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Research Article

SYNTHESIS AND CHARACTERIZATION OF MANGANESE DIOXIDE USING BRASSICA OLERACEA (CABBAGE)

SHAYANTANI CHATTERJEE, ANITA J, ADRIJA SUBRAMANIAN AND SANGEETHA SUBRAMANIAN*

School of Biosciences and Technology, VIT University, Vellore-643014, India

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ABSTRACT

Current research is focused on synthesis of sustainable and environment friendly process of particles for effluent treatment applications. To further enhance the prospects of eco-friendly approach, the current study is dedicated to the green synthesis of Manganese dioxide microparticles that has a wide range of applications from waste water treatment, heavy metal remediation to electronic applications. A procedure to obtain the Manganese dioxide particles from Brassica oleracea (cabbage) leaves has been devised. Effect of initial KMnO4 concentration, amount of Brassica oleracea (cabbage) leaves extract, pH and temperature of the solution was evaluated. The obtained Manganese oxide particles were characterized using Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) and X-Ray Diffraction (XRD). The particle size was found to be in the range of 10-20 μm with 15.98% Manganese content. The X-ray diffraction revealed the presence of tetragonal MnO2 crystals (Pyrolusite) and the sample peaks on the diffraction graph coincided with the peaks for Manganese (IV) oxide.

INTRODUCTION

Nanoparticle synthesis is one the most prominent and highlighted spheres in current researches worldwide. With a wide variety of applications, nanoparticles have been synthesized from several biological as well as chemical sources. The biosynthesis of nanoparticles of metallic, alloy or magnetic nature has been reported in various microorganisms like bacteria, fungi, algae etc. (Saba, 2015). Diverse arrays of protocols have been designed for nanoparticle syntheses that include solvent evaporation, solvent diffusion, co-precipitation, dialysis etc. (Renu, 2015). Moreover, the nanoparticles are characterized on the basis of certain parameters like the zeta potential, particle size, and thermo-gravimetric analysis, surface area, porosity, electron microscopy, x-ray diffraction patterns etc. and their applicability to a particular field is determined.

Manganese oxide (MnO_2) particles have been in focus owing to its variant catalytic and adsorptive properties. Depending on the preparation of MnO_2 particles, many structural forms have been obtained such as α, β, γ, δ, λ etc. and each of these vary in their crystalline structure, morphology and dimensions, thereby resulting in diversity in their electrochemistry (Ting-Ting, *et al*., 2012; Xiaodi, *et al*., 2013). MnO_2 synthesis has been reported through numerous processes like hydrothermal process (Xiao, *et al*., 2010; Cheng, *et al*., 2006; Luo, *et al*., 2008), Sol-gel process (Ching, *et al*., 2002), wet chemical and photochemical route (Jana, *et al*., 2009), wet chemical method for nanodisks (Wang, *et al*., 2008), co-precipitation technique (Harish, *et al*., 2013), pyrolysis process (Burçak, *et al*., 2016) and low temperature solution combustion method (Pradeep, *et al*., 2014).

Manganese oxide nanoparticles have been investigated through numerous intensive researches leading to the discovery of their applicability in several fields like immobilization of proteins (Lvov, *et al*., 2000), sensitive biosensors (Xi-Liang, *et al*., 2004), electrochemical capapcitors (Mao-wen and Shu-Juan, 2011), removal of dyes (Ramprasath,

***Corresponding authors email: sangeethasubramanian@vit.ac.in**

et al., 2016; Pradeep, *et al.*, 2014), lithium-ion batteries (Xiaodi, *et al.*, 2013), synthesis of bio-active compounds (Harichandran, *et al.*, 2014), analysis of neuro-behavior of rats (Tao, *et al.*, 2014), biomimetic catalysts (Mohammad, *et al.*, 2012) metal adsorption (Van-Phuc, *et al.*, 2015). In contrast to this, the toxicity of Manganese oxide nanoparticles has also been reported owing to their variance in morphology, structure, oxidation states that subsequently cause these variants to undergo distinct oxidation or reduction reactions (Marijan, *et al.*, 2013). The nanoparticles form free radicals or ROS due to their physicochemical reactivity, and through direct or indirect activation of oxidative enzymatic pathways, may result in oxidative stress, inflammation and damage biological systems (Javad, *et al.*, 2015). Owing to these findings, green or eco-friendly procedures for production may be the key to sustainability in several fields of nanoparticles applications.

