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Nanoceria Tween-assisted synthesis, characterization, photocatalytic efficiency and antimicrobial activity

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Abstract

Ceria nanoparticles (CeO_2 NPs) have been synthesized by wet chemical technique using NH_4OH precipitation method. CeO_2 NPs were prepared in presence of different concentration of the non-ionic surfactants Tween 20 and 80 of hydrophilic-lipophilic balance (HLB) of 16.7 and 15.0, respectively, to improve and controlling the size and shape of CeO_2 -NPs. The role of these surfactants in controlling the size of CeO_2 NPs has been discussed. The synthesized CeO_2 NPs were characterized by Fourier transform infrared (FT-IR), Raman spectroscopy, UV-Visible spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The TEM micrographs and XRD patterns confirmed the semi-spherical structure of CeO_2 NPs with ultrafine particle sizes ranging from 5.9 nm to 11.0 nm. FT-IR and Raman spectral analysis confirmed the identities of the oxides. In vitro antimicrobial studies show significant zone of inhibition against bacterial and fungal strains. The efficiency of CeO_2 NPs as a promising candidate in photocatalysis was evaluated using a methylene blue (MB) as organic contaminant dye irradiated with UV light from conventional high-efficiency low-pressure and low power (6 watt) mercury lamp is also established.

Keywords: CeO_2 NPs; Tween; MB; Photocatalysis; Antimicrobial activity

Abbreviations

T1: CeO_2 NPs synthesized in the presence 10 % Tween 20.

T2: CeO_2 NPs synthesized in the presence 5 % Tween 20.

T3: CeO_2 NPs synthesized in the presence 2.5 % Tween 20.

T4: CeO_2 NPs synthesized in the presence 10 % Tween 80.

T5: CeO_2 NPs synthesized in the presence 5 % Tween 80.

T6: CeO_2 NPs synthesized in the presence 2.5 % Tween 80.

MB: Methylene blue (3,7-bis(Dimethylamino)phenazathionium chloride).

Introduction

Nanoparticles (NPs) have become a central issue in a wide variety of industrial and commercial products as they can confer novel properties and functionalities. Cerium oxide nanoparticles (CeO_2 NPs) are one of the most produced metal oxide nanoparticles worldwide [1].

Currently, CeO_2 NPs, as important rare-earth oxide materials, have attracted interest in recent years due to its unique physical and chemical properties which are significantly different from those of bulk materials [2]. Many effective technological applications such as solid state electrolytes used for electrochemical devices [3,4], catalysis in petrochemical processing [5], fuel-borne nanoparticles

additives [6], sun screens for ultraviolet absorbents [7], oxygen gas sensors [8], substantial oxygen storage capacity (OSC) [9], polishing materials [10], as well as uses in biotechnology and medicine [11, 12].

Nano-sized CeO_2 is an n-type semiconductor with a wide band gap of (≈ 3.2 eV), and received much attention as a very promising photocatalyst for photocatalytic degradation of water pollutants under ultraviolet light (UV) [13]. In addition, Ceria has no unsafe effect on human cells compared to other metal oxides such as TiO_2 , ZnO and Al_2O_3 [14, 15] and accordingly can be used for water purification and food packaging with minimal risk for humans.

Generally, several methods are in practice for the synthesis of Ceria (CeO_2) NPs such as thermal decomposition, thermal hydrolysis,

mechanochemical processing, hydrothermal crystallization, microemulsion, flame spray pyrolysis, sonochemical, microwave, sol-gel, and co-precipitation [16-25]. However, most of the techniques are complex, time consuming, expensive and hazardous [26-35]. Recently, it has been reported that the change in experimental conditions like type of surfactant and its concentration can alter the nanostructure and particle size [36].

