Abstract. A surfactant assisted precipitation method is employed for the preparation of nanostructured magnesium oxide with flake-like nanoparticles. The influence of surfactant on the crystallite size and morphology of MgO was studied using various parameters. The synthesized MgO nanomaterials were characterized by using Fourier transform infrared spectroscopy (FT-IR), powder X-ray power diffraction (XRD), Field Emission Scanning Electron Microscopy (FFSEM) and Field Emission Transmission Electron Microscopy (FETEM) in order to evaluate the formation, crystalline phase morphologies, microstructures and chemical compositions. The XRD analysis revealed the average crystalline size of 15.34 nm with cubic structure. The crystallite size increased with increasing amount of Poly Ethylene Glycols (PEG). FFSEM and FETEM showed that the surfactant strongly affect the size and morphology of nanostructure. FT-IR spectroscopy studies indicated the formation of MgO with the characteristic vibration mode of Mg-O. Further, the antibacterial effect of MgO nanoparticles evaluated against pathogenic bacteria by agar diffusion method showed that the nanoparticles have reasonable antibacterial activity against both gram positive (S.aureus) and gram negative (E.coli) pathogenic bacterial strains and retains potential application in pharmaceutical and biomedical industries.

1. Introduction

Over the past decade, nanoparticle technology is significantly considered for a large number of practical applications as it can provide large surface area materials. Several researchers have developed simpler and inexpensive techniques to produce nanoparticles. Among the various oxide nanoparticles, magnesium oxide is widely used in various areas such as waste remediation, refractory materials, pharmaceutical, glass industry and catalysis [1]. Also used in energy storage, electronics, chemical and industrial applications based on versatile properties [2]. Now a day’s nano MgO is also used in antibacterial activity.

Shah reported that the materials prepared in the form of very small particles, change their properties significantly, sometimes to the coverage that completely new phenomenon are established [3]. A highly defective co-ordination environment is exhibited by the constituting atoms when particle size is scaled down to form nanometer. Limited papers are available about the variation of biological activities when constituent particles are decreased to nanoscale dimensions. Nanoscale one dimensional materials, such as nanorods, nanowires, nanoflowers and nanowhiskers have forced great concentration, due to their consequence in potential technological application and basic scientific research. Two dimensional (2D) materials, nano plates have received severe research due to their potential applications in energy storage, electronics and catalysis.

Nanotechnology plays an important role in improving the activity of inorganic antibacterial agents. Roselli et al. (2003) and Tang et al. (2012) [4, 5] have investigated the metal oxide nanoparticles such as CaO, ZnO and MgO as inorganic antibacterial agents. Nanoparticles are recognized as antibacterial agents due to their size, structure and surface properties [6]. The novel and useful properties of MgO are further superior when used as nano size powder. Many different synthetic ways offer MgO nano scale, including sol-gel [7], combustion aerosol synthesis [8], hydrothermal process [9], chemical precipitation [2], surfactant method [10], surfactant assisted precipitation method [11] and co-precipitation methods [12,13] etc.
In this present work, we express a simple co-precipitation method to synthesize MgO nanoparticles using sodium hydroxide as precipitating agent and magnesium nitrate as precursor in the presence of polyethylene glycols. The use of PEG with different concentrations and detailed discussion of the influence of this parameter on products properties certainly represents the originality of this work compared with the previous literature. The present approach has the advantage of easier work-up lower cost, milder conditions and more suitability without any special equipment such as high pressure and high temperature.

2. Methodology

All the chemicals were of analytical grade and they were used without further purification, Magnesium nitrate hexahydrate Mg (NO$_3$)$_2$.6H$_2$O, polyethylene glycol (PEG 6000) and sodium hydroxide were purchased from Merck products.

2.1 Experimental methods

In the typical experiment 0.2M Mg(NO$_3$)$_2$.6H$_2$O was dissolved in 40 ml distilled water and Subsequently, 40 ml of a 0.2M NaOH solution was added drop wise into Mg(NO$_3$)$_2$.6H$_2$O solution and the resulting mixture was constantly stirred for 4 hrs at room temperature to form a white suspension. After completion of this whole reaction process, white precipitate formed at the bottom of the flask was separated carefully from the supernatant liquid under vacuum pressure. The above precipitation was washed thoroughly with the help of doubly distilled water to make the precipitate free from tracer of foreign elements. The resulting precipitate was kept in air oven for proper drying at 80°C for 6 hours for drying. Then the white precipitate was calcined at 500°C for 4 hours to obtain nanoparticles. The white color of the final product resembles with the natural color of the MgO.