The green synthesis of Manganese oxide nanoparticles has been reported from *Syzygium aromaticum* i.e., clove extract (CE) to be applied as a stabilizing as well as reducing agent and the resulting nanoparticles was applied towards p-Nitrophenol (PNP) sensing (Vineet, *et al.*, 2017). In another study, manganese dioxide nanoparticles have been produced from *Kalopanax pictus* leaf extract and applied towards a methodology for degradation of dyes (Sun, *et al.*, 2015). A methodology has been reported for biosynthesis of Manganese oxide nanoparticles by using lemon extract and turmeric curcumin extract as a reducing and capping agent respectively and analyzed for their antibacterial and antifungal activities (Muhamed, *et al.*, 2017). A study analyzed *Shewanella* strains for their efficacy in oxidizing manganese and found *Shewanella loihica* strain PV-4 to be the strongest oxidizer which could produce oxides at a rate of 20.3 mg/liter/day (Wright, *et al.*, 2016).

In the current study, an approach towards manganese dioxide nanoparticles synthesis has been formulated by utilizing *Brassica olera*c*ea* i.e., cabbage leaves as a green process. The protocol was analyzed for the effects of altering pH, temperature, initial $KMnO_4$ concentration and amount of cabbage leaves used for the process. The resulting particles were characterized through Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) and X-ray diffraction (XRD) study.

MATERIALS AND METHODS

Materials

Potassium permanganate was purchased from Hi-media and used in its purest form. *Brassica oleracea* (Cabbage) was procured from local vegetable supplier cultivated under standard Indian climatic conditions.

Brassica oleracea solution preparation

Brassica oleracea was washed with distilled water and dried until water molecules were evaporated. 7.5 g of finely cut *Brassica oleracea* was added in 50 ml distilled water. Mixture was heated in microwave oven 100°C for 5 min. Obtained solution with yellowish tint was filtered and diluted to 12% for further use.

Preparation of biogenic manganese oxide particles

Brassica oleracea solution was adjusted to pH 6 and $KMnO_4$ crystals (0.2 M concentration) were added to it. This solution was stirred for four hours resulting in a brown colored suspension that was further sonicated to produce a homogenous solution. The prepared solution was subjected to Spectrophotometric analysis in the range of 300-800 nm. The obtained solution was centrifuged and dried at 100°C overnight and the microparticles were obtained in amorphous form.

Effect of significant parameters

For the synthesis of MnO_2, the effect of initial amount of cabbage leaves was studied by varying its quantity (5 g, 7.5 g and 10 g per 50 ml of solution). The resultant MnO_2 products were quantitatively analyzed and confirmed by UV- spectrophotometry to estimate the presence of desired product at 340 nm. Effect of initial concentration of $KMnO_4$ added to the *Brassica oleracea* solution was also observed by varying the molarity of $KMnO_4$ (0.05, 0.1, 0.2, 0.3, 0.4 M) and subjected to UV-spectrophotometric quantitative analysis. In many reduction reactions pH and temperature play a major role in the formation of compounds. To evaluate the effect of varying pH and temperature on the synthesis of MnO_2, the pH of the solution was varied from pH (3-8) and temperature (20-40°C) was experimented and quantified spectrophotometrically against 340 nm. During all the experimentation, rigorous mixing conditions were maintained to provide a homogenous reduction.

