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Research Article

Synthesis of manganese dioxide nanoparticles using co-precipitation method and its antimicrobial activity

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Abstract

The advancement in nanotechnology research has helped in the development of eco-friendly methods for the synthesis of nanoparticles, which gives considerable importance to expand their applications. In this work manganese dioxide nanoparticles with controlled particle size and composition were synthesized by co-precipitation method with the help of salt such as sulfates under a fine control of pH by using NaOH solution. The optical properties of the nanoparticles were analyzed using UV–VIS spectroscopy. The characteristic functional groups present in the molecule of synthesized nanoparticles were analyzed using Fourier Transform Infrared Spectroscopy. Particle size and morphology of the synthesized manganese dioxide nanoparticles were analyzed using Scanning Electron Microscope. Manganese dioxide nanoparticles are one of the most attractive inorganic materials because of its physical and chemical properties and wide application in the field of pharmaceutical industries, sensors, fuel cell electrodes and catalysis. Antimicrobial activity of manganese dioxide nanoparticles towards both gram negative bacteria (*Escherichia coli, Klebsiella pneumonia*, and *Pseudomonas aeruginosa)* and gram positive bacteria (*Staphylococcusaureus, Bacillus subtilis*) was studied using the well diffusion method.

Keywords: Manganese dioxide nanoparticles; Fourier Transform Infrared Spectroscopy; Scanning Electron microscopy; Antimicrobial activity.

Introduction

Nanotechnology is a branch of science, engineering and technology which deals with dimensions and tolerances of less than 100 nanometers of matter on an atomic or molecular scale. Nanoparticles have wide application due to the unique size dependent properties. Magnetic nanoparticles have been receiving considerable attention because of their wide range of applications, such as the immobilization of the proteins and enzymes, bioseparation, immunoassays, drug delivery, and biosensors (Madhuri et al., 2005). Nanoparticles possess high surface to volume ratio due to its small size which give very distinctive features to nanoparticles (Allaker, 2010; Morones et al., 2005; Jayendran e al., 2015).

Generally metal oxide nanoparticles are inorganic. Various nanoparticles like Fe, Ni, Co, Mn and Zn are enormously accepted magnetic material for a wide range of applications likemagnetic sensors, recording equipments, telecommunications, magnetic fluids, microwave absorbers etc (Willard et al., 2004).

Among various metal oxide nanoparticles manganese dioxide is an important transition metal oxide of P-type semiconducting materials with a band gap of 3.3 eV and 3.8 eV. Generally nanoparticles have been prepared by physical vapor deposition, chemical vapor deposition, aerosol processing, sol-gel process, reverse micelle method, mechanical milling etc. A wet chemical technique such as hydro thermal sol-gel, emulsion and conventional co-precipitation method is commercially widely used because of its cost effective nature (Kumar et al., 2013).

Manganese dioxide nanoparticles have been synthesized in several methods like hydrothermal (Kumar et al., 2013), combustion method (Khattak et al., 2012) and co-precipitation method (Verma., 2013). Two commonly used techniques for immobilizing enzyme onto nanoparticles are covalent binding and physical adsorption. Covalent binding is achieved by the formation of covalent bond between enzyme and the nanoparticle (Abraham et al., 2014). It is considered to be one of the safe route to minimize protein desorption. Advantages of Co-precipitation method include simple and rapid preparative method; ease of control of particle size and composition and also this method help to modify the particle surface state and over all homogeneity.

The present study deals with the synthesis of manganese dioxide nanoparticles using Co-precipitation method and characterization of synthesized nanoparticles. The anti-bacterial activity of manganese dioxide nanoparticles was checked towards *Staphylococcus aureus, Escherichia coli, Klebsiella pneumonia, Bacillus subtilis and Pseudomonas aeruginosa*.

Materials and methods

Synthesis of manganese dioxide nanoparticles

All chemicals used were analytical grade. Manganese dioxide nanoparticles were synthesized by co-precipitation method. 1 M manganese sulfate and 2M sodium hydroxide were used as reactant materials. Freshly prepared 100 ml aqueous solution of 2M NaOH was added drop by drop to 100 ml of 1M $MnSO_4.H_2O$solution. The solution was stirred continuously at 60ºC for 2h to precipitate the nanoparticles. The precipitate was then separated from the reaction mixture and washed several times with deionized water and dried in hot air oven at 100ºC for 12 h (Kumar et al., 2013).