The focus of the present study was to synthesize CeO₂NPs at room-temperature by a chemical precipitation process using Ce(NH₄)₂(NO₃)₂ and NH₄OH in the presence of two non-ionic surfactants, i.e. Tween 20, and Tween 80, which are basically polyethoxylated sorbitan fatty acid esters which are good stabilizers for synthesis of nanoparticles. A high hydrophilic–lipophilic balance (HLB) value of the surfactant indicates strongly hydrophilic character while a low value is an indication of a strong hydrophobic nature. Considering these points, non-ionic surfactants, i.e. Tween 80 and Tween 20 with HLB values of 15 and 16.7, respectively, were selected for the present study. The effect of the type of the surfactant and its concentration to control size of synthesized CeO₂NPs is discussed. This method has the advantages of being a simple process, easy to scale-up and to produce a low-cost nanometer-sized cerium oxide. The resulting CeO₂ NPs were fully characterized by XRD, TEM, UV–visible, FT-IR and Raman spectroscopies. Moreover, photocatalytic performance of CeO₂NPs of different particle sizes against methylene blue (MB) and antimicrobial activities were investigated and analyzed.

Experimental

2.1. Chemicals

Ce(NH₄)₂(NO₃)₂, ammonia solution (AR), tween 20, tween 80 as dispersion stabilizers and methylene blue (MB) were procured and used without further purification. Deionized water is used as a solvent. NaOH/HCl was used to adjust pH of solutions.

2.2. Synthesis of CeO₂ NPs

Ceria nano powder samples were prepared by the room temperature chemical precipitation method in presence of different concentrations of surfactant (2.5%, 5% and 10% tween). In a typical synthesis, 2 mmol of Ce(NH₄)₂(NO₃)₆ were dissolved in 20 ml of deionized water in 100 mL beaker, then 5 mL of the tween surfactant (2.5%, 5% and 10% of) was added dropwisely and the whole solution was then stirred at room temperature for □ 2 hs to ensure homogenous mixing. After that, 25 mL of NH₄OH solution (0.4 M) was slowly added with constant stirring until the required pH of the solution was obtained, making the precursor Ce(OH)₄. To complete the reaction, the reaction mixture was continually stirred for □ 2 h. The resultant pale yellow precipitate was filtered

and then washed with deionized water for several times and dried in an oven at 80 °C for 24 hs. Finally, the dried sample was calcined in a muffle at 500 °C for 2 hs. During calcination, the surfactant and the remaining base in the sample were removed and pure pale-yellow fine powder was obtained. The synthesized nanoparticles were then used for further experimental work. The main chemical reactions that take place during the synthesis can be summarized by the following reactions [37]:

2.3. Characterization of CeO₂ NPs

The XRD pattern of the powdered nanoparticles are obtained using a Bruker D8 X-ray diffractometer at a scanning speed of 5 degree/minute and in the 2θ range from (20° 0 80°) in a step size of 0.05° using CuKα radiation. The size and morphology of the samples were examined using transmission electron microscopy (TEM). TEM images were obtained using JEOL-JEM-2100, Jaban electron microscope operating at 100 KV. The UV–VIS absorption spectra of the prepared CeO₂ NPs are recorded on a Shimadzu UV-2700 spectrophotometer in the range of 200-800 nm. FTIR spectra were carried out for the samples dispersed in KBr pellets in the range of 400-4000 cm⁻¹ on a Unicam-Mattson 1000 IR-spectrophotometer. Room temperature Raman spectra were recorded by the dispersive Raman Santerra- Bruker spectrometer with a laser power of 10 mw and 9.18 cm⁻¹ resolution. The spectra were excited using 532 nm line of an air-cooled Ar-ion laser and a charge-coupled device detector.

2.4. Photocatalytic activity assessment of CeO₂NPs

To evaluate photocatalytic activity, 0.1 g CeO₂ NPs was added to 100 ml of MB solution (3×10⁻⁵mol/L) and the solution was stirred in the dark for 1 h to attain adsorption-desorption equilibrium between the catalyst and the dye. The degradation experiments were carried out in a homemade photoreactor equipped with conventional high-efficiency low-pressure mercury lamp 6 W of wavelength 254 nm, keeping a distance of 5 cm between the lamp and the surface of the solution.