Characterization of MnO_2 particles

Following the synthesis, the MnO_2 particles were characterized by subjecting to Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) study and X-Ray diffraction (XRD) study. Scanning Electron Microscopy would reveal the morphological characteristics and distribution of the synthesized particles. Further, EDX study was utilized to identify the constituent atomic percentages and elemental composition of the sample and thereby verify its purity. The crystalline structure of the compound was analyzed through X-ray diffraction where the physical properties would be deliberated based on the atomic arrangement in the sample.

RESULTS AND DISCUSSION

Synthesis of biogenic manganese oxide particles

Brassica oleracea solution was prepared successfully. Manganese oxide particles were synthesized upon the addition of 0.2 M $KMnO_4$ under stirring condition and continued for 4hrs. The change in coloration to brownish indicated the formation of manganese oxide particles by reduction of $KMnO_4$ to MnO_2 by *Brassica oleracea* solution. The resultant brownish manganese oxide solution was subjected to sonication at 20 kHz at room temperature for 30 minutes, followed by drying. Amorphous manganese oxide was thus obtained by a biogenic process.

Effect of significant parameters on synthesis

The synthesized MnO_2 solution was spectrophotometrically analyzed for confirmation of MnO_2 metal particle synthesis. A peak at 340 nm was obtained which was found corresponding to MnO_2 (Kumar, *et al*., 2013).

Further, experiments were conducted to enhance the MnO_2 synthesis process. The amount of *Brassica oleracea* leaves to be used for the procedure was analyzed using varying quantities of 5 g, 7.5 g and 10 g in 50 ml of the solution. The obtained solutions were then subjected to UV- spectroscopy. The highest peak which correlates with MnO_2 synthesis and the maximum amount of MnO_2 product was obtained for the amounts 7.5 g and 10 g at 340 nm (Fig. 1). For all further experiments, 7.5 g was selected as the amount of cabbage leaves added.

The effect of varying the initial concentration of $KMnO_4$ was also studied by utilizing 0.05, 0.1, 0.2 M, 0.3 M and 0.4 M $KMnO_4$ in preparing the micro-particles. The resulting solutions were spectrophotometrically analyzed to determine the highest peak of relevance that appeared at 0.2 M $KMnO_4$ (Fig. 2) and hence, is the optimum concentration for MnO_2 particle synthesis.

The effect of varying pH (3-8) and temperature (20-40°C) on synthesis of MnO_2 was studied. It was observed that pH 5 (Fig. 3) and room temperature, displayed maximum absorbance at 340 nm indicating the presence of manganese oxide (Deogratius, *et al*., 2013). Other pH and temperature conditions displayed similar results with lower significance in yield.

Characterization of the particles

Scanning Electron Microscopy (SEM) revealed the microparticle structure and arrangement of the MnO_2 particles in the sample. The particles were found to be in the range of 10-20 µm and were evenly distributed throughout the sample (Fig. 4). Energy Dispersive X-ray (EDX) analysis aided in determining the atomic contributions of the constituents in the sample where Manganese was found to be in high proportions (Table 1).

The sample was subjected to X-ray diffraction study and analyzed by Match! software to determine the purity and atomic arrangement in the sample. The wavelength was found to be 1.540598 Å (Cu-Ka) and the resulting graph showed high quantities of Manganese (IV) oxide beta (Pyrolusite). Pyrolusite is a stable form of MnO_2 and forms a framework structure with square cross sections. The crystal system was determined to be tetragonal with a value of 4.3880 Å and c value of 2.8650 Å and the diffraction pattern represents the synthesized MnO_2 Microparticles (Fig. 5).

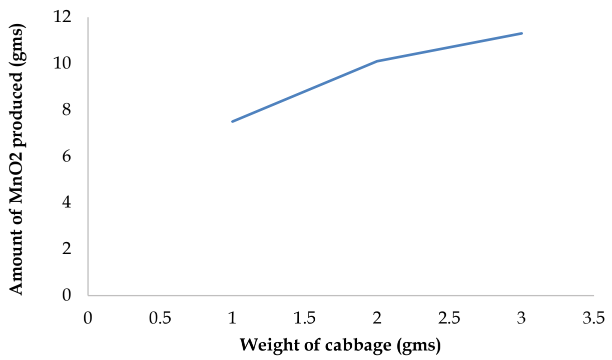

Fig. 1 Effect of amount of *Brassica oleracea* leaves on MnO_2 synthesis.