Characterization of manganese dioxide nanoparticles

Optical properties of the nanoparticles were analyzed using UV –VIS spectroscopy. UV-VIS spectrum was recorded on Systronics Double Beam UV-VIS spectrophotometer 2201. The characteristics functional groups present in the synthesized nanoparticles were analyzed using Fourier Transform Infrared Spectroscopy (FT-IR). Particle size and morphology of the synthesized manganese dioxide nanoparticles were analyzed using Scanning Electron Microscope (SEM). The weight percentage of manganese and oxygen was confirmed using Energy Dispersive x-ray Diffractometer SUPRA 55 Carl Zesis, Germany.

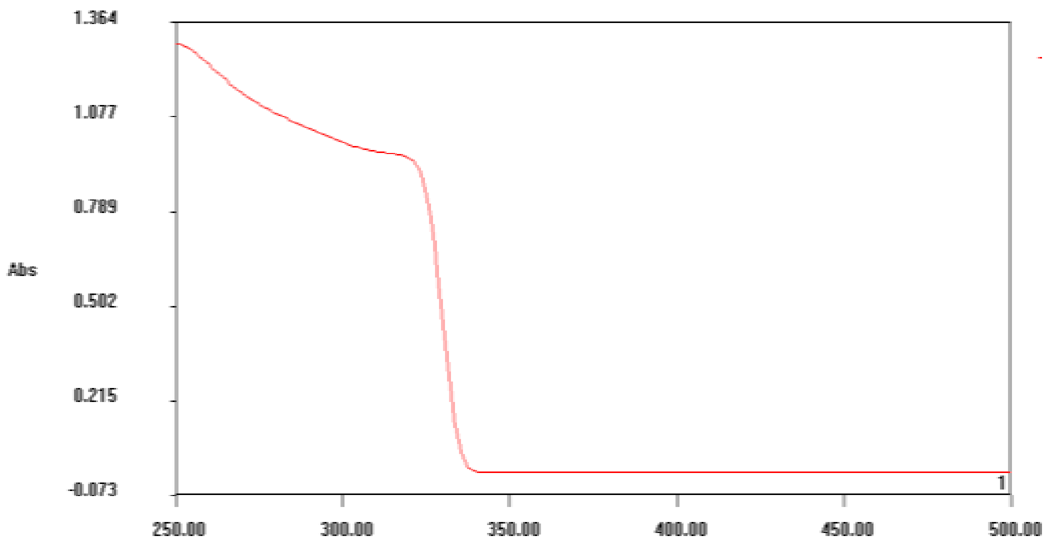
Antimicrobial Assay

Bacteria such as *Staphylococus aureus, Escherichia coli, Klebsiella pneumonia, Bacillus subtilis, and Pseudomonas aeruginosa* were used for the study. Antimicrobial activity of manganese dioxide nanoparticles towards gram positive and negative bacteria was checked using Well diffusion method. 50 µl of each fresh bacterial culture was spread on respective agar plates. Well of 5mm diameter was made in the plates using gel puncher. Wells were loaded with manganese dioxide nanoparticles. This was done for all the five bacterial strains. The plates were incubated for two days in an incubator at 37ºC. The zone of clearance was checked to find the antimicrobial activity of manganese dioxide nanoparticles (Jeeva Lakshmi et al., 2012).

Results and discussions

UV spectrum of manganese dioxide nanoparticles

Optical absorption spectra of manganese dioxide nanoparticles by UV-VIS spectrophotometer in the range of 250nm to 500 nm presented in the Figure 1. An absorption peak at 340 nm indicates the presence of manganese dioxide (Deogratius et al., 2013).



Wave length (nm)

