

Synthesis and Adsorption Study of Manganese Dioxide Nanoparticles

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Abstract : *In this study deals with the synthesis of manganese dioxide nanoparticles by Hydrothermal and Co-precipitation methods. The morphology of MnO₂ nanoparticles were analysed through various instruments like Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) to get the information related to nanoparticles. The structure of MnO₂ nanoparticle was analysed through Powder X-ray Diffraction (PXRD), Infra Red spectroscopy (IR) and Ultra Violet spectroscopy (UV). Adsorption study of Brilliant Green (BG) and Rhodamine B (RB) was applied and the adsorption behaviour of MnO₂ nanoparticle is compared with ordinary MnO₂. From the percentage removal of dyes, it was known that the MnO₂ nanoparticles are having high adsorption activity than the ordinary MnO₂ to adsorb Brilliant Green (BG) and Rhodamine B (RB).*

1. Introduction

In recent years, there has been an exponential interest in the development of novel drug delivery systems using nanoparticles. Now a days, cleaning of environment is concentrated thoroughly by the research articles. Dyes are one of the factor to cause the air pollution in the society for affecting the living style of all organism present in the land. To remove the dye is very essential from the effluent mixing in the river or other water source^[1]. This project analyses the structure and activity of nanoparticles and adsorption activity of nanoparticle to apply the nanoparticles for develop the pollutant free environment i.e., Green chemistry^[2]. Nanomaterials^[3] are having a length scale less than 100 nm which are having their potential applications of fascinating electrical, magnetic and catalytic properties^[4]. Compared to bulk active electrode materials, the corresponding nanomaterials possess more excellent electrochemical activity, such as higher capacities, larger surface areas and lower current densities, so that, nanomaterials have vastly applied in electrochemistry field. This is due to unique size dependent properties of nanoparticles, which are often thought as a separate and intermediate state

of matter lying between individual atoms and bulk material. One-dimensional manganese dioxide (MnO₂) nanostructures such as nanorods, nanowires and nanofibers^[5-10] have produced to intense science research over the decade due to their superior optical, electrical, catalytic, magnetic and electrochemical properties. MnO₂ exists in different structural forms, α -, β -, γ -, δ -, ϵ - and λ -types. The basic structural unit is [MnO₆] and it is an octahedron. Among various approaches of fabricating manganese dioxide, hydrothermal^[11-15], microemulsion^[16-18] and conventional co-precipitation method is commercially widely used because of its cost-effective^[19-24]. A number of advanced waste water treatment schemes have been proposed for water quality environment. Most of these treatment methods use a combination of biological, chemical and physical processes. Recently treatment by nano MnO₂ is used to study the adsorption of two specific dyes and compared with the ordinary MnO₂. There will be so many factors influencing adsorption like temperature, pressure, nature of the adsorbents, nature of the adsorbate, number of active sites available, pH and contact time. In this study the adsorption is carried out by fixing all the parameter with variation of initial concentration of dyes.

Aim and objectives of present work

1. To study the synthesis of MnO₂ nanoparticles by Hydrothermal and Co-precipitation methods.
2. To investigate the morphology of MnO₂ nanoparticles through various instruments like Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM)
3. To analyse the structure of MnO₂ nanoparticle through Powder X-ray Diffraction (PXRD), Infra Red spectroscopy (IR) and Ultra Violet spectroscopy (UV).
4. To apply the adsorption study of Brilliant Green (BG) and Rhodamine B (RB) by MnO₂ nanoparticles.
5. To compare the adsorption behaviour of MnO₂ nanoparticle with ordinary MnO₂.

2. Experimental Methods

In the hydrothermal method, MnCl_2 (0.18 g) mixed with isopropanol (50 mL) was heated to 83°C in a refluxing process, and then KMnO_4 (0.10 g) dissolved in Deionised water (5 mL) was added to the solution. Finally, MnO_2 nanoneedles were obtained. Singly-crystal nanowires of α - and β - MnO_2 have been prepared in a hydrothermal procedures employing Mn^{2+} with oxidizing reagents such as $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or KMnO_4 .

In a typical procedure, Mn_2O_3 powders (2g) were dispersed in NaOH aqueous solution (10 mol.dm^{-3}) and then heated at 170°C for 12 hour to 1 week. In the synthesis, KNO_3 , NaNO_3 and LiNO_3 are applied as the reaction media. α - MnO_2 and β - MnO_2 nanoparticles have been synthesized by a hydrothermal treatment of KMnO_4 in HCl solution.

