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Eco-Friendly Method for Synthesis of Mn_3O_4 Nanoparticles and Their Characterization

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Abstract

Numerous strategies are used for preparing nanoparticles. The green preparation method is environmentally friendly, economical, simple, and faster nanoparticle production. Mn_3O_4 nanoparticles were prepared by a simple green chemical route using Manganese Dichloride Tetrahydrate ($MnCl_2.4H_2O$) as a precursor with Olive leaves extract as a stabilizer agent in the presence of Sodium hydroxide at room temperature. The products (Mn_3O_4 nanoparticles) were characterized and confirmed using Fourier Transform Infrared (FTIR), powder X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), dynamic light scattering (DLS) and measure surface area. The formation of Mn_3O_4 nanoparticles was confirmed with an average size of 33.424 nm. The XRD measurements confirmed the presence of a crystalline Mn_3O_4 phase. Mn $(OH)_2$ and Mn_3O_4 nanoparticles were investigated by FESEM analysis which gave nanoparticles with scale and cubic shape, respectively. The DLS suggested the particle size distribution appeared in two areas. The surface area of Mn_3O_4 was 2.0623 cm^2g^{-1}.The majority of existing pores were with a diameter of 2–90 nm (mesopores and macropores). Therefore; this green chemical method can be used for the preparation of Mn_3O_4 nanoparticles in a less time-consuming and in an environmentally friendly way.

Keyword: Mn_3O_4 nanoparticles; Olive leaves extract; Green chemical method

1. Introduction

Adsorption is one of the most effective treatment processes compared to other techniques for treating various pollutants from water because of the low-cost factor. Different kinds of sorbents have been marketed or developed for processing wastewater.[1, 2].Metal oxide nanoparticles are classified as promising adsorbents for the removal of heavy metals from aquatic systems due to their large surface areas and high activities. Therefore, increasing attention has been focused on metal oxides such as iron, aluminum, titanium, and manganese[3].Manganese oxide (MnO) is a transition metal oxide having interesting physical and chemical properties. It has triggered optoelectronic applications. It is used as electrode materials, electrochemical capacitors, rechargeable batteries, catalysts, sensors, and magneto electronic devices [4-16]. Among nanomaterials, manganese oxide nanoparticles are very promising, because of their versatility in several application fields. However, for real-world applications, the synthesis of manganese oxide NPs should be based on readily available, inexpensive and non-toxic precursors, as well as simple synthetic methods, hopefully without intermediate steps limiting the production yield of the whole process. Numerous strategies are used for preparing nanoparticles[17]. The green preparation method is an environmentally friendly, economical, simple, and faster nanoparticle production. Integrating green chemistry principles into nanotechnology has led to the identification of environmentally friendly

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reagents that are multifunctional, which they can serve as a reducing agent and a capping agent green chemistry focuses on the production of desired products without the generation of the hazardous intermediate by-products in chemical reaction processes[18, 19]. Günay et al.[20]used an ionic liquid-assisted process to syntheses Mn_3O_4 at room temperature. Up to date, there is a rare study focused on the synthesis of manganese oxide Nanoparticles using the extractions of leaves of the olive plant. Therefore, the current study focuses on the synthesis of manganese oxide nanoparticles using the extractions of leaves of the olive plant and the characterization of the product.

2. Experimental Part

2.1. Materials

Chemicals of analytical purity (BDH), manganese tetrachloride ($MnCl_2.4H_2O$) (98%), Sodium hydroxide (NaOH), Ethanol, Deoxygenated distilled water and Olive leaves for the synthesis of Manganese oxide nanoparticles Mn_3O_4 NPs.