Figure 1. UV –VIS spectrum of synthesized manganese dioxide nanoparticles

FT-IR of manganese dioxide nanoparticles

The FTIR spectroscopy was carried out in order to ascertain the purity and nature of manganese dioxide metal nanoparticles synthesized by co-precipitation method. Functional group present in the synthesized manganese dioxide nanoparticles are shown in Figure 2. The sample have absorption peaks at of 3472cm-^{1}, 2101 cm^{-1}, 1648cm^{-1}, 1143cm^{-1}, 1108cm^{-1}, 998cm^{-1}, 797cm^{-1}, 625cm^{-1}, 567cm^{-1} and 526 cm^{-1}. Absorption bands observed at 625cm^{-1} is associated with the coupling between Mn-O stretching modes of tetrahedral A- and octahedral B- sites as expected from normal spinel structure. Thus, the FTIR spectrum further confirms that the product is manganese dioxide (Zehra et al., 2009). The peak at 1108 cm^{-1} is ascribed to the stretching vibration of C-N bond of alipahatic amine, aromatic C-H in plane bend, cyclic ethers and stretching vibration of C-O bond of alkyl substituted ether. The peak at 1143 cm^{-1} is ascribed to the stretching vibration of C-N bond of alipahatic amine or aromatic amines, stretching vibration of C-F bond aliphatic fluro compounds. The peak at 1648cm^{-1} is ascribed to the stretching vibration of N-H bond of primary and secondary amine, alkyl C=C stretch, open chain imino group. The peak at 2101 cm^{-1} is ascribed to terminal alkynes. The peak at 3472 cm^{-1} is ascribed to the stretching vibration of N-H bond of aromatic primary amine and hetero cyclic secondary amine, alkyl C=C stretch, stretching vibration of O-H bond of alcohols, phenols. The presence of these functional makes the synthesized manganese dioxide nanoparticles as effective antimicrobial agent.

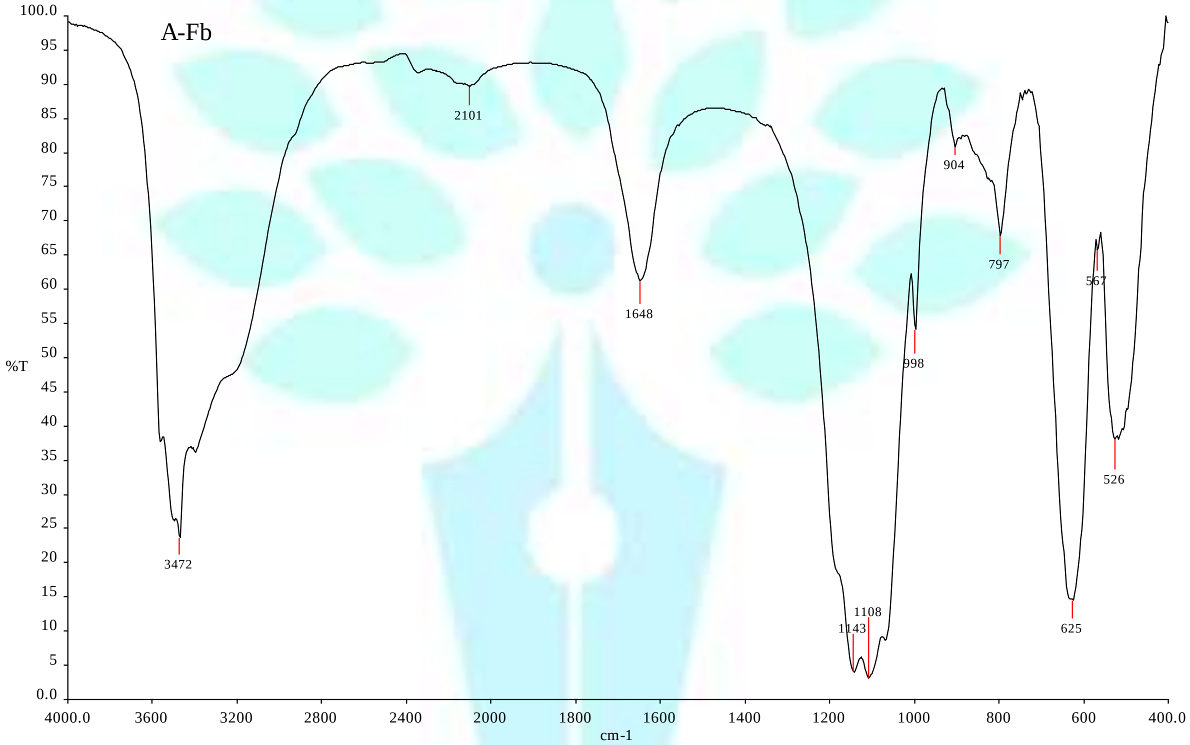


Figure 2. FT-IR spectrum of synthesized manganese dioxide nanoparticles

SEM Analysis of manganese dioxide nanoparticles

Scanning Electron Microscope was used to deduce the particle size and morphology of the synthesized manganese dioxide nanoparticles. It is concluded from Figure3 that the particles in the samples were compactly arranged and were almost spherical in shape. The size of the synthesized manganese dioxide nanoparticles were found to be in the range of 40.5 - 70 nm.