The co-precipitation method was performed by using manganese salts of two different anions which are manganese (II) sulphate and manganese oxalate. Both salts of equal concentration i.e., 0.2M are mixed with continuous stirring at a constant temperature of 60°C . While stirring, NaOH solution was added till the pH of the solutions become 12. The stirring was continued for 1 hour at constant temperature of 60°C . Brown precipitates formed was then filtered and washed with ethanol. Precipitates were dried for overnight at 100°C . Then the precipitates were kept in muffle furnace at 500°C for 4 hrs.

2.1 Characterization of MnO_2 Nanoparticles

The properties of formed MnO_2 nanoparticles prepared by hydrothermal method were determined by TEM and SEM.

Powder X-ray Diffraction (PXRD) is one of the primary techniques used by mineralogists and solid state chemists to examine the physico-chemical make-up of unknown materials. Diffraction pattern gives information on translational symmetry - size and shape of the unit cell from Peak Positions and information on electron density inside the unit cell, namely where the atoms are located from Peak Intensities. It also gives information on deviations from a perfect particle, if size is less than roughly 100 – 200nm, extended defects and micro strain from Peak Shapes & Widths. The characteristic of formed MnO_2 nanoparticle was analysed by using PXRD patterns which were obtained from a Philips PW/1050/70/76 X-ray diffractometer using $\text{CuK}\alpha$ radiation at a scan rate of $2^\circ/\text{minutes}$.

FTIR spectroscopy is widely used to study the nature of surface adsorbents in nanoparticles. Since the nanoparticles possess large surface area, the modification of the surface by a suitable adsorbate can generate different properties. Fourier Transform Infra-Red spectroscopy (FTIR) (Thermo-USA, FTIR-380) in the wavelength range $400\text{-}4000 \text{ cm}^{-1}$.

The ultraviolet spectrum for a compound is obtained by exposing a sample of the compound to ultraviolet light from a light source, such as Xenon lamp. Ultraviolet-Visible (UV-Vis) spectrophotometer (UV-500, U-2001) is used to analyse the MnO_2 nanoparticle.

2.2 Adsorption Activity of MnO_2 nanoparticles on Brilliant Green and Rhodamine B

In order to evaluate adsorption activity of the combustion derived MnO_2 sample, batch adsorption studies of Brilliant Green (BG) and Rhodamine B (RB) dyes were done. A typical experiment constitutes 50 ml of dye solutions (BG and RB) with different amount of adsorbate and MnO_2 nanoparticles were taken in a glass reactor. The mixture was stirred in dark for 30 minutes to establish the adsorption equilibrium between the dye molecules and the catalyst surface. The decolorization efficiency (%) was calculated as follows

$$\% \text{ Removal} = [C_0 - C] / C_0 \times 100$$

Where C_0 is the initial concentration of dyes and C is the concentration of dyes after adsorption.

3. Result and Discussion

The results getting by the various instruments for the characterization of MnO_2 nanoparticles prepared by hydrothermal method and co-precipitation method were analysed and confirmed. The adsorption activity of MnO_2 nanoparticles are also studied with Brilliant Green (BG) and Rhodamine B (RB) dyes.

3.1 TEM AND SEM

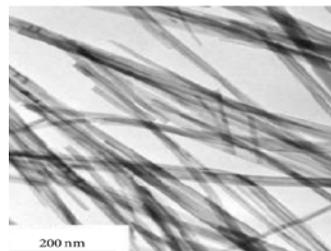


FIGURE 3.1

TEM IMAGE OF α -MnO₂ CRYSTALLINE NANOWIRES

In the hydrothermal synthesis, α -MnO is a (2 × 2) and (1 × 1) tunnel structure, and large ions (K⁺) are needed to support the framework. Then, KNO₃ was used as molten salt to prepare α -MnO nanomaterials. β -MnO is a (1 × 1) tunnel structure, so a mixture of NaNO₃ and LiNO₃ with smaller cation is selected. This is shown in Figure 3.1.

As shown in Figure 3.2, the obtained nanotubes have an average outer diameter of 200 nm and the wall thickness of 30 nm, and the length is up to several microns. It is found that the nanotubes are formed via solid nanorods.