2.2. Instruments and Apparatus

All analyzes of samples were performed at the Faculty of Science/University of Tehran - Iran. An XPERT-Pro diffractometer operating at 30 mA and 40 kV for scanning angles from 20 to 80° was used to obtain an XRD pattern by irradiating samples with a Siemens D500. The surface morphology studies were conducted using the Scanning Electron Microscope model ZEISS: Sigma VP.Also, sample size distribution studies were carried out by DLS Malvern Zetasizer Nano zs. The FTIR spectrum of Mn_3O_4 composite nanoparticles was determined at Diyala University/College of Education for Pure Sciences using Schimadzu Spectrophotometer/Japan with a resolution of 4 cm^{-1} with the range of 300 – 4000 cm^{-1}.

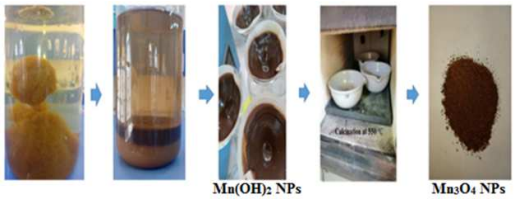
2.3. Preparation of aqueous leaves extract

The leaves of the Olive plant were taken and washed with distilled water, then ground into a fine powder. The fine powder of Olive leaves (5.0 g) were put in distilled water (100 mL) and boiled at 80 °C for 30 minutes. The extract was then filtered through filter paper (Whatman filter paper 1) and kept in a refrigerator at 4 °C for later use (Scheme 1).

Scheme 1. Preparation of Olive plant leaves extract

2.4. Green synthesis of Mn_3O_4 NPs using leaves extract

A salt solution was prepared by dissolving a 2.0 g ($MnCl_2.4H_2O$) in 100 mL of deionized water. The plant extract solution was gradually added to the precursor solution while stirring at (30°C), the temperature of the solution was raised to (80 °C), and Sodium hydroxide solution (0.1 M) was added dropwise to the mixture (brine and leaves extract), to obtain the number of pH at approximately 14 with constant stirring for 1hour. After that, the mixture is filtered; the precipitate was collected and washed with deionized water and ethanol to obtain a pH of approximately 7. Then, the precipitate $Mn(OH)_2$ NPs was collected and dried in an oven at 80°C for 1 h. Calcining the precipitated product at 450°C, for 4 h to obtain Manganese Oxide Nanoparticles Mn_3O_4 NPs (Scheme 2).



Scheme 2. Preparation of $Mn(OH)_2$ and Mn_3O_4 nanoparticles by Olive leaves extract

The formation of $Mn(OH)_2$ and Mn_3O_4 compound in the alkaline aqueous solution by Olive leaves extract may be formulated by the following reactions:

$$Mn^2 + 2OH^- \xrightarrow[\text{Plant extract}]{0.1\ NaOH} Mn(OH)_2\ NP_s \xrightarrow[450\ /hr]{Calcining} MNO + H_2O \xrightarrow[450\ /hr]{Calcining} Mn_3O_4\ NP_s$$

3. Results and Discussion

3.1. FTIR analysis

Fig. 1 represents the FT-IR spectrum of the Manganese Hydroxide $Mn(OH)_2$ (A) and (B) Manganese Oxide Mn_3O_4 nanoparticles samples that were synthesized. In (figure 1 A), the peak at 3337 cm^{-1} indicates an (O-H) stretching bond and the vibration frequency located in the range of 400–650 cm^{-1} is characteristic of Mn–O stretching modes in tetrahedral sites, whereas, in (figure 1 B) displays two significant absorption bands at 617 cm^{-1} and 509 cm^{-1} for the vibration frequency Mn–O corresponds to stretching modes in tetrahedral sites and the distortion vibration frequency the of Mn–O in an octahedral environment.