EDX Analysis *of manganese dioxide nanoparticles*

The energy dispersive X-Ray diffractive studies were done to know the elemental composition of the produced manganese dioxide nanoparticles. The Figure 4 showed the elemental analysis of MnO_2 nanoparticles. It shows a very strong signal for Mn and O confirming the existence of MnO_2.

Antimicrobial activity of manganese dioxide nanoparticles

The effect of manganese dioxide nanoparticles on *Staphylococcus aureus*, *Escherichia coli*, *Klebsiella pneumonia*, *Bacillus* *subtilis,* and *Pseudomonas aeruginosa* was studied using well diffusion method.

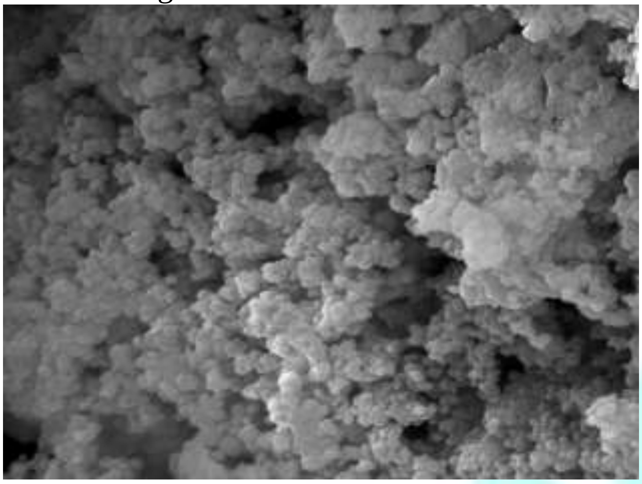


Figure 3. SEM image of synthesized manganese dioxide nanoparticles

Zone of inhibition was observed in all the plates from which it is inferred that manganese dioxide has antimicrobial activity. The antimicrobial activity of manganese dioxide nanoparticles is mainly due to the generation of highly reactive species like membrane OH^-, H_2O_2, and $O_2^{2+\cdot}$ H_2O_2 penetrate the cell. OH^- and O_2^{2+}damage the cell membrane and cell wall from outside. The effect of manganese dioxide nanoparticles on growth of bacterial strain are shown in Figure 5. The values of zone of inhibition obtained are presented in the Table1. Among Gram positive bacteria, the inhibition zone of manganesedioxide nanoparticles against *Staphylococcus aureus* was higher compared to *Bacillus subtilis*. Among Gram negative bacteria, the diameter of inhibition zone of manganese dioxide nanoparticles against *Klebsiella pneumonia*was higher compared to *Escherichia coli and Pseudomonas aeruginosa*.

