Comparative investigation of catalytic application of α/β/γ-MnO2 nanoparticles synthesized by green and chemical approaches

Hamza Shehroz
Sarmad Ali
Guria Bibi
Tahreem Khan
Saba Jamil
Shanza Rauf Khan (✉ shanzaraufkhan@gmail.com)
https://orcid.org/0000-0001-8069-6746

Muhammad Hasaan
Muhammad Ramzan Saeed Ashraf Janjua

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Abstract

It is first time reported that three phases (α, β, and γ) of manganese dioxide (MnO₂) are successfully stabilized in a single entity. For this purpose, Citrullus colocynthis (bitter apple) extract is used as natural surfactant in green synthesis. MnO₂ nanoparticles were synthesized in the presence and absence of plant extract under same conditions. The morphology of both products are analyzed by SEM and STEM to understand the role of plant extract in controlling the morphology of particles. The crystallinity and composition are analyzed by XRD and confirmed that product is comprised of multiple phases α, β, and γ. The reduction of dyes and nitroarenes are studied by using MnO₂ nanoparticles (green and chemical products) as a catalyst. Apparent rate constant, percentage reduction, time reduction and reduced concentration are determined to compare the activity of both catalysts. After comparative data analysis, the catalytic reduction of picric acid is found fastest among all the substrates. All the results are analyzed on the basis of structure, functional group and affinity towards catalyst.

1. Introduction

Composition and sizes of nanoparticle have a great impact on their chemical and physical properties [1]. Nanoparticles exceptional properties allow them to be used in domains such as electronics, catalysis, medicine delivery and nanofluids. Oxides of manganese such as manganese (II) oxide (MnO), manganese (II,III) oxide (Mn₃O₄), manganese (III) oxide (Mn₂O₃), manganese (VI) oxide (MnO₃), manganese (VII) oxide (Mn₂O₇) and manganese (IV) dioxide (MnO₂). MnO₂ is naturally existing in different phases like α, β and γ. α, β and γ- MnO₂ nanoparticles differ in their crystallinity and lattice structure [2]. The polymorphous difference of α, β and γ- MnO₂ nanoparticles is 2 × 2 tunnel or hollandite, 1 × 1 tunnel or pyrolusite, and 2 × 1 and 1 × 1 tunnels or nsutite respectively. These polymorphs have different atomic arrangements, resulting in different types of pores or tunnels in the crystal structure and these different atomic structure make them selective toward different ions and atom for kinetic and catalytic properties [3]. That’s why MnO₂ structure is considered suitable to be used in catalytic application in this work. Manganese is a 3-d transition element with multiple oxidation states start from the − 3 to + 7 and belongs to a group 7 (VIIb). Depending upon these oxidation states, MnO₂ can be acidic, basic and amphoteric oxides. MnO₂ nanoparticles have both unique chemical and physical properties because MnO₂ is utilized in a variety of catalytic reactions in combination with other catalysts [4]. There are various methods adopted for the synthesis of MnO₂ nanoparticles like hydrothermal, sol–gel, reverse micelle and co-precipitation methods but green-assisted wet chemical method has been used here for synthesis of MnO₂ nanoparticles [5]. Green assisted approach is preferred because phytochemicals are non-toxic, easily degradable and less hazardous [6–10]. Green assisted approach is preferred for the catalytic application of MnO₂ nanoparticles because of its ecofriendly effects. Different plants extracts have been used as a stabilizing agent and some are used as a reducing agent in synthesis of MnO₂ nanoparticles. Plant extracts of Citrus Limon, Kalopanax pictus, Phyllanthus amarus and Ditrichia graveolens have been used for the synthesis of MnO₂ nanoparticles: nano needles by lemon
extract, nanosphere by *Alopanax pictus* extract and, furrowed nanorod and nanosphere by *Phyllanthus amarus* extract [11]. Here the plant extract of Bitter apple (*Citrullus colocynthis*) is firstly used for synthesis of MnO$_2$ nanoparticles by green-assisted wet chemical approach. In this work bitter apple desert plant grows in sandy areas in Pakistan. This plant is native to the desert area like Cholistan and Thar dessert that's why this is also called guava desert. In this work $\alpha/\beta/\gamma$-MnO$_2$ nanoparticles has been synthesized by using bitter apple extract. The combination of these three phases of MnO$_2$ nanoparticles, oxidation states and lattice structure cause the fast transfer of electrons which helps the fast reduction of organic compounds, that's why these nanoparticles are considered as good catalyst. MnO$_2$ nanoparticles are used as a catalyst for the reduction of organic dyes such as 2,4-dinitrophenylhydrazine (2,4-DNPH), 4-nitrophenol (4-NP), Rhodamine B (RhB), Congo red (CR), methyl orange (MO) and methylene blue (M) because organic dyes and these nitro compounds are hazardous for environment. The reduction of pollutants has been enhanced by the use of composite metal-based nanoparticles as catalysts [12, 13].