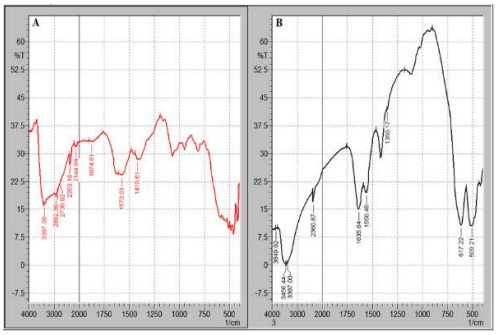


Fig. 1. FTIR spectra of $Mn(OH)_2$ nanoparticles (A), and Mn_3O_4 nanoparticles (B)

Fig. 2 shows XRD patterns of as-prepared Mn_3O_4 nanoparticles. The diffraction peaks correspond to the tetragonal Mn_3O_4 single phase (JCPDS Card 01-080-0382). The average crystallite size has calculated by using the Scherrer equation; D = KA / B cos 0 where; the symbols usual meaning: D is the crystallite size, ß the full - width at half maximum (FWHM) of the most intense diffraction peak in radians, 0 the diffraction angle and λ the wavelength of X - ray radiation. The crystallite sizes were calculated using the Debye Scherrer approximation and are about 33.424 nm.

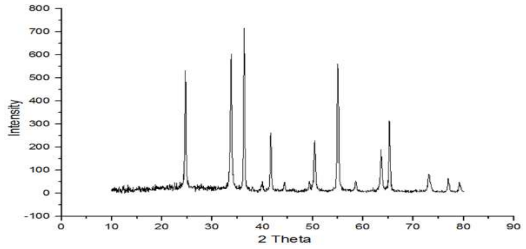


Fig. 2. XRD pattern of Mn_3O_4 NPs prepared by green synthesis

3.2. Crystal Structure, Size and Morphology

The morphology of $Mn(OH)_2$ and Mn_3O_4 nanoparticles are studied by the FESEM technique, (Figures 3, and 4) show the formation of $Mn(OH)_2$ and Mn_3O_4 nanoparticles is confirmed with a size average of 104 (plates shape) and 100 nm (cubic shapes), respectively. FESEM images show that both samples are always constituted by disordered assemblies of large and small particles, which form large mesoporous aggregates with plates and cubic shapes.

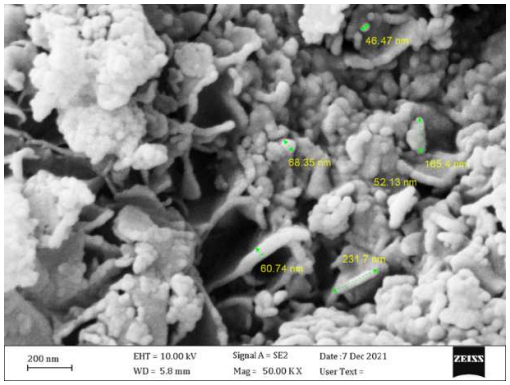


Fig. 3. XRD pattern of Mn_3O_4 NPs prepared by green synthesis

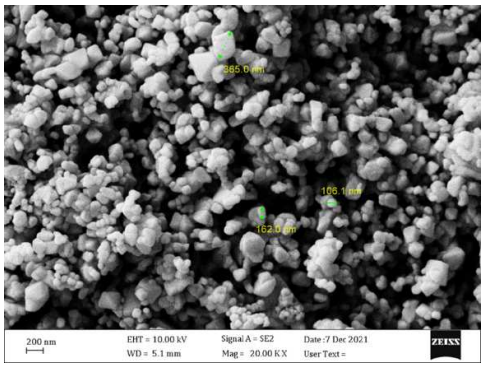


Fig. 4. FESEM images of Mn_3O_4 NPs prepared

3.3. DLS analysis

The particle size distribution curves for Mn3O4 nanoparticles are shown in Fig. 5. The dynamic light scattering (DLS) data for Mn3O4 NPs displayed two peaks (Fig. 5) having a diameter of 464.9 and 2603 nm. The average particle size was found to be 324.1 nm, showing that all the particles were not of the same size. The increase in the mean particle size is attributed to the agglomeration of smaller particles.

