniques .The FE-SEM micrographs indicated that the prepared manganese (III) oxide powder after calcination at 500° C was porous nature of surface. According to the EDXRF data, 88.64% Manganese oxide was observed. The XRD diffractogram of prepared manganese (III) oxide were well matched with JCPDS-41-1442of Mn_2O_3 and reveal the cubic structure. By using Scherrer's equation, the average crystallite size of the prepared manganese (III) oxide was found to be 35.09 nm at calcination temperatures of 500° C.

Catalytic degradation properties of prepared manganese (III) oxide nanoparticles was studied by using textile wastewater sample. The applications was done in two successive processes. The percent degradation of green colour of textile wastewater was found to be 57% in 1st cycle for 4 hours contact time. After 2nd cycle, percent degradation of wastewater sample was found to be 71% for 30 minutes contact time.

Acknowledgements

We would like to express my deep appreciation to Dr Tin Htwe, Rector of Hinthada University and Dr Mar Lar, Pro-Rector of Hinthada University, for their kind permission to carry out this research. We would like to express my profound gratitude to Dr Cho Cho Than, Professor and Head, Department of Chemistry, Hinthada University, for her numerous invaluable suggestions, kind encouragement and comments without which this work would not have been completed.

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