Keeping the molar concentration of 0.2M Mg (NH$_3$)$_2$.6H$_2$O and 0.2M NaOH as constant, PEG is varied. In this process, a mixture of a specific amount of PEG and 2.05g Mg (NO$_3$)$_2$. was dissolved in 40ml distilled water under stirring condition. 40ml of a 0.32g NaOH solution was then added drop wise into as obtained liquid, and same procedure was carried out for synthesis of sample A (ie absence of PEG). Finally, a series of samples was produced and denoted as B, C and D respectively, according to different PEG amounts (0.1, 0.2 and 0.3g) used.

2.2 Disc diffusion method for antibacterial activity

The agar disc diffusion method was carried out to establish the antibacterial activity of the MgO nanoparticles against the test pathogens of S. aureus and E. coli are selected (Sundararajan et al.,) [14]. Bacterial cultures were grown overnight at 37˚C by adding a single colony in 100 ml Luria Bertani Broth. Transfer inoculums from the tube onto a nutrient agar plate using a 10 ml loop incubating disk diffusion agar plates at 37˚C for 16 to 18 hours in ambient air. E. coli and S. aureus cultures (0.1 ml each) were plated out onto individual Nutrient Agar plates using the Aseptic technique. Holes/Wells were made on the nutrient agar inoculated with bacteria and (about 0.5 mg) MgO nanoparticle suspensions were decanted into the wells and the plates were incubated overnight at 37˚C. Control was maintained with solvent alone [15]. The Zone of inhibition is the area in which the bacterial growth is stopped due to bacteriostatic effect, the diameter of which is measured against the control strain and measured using calipers.

2.3 Characterization

Thermal gravimetric and differential thermal gravimetric (TGA/DTA) analyses were performed under Argon flow at a heating rate of 10 C/min using NETZSCH-STA 449 F3 JUPITER instrument. The powder samples were then analyzed with an X-ray diffract meter (PANalytical X’Pert-Pro) using the Cu-ka radiation of wave length 1.5406 Å to determine their crystal structure and phase. The FTIR spectra were recorded using a SHIMADZU-8400 spectrometer with KBr pellets in the range of 400-4000 cm. The FESEM with EDAX images were recorded using JSM 6701F SEM instrument in order to analyze the structure and morphology of synthesized MgO samples. FE-TEM with SAED patterns have been used for morphology was performed using JEM.
2100F. Antibacterial activity studies were carried out the agar disc diffusion method. The zone of inhibition was measured around the discs (mm diameter).

3. Results and discussion

3.1 TG-DTA

![Fig. 1. A) TG-DTA analysis of the precursors Mg(OH)\(_2\) without PEG modification; B) TG-DTA analysis of the precursors Mg(OH)\(_2\) with PEG modification.](image)

Fig. 1 shows decomposition behavior and thermal stability of precursors for both samples MgO and MgO-PEG. A typical TG-DTA profile (Fig. 1A) shows weight loss occurring in two steps. The first small weight loss is due to the removal of adsorbed water/alcohol below 100 °C. A pronounced weight loss occurs in the temperature range of 310°C to 450°C, and a corresponding well-defined endothermic peak is observed at 405°C in the DTA curve that could be attributed to the decomposition of Mg (OH)\(_2\) into MgO.

\[
\text{Mg (OH)}_2 \xrightarrow{\text{decomposition}} \text{MgO + H}_2\text{O}
\]

However, the observed weight loss from 310 to 450°C is 30% weight loss which is slightly lower than the theoretical value from Mg (OH)\(_2\) to MgO transformation (30.8% weight loss), which could be due to the incompleteness of the decomposition of Mg (OH)\(_2\) in a short time during this temperature range [2].

A typical TG-DTA profile (Fig. 1B) shows weight loss occurring in two steps. The first small weight loss at below 100 °C is related to the loss of free water. The major (second) weight loss in the temperature range of 310°C - 450 °C is related to decomposition of Mg (OH)\(_2\) and crystallization of MgO particles. The strong endothermic peak observed at about 405 °C in the DTA curve could be attributed to the decomposition of Mg (OH)\(_2\). The 29.5 % weight loss observed from 310 °C to 450 °C, which is in a good agreement with the theoretical value from Mg(OH)\(_2\) to MgO transformation (30.7 wt.%), which could be due to the incompleteness of the decomposition of Mg (OH)\(_2\) in a short time during this temperature range. Thus DTA/TGA results indicated that the formation of MgO was observed in the temperature 500°C in air and this analysis is in good agreement with the reported survey of Mehran Rezaei et.al., [10].