3.4. BET analysis

For the surface analysis, the N_2 adsorption-desorption isotherms were carried out by the 3 Flex analyzer (Micromeritics, USA) at 77 K. The specific surface area (SBET) was calculated using multi-point adsorption data from the linear segment of the N_2 adsorption isotherms using BET theory. The surface characterization of the Mn_3O_4 nanoparticles based on the N_2 adsorption-desorption isotherms showed the IV-type isotherm with hysteresis loop, which was representative of the mesoporous ordered framework textural pores as judged from Fig.6. As well as the mesoporous Mn_3O_4 NPs exhibited significant-small surface area (SBET), pore-volume, and pore-diameters according to the data analysis. Also, the N_2 isotherm indicated the uniform channels with well pore size having a surface area of 2.0623 cm^2g^{-1}, a high pore volume of 0.0181 cm^3g^{-1} and a pore diameter of 35.233 nm. The law surface area of the mesoporous Mn_3O_4 NPs exhibited case cavities from the oxidation of reactant precursors using alkaline medium. The BJH pore size distribution of Mn_3O_4 NPs is peaked in the range 3–81 nm, an average BJH pore diameter of 39.7 nm is observed as well (Figure 7).

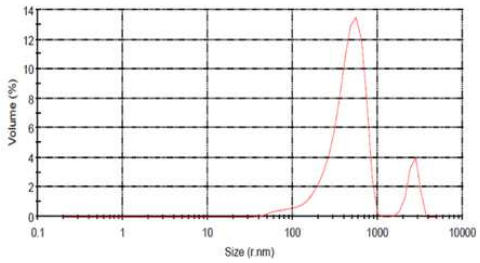


Fig. 5. . DLS studies of Mn_3O_4 nanoparticles

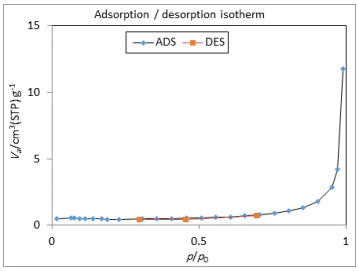


Fig. 6. BET analysis for Mn_3O_4 NPs by using N_2 adsorption desorptionIsotherms

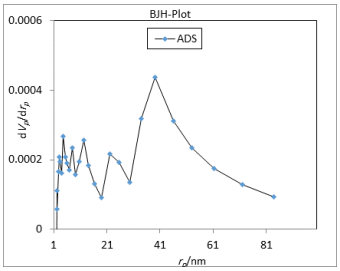


Fig.7. Barrett–Joyner–Halenda (BJH) distributions for the desorption branch of the isotherms of Mn_3O_4 NPs

4. Conclusions

The present study shows that pure Manganese Oxide NPs can be synthesized by means of a time and energy-saving method, characterized by a very high production yield, based on a green chemistry process. The characterization analyses reveal that produce large and small NPs, due to a higher degree of calcination and a greater nucleation rate. The $Mn(OH)_2$ and Mn_3O_4 NPs, organized in quite ordered and microporous /mesoporous aggregates, are scale and cubic shape monodispersed and agglomerates, with size dimensions of 46-365 nm. A BET surface area up to 2.0623 cm^2 g^{-1}, values were lower than those previously reported in the literature for Mn_3O_4 NPs samples.

5. Conflicts of interest

There are no conflicts to declare.

6. Acknowledgments

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7. References

[1] [1] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study, Dyes and pigments 51(1) (2001) 25-40.
[2] [2] Y. Yu, Y.-Y. Zhuang, Z.-H. Wang, Adsorption of water-soluble dye onto functionalized resin, Journal of colloid and interface science 242(2) (2001) 288-293.
[3] [3] R. Taman, M. Ossman, M. Mansour, H. Farag, Metal oxide nano-particles as an adsorbent for removal of heavy metals, J. Adv. Chem. Eng 5(3) (2015) 1-8.
[4] [4] M.S. El-Deab, T. Ohsaka, Manganese oxide nanoparticles electrodeposited on platinum are superior to platinum for oxygen reduction, Angewandte Chemie International Edition 45(36) (2006) 5963-5966.