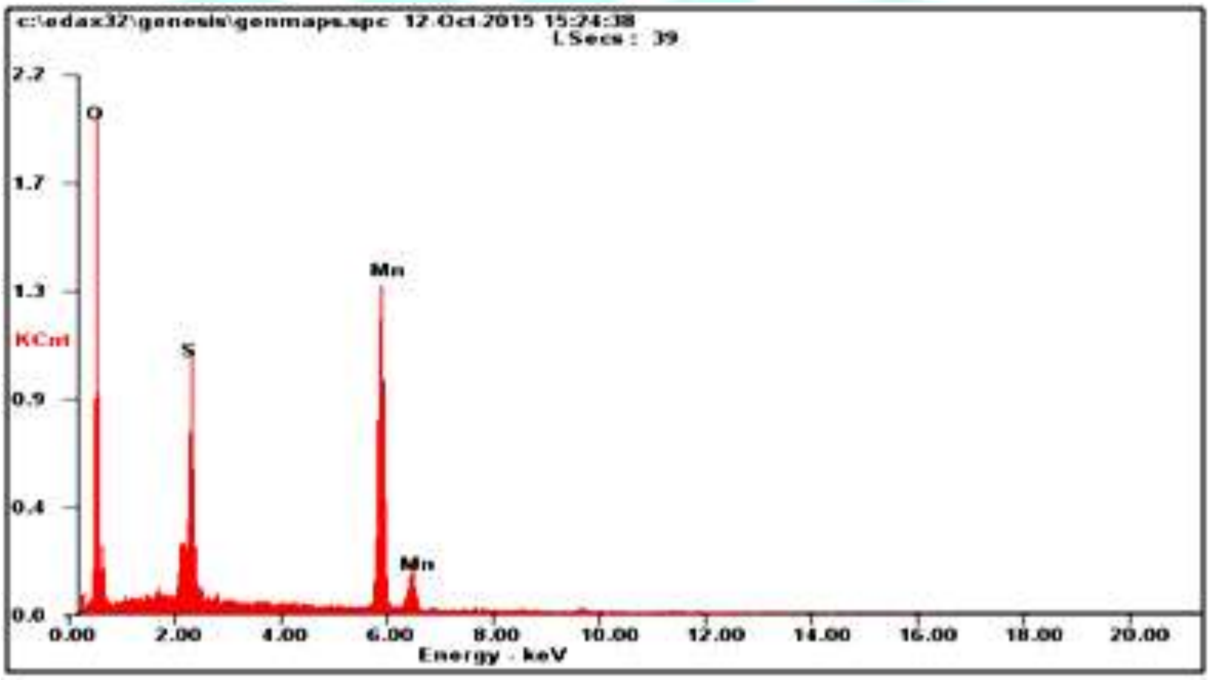


Figure 4. EDX pattern of the manganese dioxide nanoparticles

Table 1. Antibacterial activity of synthesized manganese dioxide nanoparticles at different concentration (I-250 µg/ml), (II-500 µg/ml), (Ш-750 µg/ml), (IV-1000 µg/ml) against pathogenic bacterial species

Label	Bacteria	Zone of Inhibition (mm)			
		I (250 µg/ml)	II (500 µg/ml)	III (750 µg/ml)	IV (1000 µg/ml)
A	*Klebsiella pneumonia*	23	27	28	30
B	*Pseudomonas aeruginosa*	20	23	25	27
C	*Escherichia coli*	16	18	19	21
D	*Staphylococcus aureus*	23	25	28	30
E	*Bacillus subtilis*	22	23	26	30