A endothermic peak at 405 °C is observed in both cases of pure and PEG added precursor, and also similar TG-DTA curves are obtained for both pure and PEG added precursors Mg (OH)2. No weight loss occurred above 500°C in both cases reveal the formation of MgO and MgO-PEG.

3.2 XRD Analyses

Keeping the molar concentration of 0.2M Mg (NH\(_3\))\(_2\) 6H\(_2\)O and molar concentration of O.2M NaOH as constant, the same preparation procedure was followed for MgO with different amount of PEGs. XRD patterns of the prepared MgO calcined at 500°C (i.e sample A) and with different amount of PEGs 0.1g, 0.2g and 0.3g are named as B, C and D respectively. The obtained fundamental peaks due to the diffraction of MgO on the plane ( 111), (200), (220), (311) and (222) for the synthesized sample A, is in good conformity with the standard data (JCPDS Card no. 74-1225) [16]. Absence of additional peaks due to impurities shows the pure form of MgO.
nanoparticles. Similar reflections from the planes (111), (200), (220), (311), and (222) were observed for samples B, C and D indicating the cubic structure of magnesium oxide. The crystallite sizes were calculated on the (111), (200) and (220) diffraction maxima from the half-width of diffraction peaks using Debye Scherrer’s formula. The calculated crystallite sizes are 14.76nm, 15.48nm and 15.78nm for the samples B, C and D respectively. As it can be seen, the crystallite size increases with the increase in concentration of PEGs. The XRD patterns indicate that the addition of polymer does not change the structure of MgO crystal [17]. The MgO crystallites are about 8.62 nm and this increased to 15.34 nm with when the addition of PEG. The increase in intensity of the peak corresponding to the plane (200) with increasing PEG content indicates that under this experimental conditions PEG favors the growth along the atomic plane (002) [18].

![X-ray diffraction patterns](image_url)

**Fig. 2.** X-ray diffraction patterns of MgO samples prepared with different amount of PEG used: A) 0g B) 0.1g C) 0.2g and D) 0.3g are named as samples A, B, C and D respectively.

**Table 1.** Different amount of surfactant added with precursor MgO nanoparticles.

| S.no | MgO nanoparticles samples | Amount of surfactant | Average grain size |
|------|---------------------------|----------------------|--------------------|
| 1    | A                         | _                    | 8.62               |
| 2    | B                         | 0.1                  | 14.76              |
| 3    | C                         | 0.2                  | 15.48              |
| 4    | D                         | 0.3                  | 15.78              |

3.3 FTIR

Fig. 3A shows the FTIR spectrum of MgO nanoparticles. The sharp and intense peak at 3699 cm⁻¹ was due to the OH group in Mg (OH)₂ and the strong peak at around 445 cm⁻¹ corresponds to Mg-O stretching vibrations. The weak absorption band at 2372 cm⁻¹ is ascribed to the stretching vibrations of CO₂ due to adsorption of atmospheric carbon dioxide [19].

In the FTIR spectrum Fig. 3B of the MgO-PEG, the sharp and intense peak at 3695 cm⁻¹ was due to the OH group in Mg (OH)₂, the strong peak at around 513 cm⁻¹ was assigned to the Mg–O stretching vibration. Bands in the range of 1419, 1463 and 1514 cm⁻¹ were attributed to the –OH stretching mode in water. In addition, the FTIR spectrum of MgO-PEG shows the peaks 1118 and 1091 cm⁻¹ are also corresponded to the existence of the block copolymer surfactant [10]. A slight shift in stretching vibration band (i.e. from 445 cm⁻¹ to 513 cm⁻¹) is observed, when PEG is added into precursor.
Fig. 3. FTIR spectrum of A) MgO nanoparticle and B) addition of surfactant (i.e MgO-PEG).

Fig. 4. FESEM micrographs of samples prepared A) MgO B) with addition of surfactant C) EDAX image of with addition of surfactant.