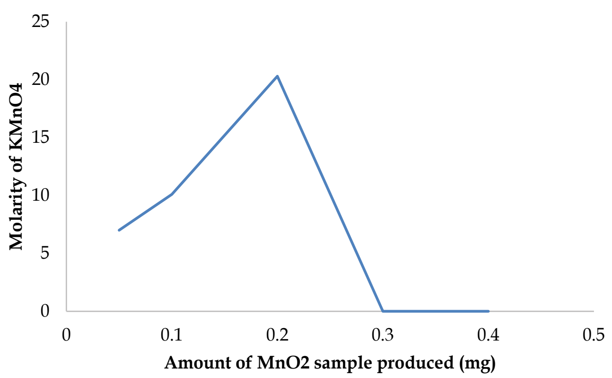

Fig. 2 Effect of initial concentration of $KMnO_4$ on MnO_2 synthesis.

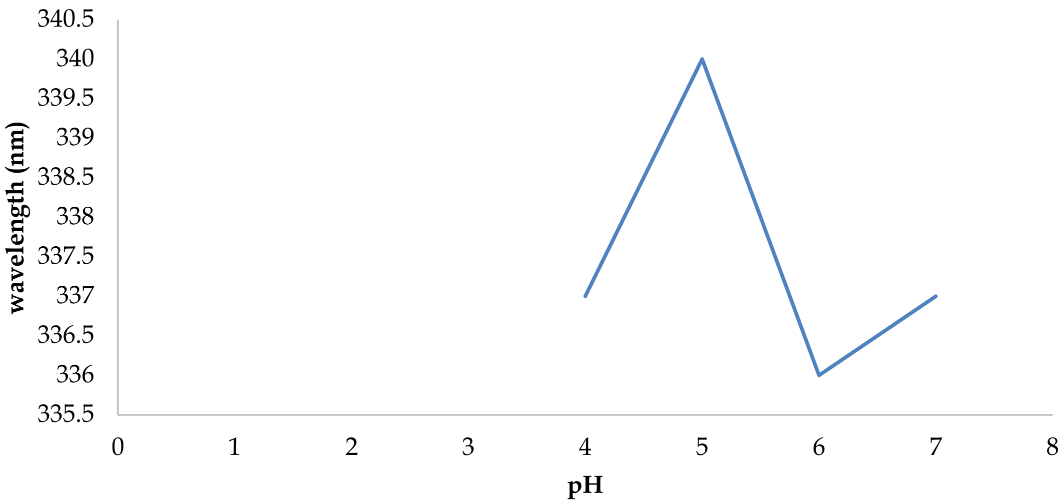

Fig. 3 Effect of varying pH on synthesis of MnO_2.