The experiment was carried out at different pH values by adding small volumes of either HCl or NaOH using a micropipette. The progress of the reaction is subsequently followed by withdrawing 2.5 mL of test sample at different time intervals followed by centrifuging to remove the dispersed catalyst particles, and the absorbance of MB at 664nm was measured by using a UV-Visible spectrophotometer. The absorbance for MB was an indication of catalytic activity of CeO₂ NPs. The efficiency of the synthesized CeO₂ NPs in terms of photocatalytic degradation percentage (%PDP) was calculated using the following equation:

$$\%PDP = (A_0 - A_t) / A_0 \times 100 \quad (1)$$

where, A₀ and A_t are the absorbance of MB before and after exposure to UV irradiation, respectively.

2.5. Antimicrobial Screening

The invitro antimicrobial activity of the synthesized nanoceria samples of different particle sizes were individually investigated against a panel of gram-positive, gram-negative bacterial pathogens and fungi. The (gram +ve) bacteria: Staphylococcus aureus, Staphylococcus epidermidis and Stryptococcus pyogenes and the

(gram -ve) bacteria: *Escherichia coli*, and *Klebsiella pneumoniae* and fungi: *Aspergillus fumigatus*, *Geotrichum candidum* and *Candida albicans*. The antibacterial and antifungal activities were done at 20 mg/mL concentrations in DMSO solvent. Antimicrobial activity of the tested samples were carried out using the agar well diffusion method, pathological tested bacteria, 1×10^6 CFU/mL yeast and 1×10^4 spore/mL fungi spread on (NA), Sab. Dextrose agar (SDA) and malt extract agar (MA), respectively [38]. After the media, had cooled and solidified, wells (6 mm in diameter) were made in the solidified agar and loaded with 100 μ L of the tested compound solution prepared by dissolving 20 mg of the chemical compound in 1 mL of (DMSO). The inoculated plates were then incubated for 24 hours at 37 °C for bacteria and yeast, 48 hours at 28° C for fungi. Negative controls were prepared using DMSO employed for dissolving the tested compounds. Ampicillin, Gentamycin and Amphotericin B were used as standards for Gram positive bacteria, Gram negative bacteria and fungi, respectively, to evaluate the potency of the tested compounds under the same conditions. After incubation, antimicrobial activity was evaluated by measuring the zone of inhibition against the test organisms and compared with that of the standard. At general procedure, standard antibacterial (Tetracycline) and antifungal drug (Amphotericin B) were used as references. Antimicrobial activity was expressed as inhibition diameter zones in millimeters (mm). The experiments were carried out in triplicates and the data were expressed as mean $\pm$ SD.

Results and discussion

3.1. Characterization and Measurements

3.1.1. Powder XRD studies

X-ray diffraction peak profile analysis is a widely-used method for the determination of crystallite size in crystalline materials. The formation of the CeO₂ NPs was confirmed by XRD measurement. Fig. 1 represent the measured XRD profile of CeO₂ particle sizes in the presence of different concentrations of Tween 20 and Tween 80. The diffraction peaks at 28.5, 33.1, 47.4, 56.2, 59.3, 69.5, 76.6 and 79° are assigned to diffraction from the (111), (200), (220), (311), (222), (400), (331) and (420) planes of single phase cubic fluorite structure of ceria and no other impurities were detected. The positions and intensities of the peaks are in a typical agreement with the literature values [39]. The lattice parameters from XRD data were found to be $a=b=c=5.411$ Å and $\alpha=\beta=\gamma=90^\circ$, which are in a good agreement with the data documented in literature data [40]. The average crystallite size of CeO₂ NPs is calculated from the full-width-half-maximum (FWHM) of the diffraction peaks using Scherrer equation [41]:

$$D = k\lambda / \beta \cos \theta \quad (2)$$

where D is the crystallite size, λ is the wavelength of the incident x-ray radiation, typically 1.54Å, θ is the Bragg angle, β is the FWHM in radians and k is the shape factor equals to 0.89.