MnO$_2$ nanoparticles has been synthesized by using plants extract and lattice structure is characterized by XRD and morphology is analyzed by STEM. MnO$_2$ nanoparticles has been used as a catalyst for the reduction of organic dyes and other nitro compounds.

## 2. Materials And Methods

### 2.1 Materials

All chemicals were of analytical grade. Manganese chloride tetrahydrate (MnCl$_2$.4H$_2$O), sodium acetate (CH$_3$COONa), isopropanol (C$_3$H$_8$O), sodium borohydride (NaBH$_4$), 2,4-dinitrophenyl hydrazine (2,4-DNPH; C$_6$H$_6$N$_4$O$_4$), 4-nitrophenol (4-NP; C$_6$H$_5$NO$_3$), Rhodamine B (RhB; C$_{28}$H$_{31}$N$_2$O$_3$Cl), Congo red (CR; C$_{32}$H$_{22}$N$_6$Na$_2$O$_6$S$_2$), methyl orange (MO; C$_{14}$H$_{14}$N$_3$NaO$_3$S) and methylene blue (MB; C$_{16}$H$_{18}$ClN$_3$S) were purchased from Sigma-Aldrich USA. Distilled water was also used for solution preparation and washing.

### 2.2 Synthesis of $\alpha, \beta$ and $\gamma$-MnO$_2$ nanoparticles

5 g of MnCl$_2$.4H$_2$O and 2 g of CH$_3$COONa were added in 50 mL of isopropanol separately. Both the solutions were mixed with 5 mL of plant’s extract and refluxed at 75°C until reddish brown color was appeared. The reaction mixture was further refluxed for 2 hr after appearance of reddish brown. The product was collected by centrifugation and five time washed with distilled water and dried in oven at 100°C. The dried form of product was ground with pestle and mortar and labeled as product A. Parallel experiment has performed to prepare the product in the absence of plant’s extract and that product is labeled as product B.

### 2.3. Catalytic application of $\alpha/\beta/\gamma$-manganese dioxide nanoparticles
Catalytic activity of both products (A and B) has been analyzed by the studied by reduction of organic dyes and nitro-compounds such as 2,4-dinitrophenyl hydrazine (2,4-DNPH), 4-nitrophenol (4-NP), Rhodamine B (RhB), Congo red (CR), methyl orange (MO) and methylene blue (MB) in the presence of sodium borohydride (NaBH4). 0.01 g of catalyst and 0.01 g of NaBH4 and 0.1 mL of 0.1 mM substrate i.e. dyes and nitro-compounds were added in cuvette. UV-Visible spectrophotometer is used to monitor the progress of chemical reaction. Catalytic reduction of all of substrates was monitored by change in absorbance at their \( \lambda_{\text{max}} \) at different time intervals \([14]\). Absorbance has been measured at \( \lambda_{\text{max}} \) till its value does not change with time. \( \ln(A_t/A_0) \) is plotted versus time and kinetics of reaction followed the pseudo first order (i.e. \( A_t \) and \( A_0 \) are absorbance at time \( t \) and at time 0 respectively).

### 2.4. Characterization

Product has been characterized on X-ray powder diffractometer, Rigaku D/max Ultima III, operating at 0.130 ampere current and 40 kV voltage X-ray diffractometer was equipped with Cu-K\( \alpha \) radiation source producing radiations of wavelength 0.15406 nm. MDI JADE 5.0 and Match 3.0 software was used to analyze XRD pattern. SEM Quanta 250, FEG (USA) was used for analyzing the morphology of products. The catalytic reduction of organic dyes and nitrocompounds has been monitored by using VIS-1100 UV-Visible spectrophotometer, Biotechnology medical service (BMS) Limited.