3.4 Morphological Analysis
3.4.1 FESEM with EDAX Analysis
The FESEM images of the pure MgO (sample A) and with surfactant (sample B) are shown in Fig. 4A and B respectively. It is seen that the morphology of particles in these two samples are different. In sample A, MgO nanoparticles are agglomerated together [20], where as flakes shape is observed in sample B. FESEM image reveals the change in morphology of particles with the addition of surfactant. FESEM image of sample B exhibit flakes-like structures formed due to the aggregation of several thousands of nanoparticles. The flakes are dense and interconnected with each other such that no clear boundaries exist between one another [19]. The EDAX analysis of MgO-PEG is shown in Fig. 4C. The EDAX spectrum confirms the presence of elements Mg and O, along with Au and C due to the coating material used.
Fig. 5. A) FETEM micrographs of prepared MgO samples with B) SAED pattern. C) FETEM analysis of prepared MgO-PEG nanoflake-like structure nanoparticles with D) SAED pattern.

3.5 Antibacterial study

MgO nanoparticles showed the bactericidal activity against both gram-positive and gram-negative bacteria. Yamamoto et al. investigated antibacterial activity of MgO against E.coli and S.aureus and reported that good antibacterial activity of MgO nanocomposites was observed against gram-positive (S.aureus) than against gram-negative (E.coli) bacteria [22]. The pure MgO and PEG-MgO nanoparticles are taken for antibacterial activity and tested against two bacteria namely S. aureus and E. coli are tabulated (Table 2). Antibacterial activities towards bacteria E.coli MTCC1195 and S.aureus MTCC3160 at different concentrations of pure and addition of PEG-magnesium oxide nanoparticles. The zones of inhibition, the clearing zones around the disc without visible bacterial growth, were measured from plates. The zone of inhibition of MgO-PEG is slightly increased compared to pure MgO nanoparticles. Gentamycin is a positive control, for which the zone of inhibition, is ranged from 13 to 29 mm. The highest mean zone of inhibition 15 mm, is recorded for 600 mg / ml against S. aureus. The maximum bacterial effect is observed S. aureus, which is because of the easier interaction with the bacteria, and this causes the distortion of the membrane structure of cell wall of bacteria. The zone of inhibition is observed to be 11mm and 13 mm for 500 mg / ml for pure MgO which may be due to minimum generation of oxygen species from the pure MgO nanoparticles. The mechanism of antibacterial effect of MgO was due to the formation of superoxide on their surface. The positively charged particles can interact strongly with negatively charged bacteria.
Fig. 6. Antibacterial activity (zone of inhibition) images of A) pure MgO nanoparticles against pathogen S. aureus bacteria, B) pure MgO nanoparticles against pathogens E. coli bacteria, C) addition of PEG-MgO nanoparticles against pathogens S. aureus bacteria and D) addition of PEG-MgO nanoparticles against pathogens E. coli bacteria.

Table 2. Antibacterial assessment by agar diffusion method.

| Concentration (mg / ml) | Zone inhibition diameter(mm) | S.aureus(Gram negative) | E.coli (Gram positive) |
|-------------------------|------------------------------|--------------------------|------------------------|
|                         | Pure MgO                     | MgO-PEG                  | Pure MgO               | MgO-PEG |
| 500                     | 12                           | 13                       | 10                     | 11      |
| 600                     | 14                           | 15                       | 12                     | 13      |

4. Conclusions

Nanocrystalline MgO nanoflakes were synthesized by co-precipitation method in the presence of a non ionic surfactant polyethylene glycol (PEG-6000) at 500°C. The powder x-ray analysis confirmed the crystalline size and the fundamental diffraction patterns of MgO. FTIR studies confirmed the formation of MgO with the characteristic vibration mode of Mg-O and large number of hydroxyl radicals on the surface. The field emission scanning electron microscopy (FESEM) and EDAS analysis reveals the flake-like structure and elements present in the samples. The MgO nanoparticles with flake-like structure were obtained with the addition of PEG also the agglomeration seems to be less. The observation shows the important role played by surfactant in controlling the morphology. The FETEM and SAED results confirmed that the nanoparticles are cubic in nature and supported by XRD reports. The antibacterial activity of the prepared MgO nanoparticles was studied using agar diffusion method. The antibacterial activity of the prepared samples shows good performance against S. aureus (gram positive) compare to E. coli (gram negative) bacteria.
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