The powder XRD patterns of the prepared CeO₂NPs show relatively broad peaks which confirmed the formation of small-sized nanoparticles. As shown in Fig. 1 as the concentration of surfactant increased, the peaks become broader to an extent

Fig 1. XRD spectra of CeO₂ NPs synthesized in the presence of different concentrations of Tween 20 (a) and Tween 80 (b).

reflecting smaller particle sizes. From the various replication peaks of the XRD pattern, the average crystallite sizes were found to be 13.59, 10.88 and 10.6 nm for CeO₂NPs prepared in the presence of 2.5%, 5% and 10% tween 20 and found to be 21.76, 15.54, and 10.88 nm in the presence of 2.5%, 5% and 10% tween 80, respectively. Hence, it can be concluded that the concentration of surfactant controls the crystallite size, as expected [42].

3.1.2. TEM studies

Data concerning the shape and size distribution of the prepared nanoparticles samples were obtained by Transmission Electron Microscope (TEM) studies. The transmission electron micrographs (TEM) of the synthesized CeO₂ NPs are depicted in the Figs. 2 and 3. Fig.2, reveals that the sizes of as-synthesized CeO₂NPs, T1, T2 and T3 are 5.9, 6.9 and 9.2 nm respectively, while the sizes are 7.1, 7.9 and 11.0 nm of T4, T5 and T6 (Fig.3), indicating that as the concentration of the surfactant increases, the particle size decreases. Moreover, the shapes of the particles are semi-spherical which is predicted since the temperature in the synthetic procedure is low and there is no enough energy for the particles to achieve an equilibrium shape [43]. Additionally, the agglomeration on the TEM images resulted from the ultrafine particle sizes and the

Fig. 2. TEM images of CeO₂ NPs T1, T2 and T3.

Fig. 3. TEM images of CeO₂ NPs T4, T5 and T6.

irregular shapes of CeO₂ NPs which promoted the formation of larger particles to minimize their exposed surfaces and surface energies [44]. Moreover, the average particle size measured from TEM micrographs proves the formation of smaller CeO₂ NPs from tween 20 stabilized synthetic route compared to that of tween 80. The average crystallite size measured from XRD peaks also corroborates with TEM results. Subsequently, tween 20 with higher HLB value has been found to be more effective in producing smaller sizes of CeO₂ NPs.

3.1.3. UV-visible absorption spectral studies

UV-visible absorption spectroscopy is most widely used method for characterizing the optical properties and electronic structure of nanoparticles. Absorption bands are related to the diameter [45, 46]. UV-visible absorption spectra of the as-synthesized ceria nano powder samples were measured and represented in Fig. 4. A careful inspection of the spectra shows a strong absorption band in the UV-region (200-350 nm) which is assigned to charge-transfer transition from 2p-orbital of O²⁻ to 4f-orbital of Ce⁴⁺ [47]. The

broadness of the absorption shoulder in the UV-region is attributed to the self-assembly of the nanoparticles.

It has been found that the different CeO₂ samples T1, T2 and T3 exhibited strong absorption peaks at 221, 224 and 228 nm, while T4, T5 and T6 are found at 240, 214 and 238 nm. Also, the intensity of the band absorption increased as the concentration of the surfactant increases. To reveal the relationship between the band gap energies and particle sizes of the prepared samples, the direct band gap energy (E_g) was determined by fitting the absorption data to the direct transition equation:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (3)$$

Where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the direct band gap of the material and A is a constant. Band gap of CeO₂ NPs samples have been measured by plotting $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) and extrapolating linear portion of the curve to absorption equal to zero [48]. The plots of $(\alpha h\nu)^2$ versus ($h\nu$) are shown in Fig. 5. The corresponding band gaps depending

Fig. 4. UV-Visible absorption spectra of CeO₂ NPs sythesized in the presence different concentrations of Tween 20 (a) and Tween 80 (b).