### 3. Results And Discussion

#### 3.1. X-ray Diffraction Powder Analysis

XRD pattern of product A is shown in Fig. 1. The peaks are identified and indexed by comparing with XRD standard pattern using MATCH 3.0 software. The peaks are identified at specific 2\( \theta \) values. The peaks are observed at 2-theta 10.14°, 19.14°, 29.14° 38.77°, 48.79° and 67.48° which are indexed to (110), (200), (310), (211), (600) and (541) miller indices respectively (JCPDS # 44–141). This set of peaks and miller indices indicate that synthesized product A is consist of \( \alpha \)-MnO\(_2\). Few additional peaks are also observed at 2-theta 28.14°, 33.98° and 59.62° which are indexed to (110), (101) and (220) miller indices respectively (JCPDS # 24–73). These peaks are characteristic to \( \beta \)-MnO\(_2\). Moreover, the peaks are observed at 20.99°, 32.22°, 57.40°, 62.20° which are indexed to (120), (131), (160) and (421) respectively (JCPDS # 16–644) which are characteristic to \( \gamma \)-MnO\(_2\). This indicates that synthesized product A is consist of three phases of MnO\(_2\). No extra peak is observed in pattern \([15]\). So the product is pure. All the peaks are very sharp indicate that the product is highly crystalline. It is difficult to stabilize multiple phases at same time using chemical synthesis approach \([16]\). Bitter apple contains verity of compounds like phenols, flavonoids, phytochemicals etc. which act as stabilizing agents. The stabilizing/capping property of all these compounds are different from each other. So presence of variety of biomolecules help in stabilization of these three phases (\( \alpha \), \( \beta \) and \( \gamma \)) of MnO\(_2\) \([17]\). The prepared product belongs to space group P 12/m (10) monoclinic system. No atom is present at center of unit cell. Four atoms of
manganese and four atoms of oxygen are present per unit cell. Two Mn-O are present as each face [18]. The distance between two Mn-O present in same face is same on both faces.

### 3.2. Effect of Plant Extract on the Morphology of Products

Product A is synthesized by green method and its SEM images are shown in Fig. 2(a-d) at magnification 50,000X, 100,000X and 200,000X. Small size of nanoparticles is observed from Fig. 2a. Some particles are observed semispherical at higher magnification. Some particles of irregular shape of average size 65 nm are also observed at higher magnification. The morphology of these particles is heterogeneous semispherical with distinct boundaries [19]. Uneven morphology with wide size distribution may be attributed to cause particle agglomeration [20]. Product is highly aggregated even at higher magnification (200000X). STEM mode images of α/β/γ-MnO₂ are shown in Fig. 2(Ha, #132) at various magnification and morphology is not seen clearly. STEM images also show that boundaries are not regular and particles are fused with each other. The boundaries are fused, that’s why shape is not clearly observed [21].

SEM images of product B synthesized by chemical method are shown in Fig. 3(a-b). Some particles are in semispherical shape and some are in irregular shape. The particles possess irregular morphology and the boundaries are not clear even at higher magnification (Fig. 3(c-d)) [22]. Average size of these particles is around ~ 20 nm. STEM images of product B synthesized by chemical method is shown in Fig. 3(e-f). Figure 3e represents the overall view of the product. Figure 3f shows that the product consists of fused particles and boundaries are not defined clearly. Morphology of the product is not clear, even at higher magnification the particles show agglomeration as it can be seen from the Fig. 3g-3h. Size distribution histogram of both products are given as Fig. 4 (a-b). Size of particles is calculated from high magnification SEM and STEM images. Particles size of product A is ranged from 10–60 nm while the size of majority of particles is in between 20–50 nm (Fig. 4a). The size of particles of product B is ranged from 5 to 35 nm. The majority of particles are lied around 20–25 nm (Fig. 4b). Both the graphs do not follow Gaussian Bell-shape distribution.

### 3.3. Catalytic Application of Products A and B

Organic dyes and nitro-compound are reduced by using α/β/γ-MnO₂ nanoparticles as catalyst in the presence of sodium borohydride (NaBH₄). The absorbance of substrate is observed at their λ_max after regular time intervals. The absorbance is decreased with time and graph become parallel to x-axis which indicates that reaction has been completed and solution become colorless [23]. It follows the pseudo-first order reaction kinetics and values of k_app is calculated from slope. The wavelength of maximum absorbance of substrates such as CV, MB, CR, MR, MG, EBT, RB, PA, 2-NP, 2,4-DNP, and 4-NP are 590, 670, 495 430, 617, 510, 595, 414, 400, 520 and 400 nm respectively. Electrons are transferred from BH₄⁻ to substrate molecule via surface of α/β/γ-MnO₂ nanoparticle and substrates are reduced into corresponding amino products. Plots of ln(A_t/A_o) as a function of time are given as Fig. 5. Plot of reduction of substrates by catalyst A are shown in Fig. 5(a-b) while plots of reduction of substrates by catalyst B are shown in Fig. 5(c-d). Initial decrease in value of ln(A_t/A_o) with time is showed that
reduction is in progress and concentration of substrates are decreased with time (according to Beer-Lambert’s law, absorbance is directly proportional to the concentration). The slope of all of these plots is different from each other which indicates that reduction of few substrate is fast while few substrates are reduced slowly [24].