[5] [5] O. Giraldo, S.L. Brock, W.S. Willis, M. Marquez, S.L. Suib, S. Ching, Manganese oxide thin films with fast ion-exchange properties, Journal of the American Chemical Society 122(38) (2000) 9330-9331.
[6] [6] N.R. Jana, Y. Chen, X. Peng, Size-and shape-controlled magnetic (Cr, Mn, Fe, Co, Ni) oxide nanocrystals via a simple and general approach, Chemistry of materials 16(20) (2004) 3931-3935.
[7] [7] H.-S. Kim, P.A. Pastén, J.-F. Gaillard, P.C. Stair, Nanocrystalline todorokite-like manganese oxide produced by bacterial catalysis, Journal of the American Chemical Society 125(47) (2003) 14284-14285.
[8] [8] G.H. Lee, S.H. Huh, J.W. Jeong, B.J. Choi, S.H. Kim, H.-C. Ri, Anomalous magnetic properties of MnO nanoclusters, Journal of the American Chemical Society 124(41) (2002) 12094-12095.
[9] [9] A. Narayanaswamy, H. Xu, N. Pradhan, X. Peng, Crystalline nanoflowers with different chemical compositions and physical properties grown by limited ligand protection, Angewandte Chemie International Edition 45(32) (2006) 5361-5364.
[10] [10] T. Ould-Ely, D. Prieto-Centurion, A. Kumar, W. Guo, W.V. Knowles, S. Asokan, M.S. Wong, I. Rusakova, A. Lüttge, K.H. Whitmire, Manganese (II) oxide nanohexapods: insight into controlling the form of nanocrystals, Chemistry of materials 18(7) (2006) 1821-1829.
[11] [11] W.S. Seo, H.H. Jo, K. Lee, B. Kim, S.J. Oh, J.T. Park, Size-dependent magnetic properties of colloidal Mn3O4 and MnO nanoparticles, Angewandte Chemie International Edition 43(9) (2004) 1115-1117.
[12] [12] X. Sun, Y.W. Zhang, R. Si, C.H. Yan, Metal (Mn, Co, and Cu) oxide nanocrystals from simple formate precursors, Small 1(11) (2005) 1081-1086.
[13] [13] A. Vijayamari, K. Sadayandi, S. Sagadevan, P. Singh, A study of optical, surface morphological and electrical properties of manganese oxide nanoparticles, Journal of Materials Science: Materials in Electronics 28 (2017) 2739-2746.
[14] [14] M. Yin, S. O'Brien, Synthesis of monodisperse nanocrystals of manganese oxides, Journal of the American Chemical Society 125(34) (2003) 10180-10181.
[15] [15] T. Yu, J. Moon, J. Park, Y.I. Park, H.B. Na, B.H. Kim, I.C. Song, W.K. Moon, T. Hyeon, Various-shaped uniform Mn3O4 nanocrystals synthesized at low temperature in air atmosphere, Chemistry of Materials 21(11) (2009) 2272-2279.
[16] [16] D. Zitoun, N. Pinna, N. Frolet, C. Belin, Single crystal manganese oxide multipods by oriented attachment, Journal of the American Chemical Society 127(43) (2005) 15034-15035.
[17] [17] A. Sharma, G. Oza, Synthesis, Characterization and Applications.
[18] [18] S. Iravani, Green synthesis of metal nanoparticles using plants, Green Chemistry 13(10) (2011) 2638-2650.
[19] [19] S. Saif, A. Tahir, T. Asim, Y. Chen, Plant mediated green synthesis of CuO nanoparticles: comparison of toxicity of engineered and plant mediated CuO nanoparticles towards Daphnia magna, Nanomaterials 6(11) (2016) 205.
[20] [20] M. Günay, A. Baykal, M.S. Toprak, H. Sözeri, A green chemical synthesis and characterization of Mn 3 O 4 nanoparticles, Journal of superconductivity and novel magnetism 25 (2012) 1535-1539.