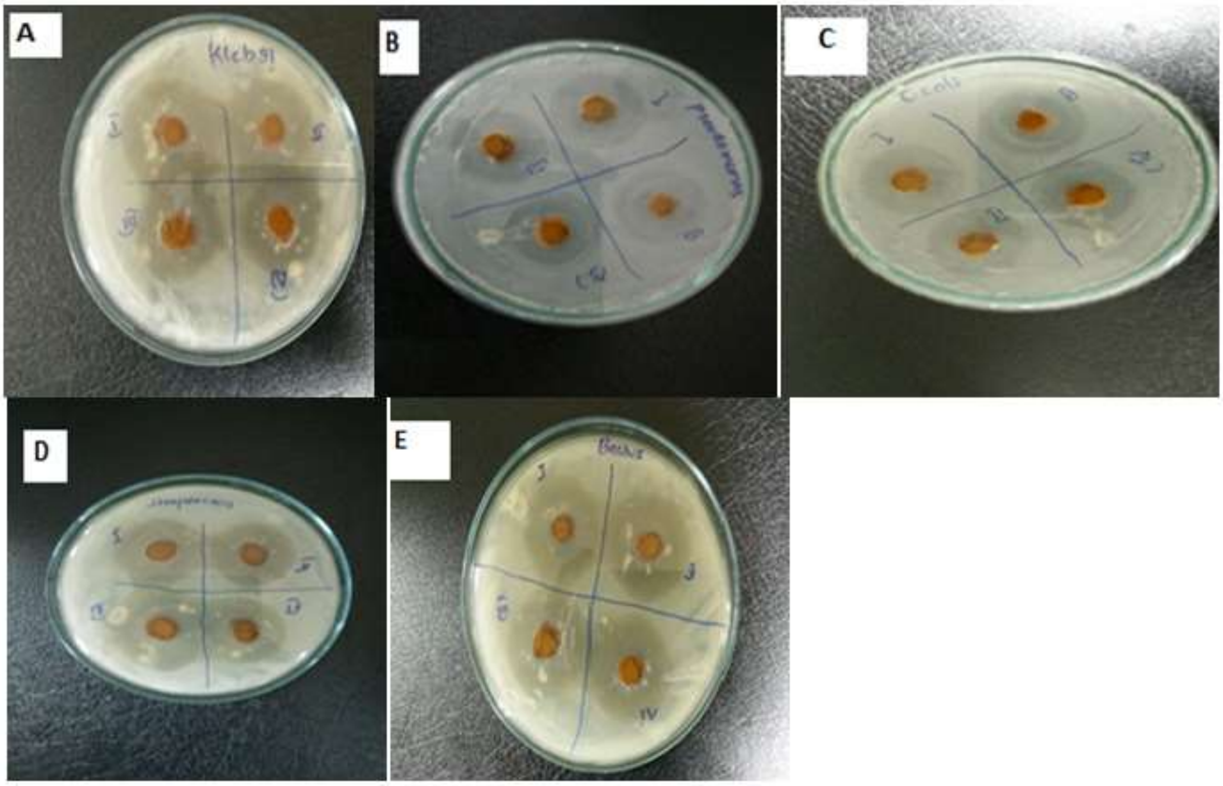


Figure 5. Antimicrobial activity of synthesized manganese dioxide nanoparticles nanoparticles against (a) *Klebsiella pneumonia,* (b) *Pseudomonas aeruginosa,* (c) *Escherichia coli,* (d) *Staphylococcus aureus,* (e) *Bacillus subtilis* at different concentrations

Conclusions

The above study demonstrated the synthesis of manganese dioxide nanoparticles by co-precipitation method. The UV–VIS spectroscopy study confirmed the presence of manganese dioxide nanoparticles. The FT-IR spectral analysis revealed the characteristics peaks of manganese dioxide nanoparticles. Spherical shape with a diameter rage from 40.5 to 70 nm was found out using SEM analysis. Antimicrobial study revealed that synthesized manganese dioxide nanoparticles can be used as antimicrobial agent.

References

1. Madhuri Mandal, Subrata Kundu, Sujit Kumar Ghosh, Sudipa Panigrahi , Tapan K. Sau, Yusuf SM, Tarasankar Pal, Magnetite nanoparticles with tunable gold or silver shell, J Colloid Interface Sci 286 (2005) 187-194
2. Allaker RP, The use of nanoparticles to control oral biofilm formation, J Dent Res 89 (2010) 1175-1186
3. Morones JR, Elechiguerra JL, Camacho A, Holt K, Kouri JB, Ramirez JT, Yacaman MJ, The bactericidal effect of silver nanoparticles, Nanotechnology 16 (2005), 2346-2353
4. Jayendran M, Haneefa M Muhamed, and Balasubramanian VS. Synthesis, Characterization and antimicrobial activities of turmeric curcumin and curcumin stabilized zinc nanoparticles-A green approach. Research Journal of Pharmacy and Technology 8(4) (2015) 445-451.
5. Willard MA, Kurihara LK, Carpenter EE, Calvin S and Harris VG, Chemically prepared magnetic nanoparticles, Int Mater Rev 49 (2004) 125-170.
6. Kumar H, Manisha, Sangwan P. Synthesis and Characterization of MnO_2 nanoparticles using co-precipitation technique, Journal of Chemistry and Chemical Engineering 3(3) (2013) 155-160.
7. Khattak WA, Ul-Islam M and Park JK. Prospects of reusable endogenous hydrolyzing enzymes in bioethanol production by simultaneous saccharification and fermentation, Korean J Chem Eng 29(11) (2012) 1467-82.
8. Verma ML, Chaudhar R, Tsuzuki T, Barrow CJ and Puri M. Immobilization of β-glucosidase on a magnetic nanoparticle

improves thermostability: application in cellobiosehydrolysis, Bioresour Technol 135 (2013) 2-6.

9. Abraham RE, Verma ML, Barrow CJ and Puri M. Suitability of magnetic nanoparticle immobilized cellulases in enhancing enzymatic saccharification of pretreated hemp biomass, Biotechnol Biofuels 7 (2014) 90.
10. Jeeva Lakshmi V, Sharath R, Chandraprabha MN, Neelufar E, Hazra A and Patra M, Synthesis, characterization and evaluation of antimicrobial activity of zinc oxide nanoparticles, J Biochem Tech 3(5) (2012) 151-154.
11. Deogratius J, Mohammad A and Isaac W. Synthesis and characterization of whisker-shaped MnO_2 nanostructure at room temperature, Applied Nanoscience 3(4) (2013)329-333.
12. Zehra D, Huseyin K, Abdulhadi B and Toprakc MS, A green chemical route for the synthesis of mangansese dioxide nanoparticles, Cent Eur J Chem 7(3) (2009) 555-559.

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