3.4. $k_{app}$ of Catalyst A and B

The values of the $k_{app}$ of substrates by using $\alpha/\beta/\gamma$-MnO$_2$ nanoparticles (Product A) as a catalyst is shown in Fig. 6a. The trend of $k_{app}$ of the substrates is PA > MB > MR > MG > 2-NP > EBT > CV > RB > CR > 2,4-DNP. The value of $k_{app}$ of PA is highest among substrates because it has three nitro-groups and accessibility easy towards active site of catalyst and Greater affinity between catalyst and substrate favors its test reduction while in the case of methyl blue it acts as electrophile in aqueous solution with respect to catalyst and accept electron from the reducing agent the nucleophile BH$_4^-$ can offer electrons to the catalyst and catalyst acts as electron relay for MB reduction in NaBH$_4$ solution that’s why the $k_{app}$ is larger than other remaining substrates of and 2, 4-DNP has lowest value of $k_{app}$ among all the substrate. Values of the $k_{app}$ of substrates by $\alpha/\beta/\gamma$-MnO$_2$ nanoparticles as a catalyst is shown in Fig. 6a. The trend of $k_{app}$ of the substrates is MB > 2,4-DNP > RB > CV > MG > CR > PA > MR > EBT > 2-NP. The trend of substrate is not same for catalyst B because this product is synthesized by chemical method and no plants extract is added in it. For example, in for product A PA has highest $k_{app}$ while in the case of product B MB has highest value and for product A 2,4-DNP has lowest $k_{app}$ and for product B there is 2-NP has lowest $k_{app}$.

3.5. Reduction time of catalyst A and B

Histogram of substrate versus reduction time by using product A as a catalyst is given as Fig. 6b. The trend of reduction time is 2,4-DNP > PA > CV > MR > EBT > CR > MG > RB > 2-NP > MB. The reduction time of nitrocompounds are comparatively greater to other dyes because of more contact time and high adsorption rate of nitro compounds on the surface of manganese-based-nanoparticles catalyst. Reduction time of 2,4-DNP is highest among other substrates because two nitro-groups are present one is present at ortho which form hydrogen bonding with hydroxyl group of phenolic part of the compound which stabilizes the structure, due to which adsorption of substrates over catalyst takes more time that’s why substrate takes longer time to reduce. Reduction time of MB is lowest because nitrogen of azo group is present at the outside of the ring and accessibility of the catalyst is increase towards the substrate and reactivity is enhanced therefore its reduction time is lowest [25]. The plot of reduction time versus substrates by using Product B as a catalyst is given in Fig. 6b. The trend for reduction time is MB > 2-NP > MR > 2,4-DNP > PA > MG > EBT > CR > CV > RB. MB shows stability because it has two N, N-dimethyl groups that cause steric hindrance that’s why MB highest reduction time. RB shows least stability because it contains SO$_3$ group due to which the accessibility of substrate towards the catalyst is increased and it also contain azo and hydrazine group which triggers the reactivity of RB [26]. The trend is not same for both products e.g. in Product A 2,4-DNP has greater reduction time while in the case of Product B MB has greater reduction time this trend indicates that there is irregular trend of reduction time for both products.
for example in the case of product A 2,4-DNP has highest reduction time while for product B 2,4-DNP forth highest value. In the case of product B MB has highest reduction time while in the case of product A it in last. RB has same reduction time in both product A and B and PA also have same reduction time in both catalysts [27].