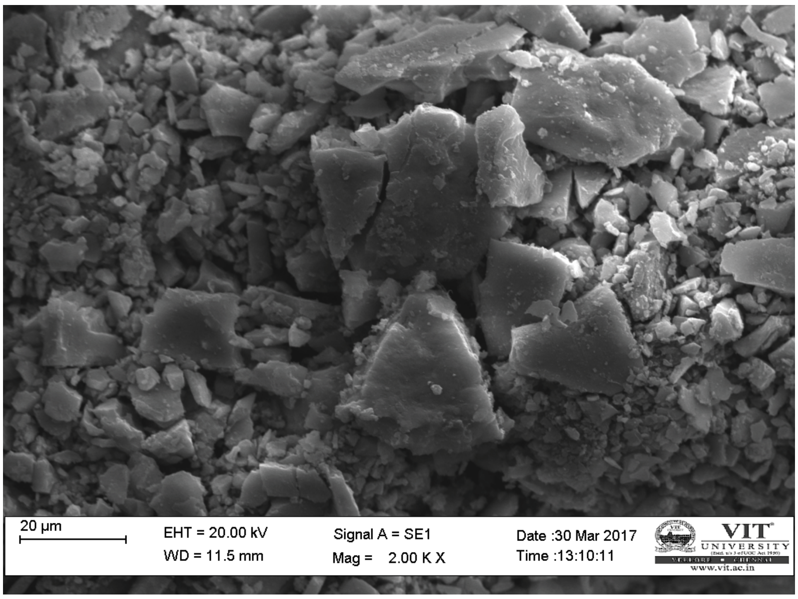

Fig. 4 SEM image of MnO_2 microparticles.

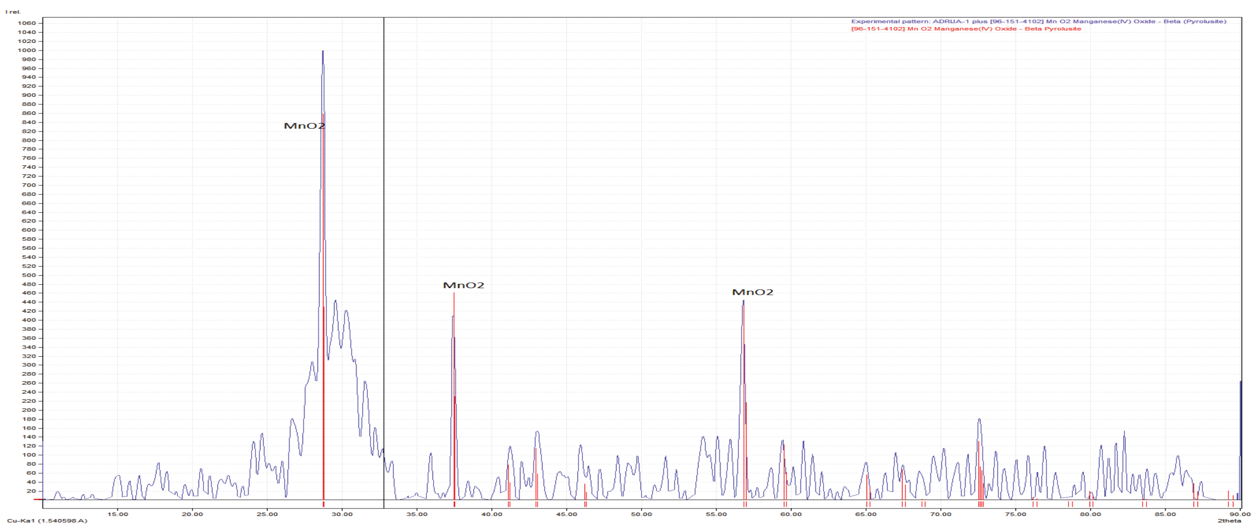

Fig. 5 Diffraction pattern obtained for MnO_2 microparticles.

Table 1. EDX of sample containing MnO_2 microparticles

Element	Weight %	Atomic %
C, K	21.15	36.60
O, K	36.45	47.36
Mn, K	42.40	16.04

CONCLUSION

Manganese oxide was synthesized successfully using *Brassica oleracea* leaves as the reducing agent. Potassium Permanganate was used as the source for the production of Manganese oxide. Physical characterization of these synthesized particles by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) and X-Ray Diffraction (XRD) revealed that a flaky structure with presence of significant amounts of Manganese oxide. Further, effect of significant parameters was evaluated to enhance the overall yield. Spectroscopic analysis was performed against the obtained product to ensuring the presence of Manganese at 340 nm with a high absorbance. The synthesized biogenic Manganese oxide microparticles could be a competent replacement for chemically synthesized Manganese oxide particles. The synthesis process proved to be eco-friendly and sustainable. It could be significantly applicable in the adsorptive, catalytic treatment processes of waste water, industrial dyes, and other effluents.

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