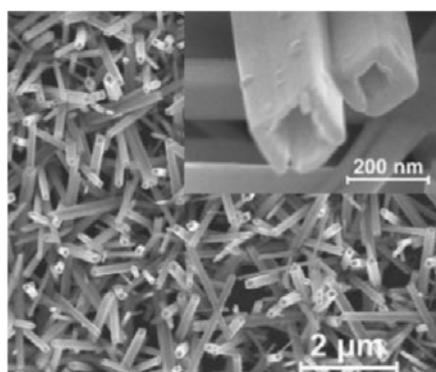


FIGURE 3.2
SEM IMAGE OF MnO₂ NANOTUBES

3.2 Powder X-ray Diffraction

The result shows the PXRD pattern of the MnO₂ powder prepared using ODH as fuel in stoichiometric fuel-to-oxidant ratio at 300°C. The typical PXRD patterns show broad diffraction peaks corresponding to Bragg's reflections from (120), (131), (300), (160) and (003) planes which corresponds to gamma phase MnO₂ (according with JCPDS 14-644) with no other impurity peaks. The crystallite size was estimated using Scherrer's formula given by the relation Powder X-ray diffraction study of manganese oxide metal nanoparticles synthesized by co-precipitation method were shown in Figure 3.3.

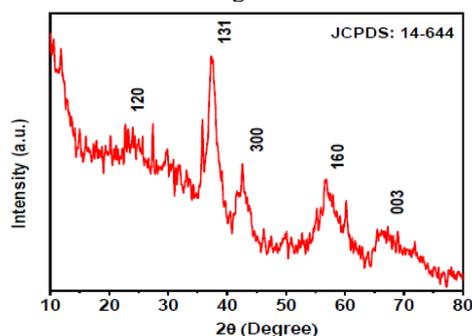


FIGURE 3.3
PXRD PATTERN OF MnO₂ NANOPOWDER

SYNTHESIZED BY CO-PRECIPITATION METHOD.

$$D = 0.9 \lambda / \beta \cos\theta$$

The crystallite size estimated by this method is found to be in the range 15-20 nm.

3.3 FT-IR Spectroscopy

FTIR spectroscopy was carried out in order to ascertain the purity and nature of manganese dioxide metal nanoparticles as synthesized by co-precipitation method. FT-IR spectra of manganese dioxide metal nanoparticles synthesized by co-precipitation method is shown in Figure 3.4.

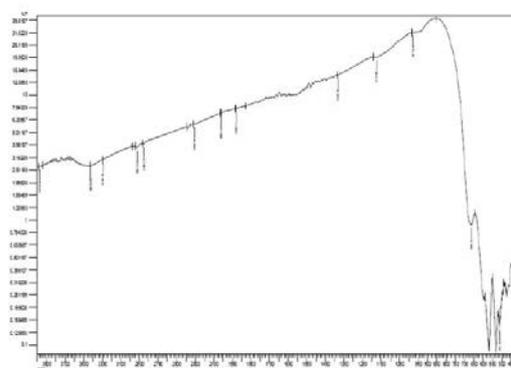


FIGURE 3.4
FT-IR SPECTRA OF MnO₂ NANOPARTICLES SYNTHESIZED BY CO-PRECIPITATION METHOD.

Oxides and hydroxides of metal nanoparticles generally gives absorption peak in the finger print region i.e. below wavelength of 1000 nm arising from inter-atomic vibrations. The bands at 515 and 480 cm⁻¹ correspond to the Mn–O bond. From the above result we conclude that the synthesized nanomaterial is manganese oxide. Absorption peak observed at 2924.09 cm⁻¹ may be due to -CH₃ stretching vibrations.

The absorption peaks at 2852.72 cm⁻¹, 2021.40 cm⁻¹ and 1382.96 cm⁻¹ may be due to –CH₂ stretching, =C–H stretching and –C–H stretching vibrations.

3.4 UV- VISIBLE Spectroscopy

The MnO₂ nanoparticles were analysed by using UV-visible spectroscopy. The UV-visible absorption shows sharp absorption at 339.60 nm due to manganese oxide metal nanoparticles. UV-Visible spectra of manganese oxide metal nanoparticles synthesized by co-precipitation method as a function of wavelength is shown in Figure 4.5.

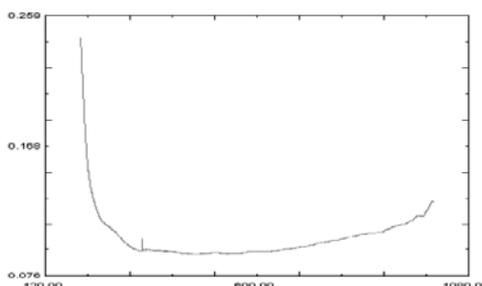


FIGURE 4.5
UV-VISIBLE SPECTRA OF MnO₂ NANOPARTICLES

MnO₂ nanoparticles of simple cubic structure were synthesized by co-precipitation method using green chemistry. The FT-IR spectral analysis reveals the characteristics peaks of Mn-O stretching. The UV-visible absorption shows sharp absorption at 339.60 nm due to metal nanoparticles.