3.6. Percentage reduction of Product A and B

The percentage reduction of all substrate is shown in Fig. 6c. The trend of %reduction is PA > MG > CV > MB > EBT > 2-NP > RB > 2,4-DNP > CR. PA shows the higher percentage reduction because three nitro groups are present in the PA which increases the accessibility of the active sites of the catalyst for the substrate, therefore the % reduction of the PA is highest among other substrate. Among all the nitrocompounds, 2,4-DNP has lowest % reduction because intramolecular hydrogen bonding stabilizes the structure of 2,4-DNP. MG shows greater % reduction among all the organic dyes because methyl group is present outside the ring which has electron donating effect while CR have lowest percentage reduction among all the substrate because there are two phenyl rings are joined by diazo linkage and two sulphonic groups are present in the structure of the CR and the reaction is kinetically less favorable as compared to the other substrates due to which CR reduced slowly and show lowest reduction potential nanoparticles as catalyst. The percentage reduction of all substrate is shown in Fig. 6c. The trend of %reduction is RB > CR > PA > CV > MR > EBT > 2-NP > 2,4-DNP > MG > MB. RB shows least stability because it contains $\text{SO}_3$ group due to which the accessibility of substrate towards the catalyst is increased and it also contain azo and hydrazine group which triggers the reactivity of RB [26]. Therefore, the % reduction of the RB is higher than the other substrate. MB shows stability because it has two N, N-dimethyl groups that cause steric hindrance that’s why MB shows greater stability and least reactive. The % reduction of substrates by using both catalyst is different in product A PA has highest % reduction while in Product B RB has highest % reduction [28].

3.7. Reduced Concentration by Product A and B

Trend of reduced concentration by both catalysts are plotted in Fig. 6d. The trend of reduce by product A concentration for MB the reduced concentration is 0.075 for CR 0.091, EBT 0.083, For MR 0.043 for MG 0.078, for 2-NP 0.082, 2,4-DNP 0.08 and PA 0.095. in the case of product B reduced concentration for MB the reduced concentration is 0.035 for CR 0.0935, EBT 0.062, For MR 0.052, for MG 0.065, for 2-NP 0.062, 2,4-DNP 0.063 and PA 0.017. The values of substrates reduced by both catalysts are different for example MB is reduced by the green catalyst has different value while MB reduced by the Product has different and same is the case of other substrates which are reduced by the both product have different reduced concentration [29].

4. Conclusions

Bitter apple is proved to be a good extract that’s stabilizing the metastable phases of metal oxide ($\alpha/\beta/\gamma-$MnO$_2$). The nanoparticles obtained from green method possess smooth surface and semispherical shape. The average size of Product A lies in 20–50 nm but the nanoparticles obtained from chemical
method is in range of 20–25 nm. Green synthesized nanoparticles show better catalytic activity as compared to chemically synthesized nanoparticles. Nitroarenes are easily reduced by nanoparticles as compared to dyes because complete reduction of dyes is not possible due to complex structure. $k_{app}$ value of PA, reduction time of 2,4-DNP, % reduction of PA, reduced concentration of PA using green synthesized catalyst are highest among all substrates. $k_{app}$ value of MB, reduction time of MB, % reduction of RB and reduced concentration of CR by chemically synthesized catalyst are highest among all substrates has highest value.

Declarations

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Compliance with Ethical Standards

Conflict of interest All the authors have declared no financial and nonfinancial interests.

References

3. S.K. Ghosh, Diversity in the family of manganese oxides at the nanoscale: from fundamentals to applications. ACS omega 5, 25493–25504 (2020)


19. K. Opatová, I. Zetková, L. Kučerová, Relationship between the size and inner structure of particles of virgin and re-used MS1 maraging steel powder for additive manufacturing, Mater.13, (2020).956


Figures
Figure 1

XRD pattern of product A α/β/γ-MnO₂ synthesized by green method.
Figure 2

SEM and STEM analyses of product α/β/γ-MnO₂ synthesized by green method. (a) Overall view of product, (b-c) randomly aligned fused particles, (d) close analysis of rough surface of particles, (e) solid nanoparticles, (f) fused boundaries of nanoparticles oval shaped nanoparticles.
**Figure 3**

SEM and STEM images of MnO$_2$ nanoparticles synthesized by co-precipitation chemical method. (a-b) Overall view of product, (c-d) fused particles, (e) overview of product, (f) small fused particles, round/oval shaped particles.
Figure 4

Size distribution histogram of MnO₂ nanoparticles synthesized by (a) green method (Product A), and (b) chemical method (Product B).
Figure 5

Plot of $\ln(A_t/A_0)$ versus time for reduction of various substrates using both catalysts: (a-b) product A and (c-d) Product B. (Conditions: $[\text{substrate}] = 0.1$ mM, $[\text{NaBH}_4] = 3.3$ mg/mL and $[\text{catalyst}] = 3.3$ mg/mL).
Figure 6

Plot of comparison of $k_{app}$, reduction time, % reduction and reduced concentration of different substrate by using Product A and B.