3.5 ADSORPTION ACTIVITY OF MnO₂ NANO PARTICLES ON BRILLIANT GREEN AND RHODAMINE B

About 20 mg of MnO₂ nanoparticle and ordinary MnO₂ were kept together with the Brilliant Green (BG) and Rhodamine B (RB) dyes prepared in various different concentration at neutral pH and 30 minutes contact time. It was observed that both adsorbents (MnO₂ nanoparticle and ordinary MnO₂) gives the increasing adsorption increases up to certain level and beyond this level there was a sudden reduction.

TABLE 3.1
ADSORPTION OF BRILLIANT GREEN (BG) AND RHODAMINE B (RB) DYES BY NANO AND ORDINARY MnO₂

Concentration (ppm)	BG by Nano MnO ₂	RB by Nano MnO ₂	BG by Ord. MnO ₂	RB by Ord. MnO ₂
6	62.89	57.56	37.9	33.87
7	62.91	57.99	38.29	34.10
8	63.89	58.34	39.12	35.29
9	63.98	58.44	40.22	36.89
10	65.43	59.02	40.57	39.88
11	65.43	59	41.60	38.56
12	66.72	58.88	41.64	38.29

The increase in the adsorption efficiency may be due to increase in the active sites available on the adsorbent. Decrease in adsorption beyond certain level is due to desorption of dye due to increased collisions between adsorbent.

The data related to the adsorption activity of Brilliant Green (BG) and Rhodamine B (RB)

dyes on ordinary and nano MnO₂ were tabulated in Table 3.1 and picturised in Figure 3.6 and 3.7.

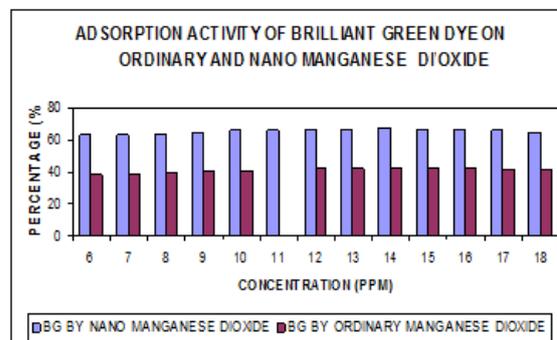


FIGURE 3.6
ADSORPTION OF BG DYE ON NANO AND ORDINARY MnO₂ NANOPARTICLES

The percentage removal of MnO₂ nanoparticle for Brilliant Green (BG) and Rhodamine B (RB) were found as 67 %, 59.02% and ordinary MnO₂ was found as 42.13 %, 39.88 % respectively.

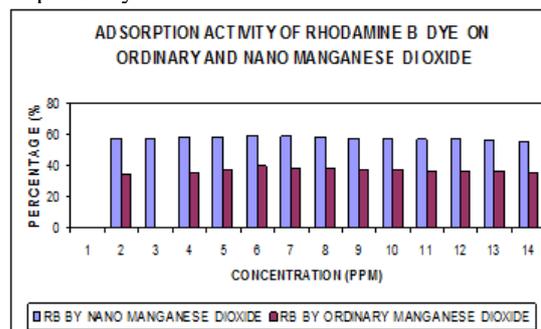


FIGURE 3.7
ADSORPTION OF RB DYE ON NANO AND ORDINARY MnO₂ NANOPARTICLES

Thus MnO₂ nanoparticles are having high adsorption activity than the ordinary MnO₂ to adsorb Brilliant Green (BG) and Rhodamine B (RB).

4. Conclusion

The present study deals with the synthesis of MnO₂ nanoparticles by Hydrothermal and Co-precipitation methods. The morphology of MnO₂ nanoparticles were analysed through various instruments like Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) to get the information related to nanoparticles. The structure of MnO₂ nanoparticle was analysed through Powder X-ray Diffraction (PXRD), Infra Red spectroscopy (IR) and Ultra Violet spectroscopy (UV). The PXRD pattern

shows the crystallite size estimated is found to be in the range 15-20 nm. The UV-visible absorption shows sharp absorption at 339.60 nm due to metal nanoparticles. Adsorption study of Brilliant Green (BG) and Rhodamine B (RB) was applied by MnO₂ nanoparticles. Adsorption behaviour of MnO₂ nanoparticle is compared with ordinary MnO₂. The percentage removal of MnO₂ nanoparticle for Brilliant Green (BG) and Rhodamine B (RB) were found as 67 %, 59.02% and ordinary MnO₂ was found as 42.13 %, 39.88 % respectively. The MnO₂ nanoparticles are having high adsorption activity than the ordinary MnO₂ to adsorb Brilliant Green (BG) and Rhodamine B (RB).

6. References

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