Fig. 5. Band gap energies of CeO₂ NPs T1, T2 and T3 (a) and T4, T5 and T6 (b).

Table 1: The optical band gaps of the as-synthesized CeO₂ NPs

CeO ₂ NPs	Optical band gap (E _g eV)
T ₁	2.90
T ₂	2.86
T ₃	2.8
T ₄	3
T ₅	2.95
T ₆	2.93

upon these plots are summarized in Table 1.

Also, it can be seen that the absorption edge expands up to a wavelength of 500 nm and no further absorption was revealed. This property of nanoceria signifies that the as synthesized CeO₂ NP's can act as a UV-blocking material in different applications. It can be concluded that the particle size of CeO₂ samples affects the band gap, as the large size of particles broadens both the energy levels in the valence band and in the conduction band leading to narrowing of the band gap.

3.1.4. FT-IR and Raman spectra studies

FT-IR spectroscopy can be used to identify the function groups of NPs samples. The most prominent bands are summarized in Table 2. FT-IR spectra of the CeO₂ NPs synthesized in the presence of

Table 2: The infrared (cm⁻¹, KBr) of the as-synthesized CeO₂ NPs.

Compounds	$\nu(\text{OH})$	$\delta(\text{OH})$	$\nu(\text{Ce-O})$
T1	3343	1529	466
T2	3388	1622	473
T3	3408	1620	435
T4	3407	1617	408
T5	3420	1629	430
T6	3425	1621	480

T2 and T5 using the KBr pellet method in the wave number range 4000-400 cm⁻¹ are presented in Fig. 6. The ceria nanoparticles showed prominent strong intense bands in the regions 3343-3425 cm⁻¹, 1529-1629 cm⁻¹ and 408-480 cm⁻¹. The first two bands are assigned to $\nu(\text{OH})$, $\delta(\text{OH})$ modes of H-bonded water molecules, respectively. Whereas, the strong broad band below 700 cm⁻¹ corresponds typically to Ce-O stretching vibration mode [49] confirming the formation of pure ceria (CeO₂). Residual water and hydroxyl groups absorbed from atmosphere are usually detected in the as-synthesized nanoceria samples regardless the synthetic method used [50-53].

The microscopic nature of structural and/or topological disorder of CeO₂ NPs was studied via Raman. The effect of the microstructure of CeO₂ NPs on the shape of the Raman spectra was observed

by the broadening of the line and by increasing its asymmetry, which are attributed to the reduction of the phonon lifetime in the nanocrystal line regime [54-56].

Fig.7 show Raman spectra of CeO₂ NPs in the frequency ranging from 250-2250 cm⁻¹. The Raman active modes for the CeO₂ samples exhibited a strong intense band at 465.0, 465.5, 465.0, 463.0, 463.5, 462.5 cm⁻¹ for T1, T2, T3, T4, T5 and T6, respectively, which corresponds to the F2g Raman active mode, confirming the crystalline fluorite cubic structure of the prepared CeO₂ samples [53, 57].

According to the Raman line broadening, the particle size of the CeO₂ can be also estimated using the good correlation reported for nano crystalline CeO₂ powder specimens [58-60].

$$\Gamma(\text{cm}^{-1})=10 + (127.4)/D_r \quad (4)$$

where Γ (cm⁻¹) is the full-width at half-maximum of the Raman active mode peak and DR is the particle size of a CeO₂ sample. By substituting $\Gamma(\text{cm}^{-1}) = 465.0$ (T1) and 462.0 (T5) into Eq. (4), it was found that, that the sizes of as-synthesized CeO₂NPs were 5.8 and 6.9 nm which are in accordance with that obtained from TEM studies.

3.2. Photocatalytic performance

Organic synthetic dyes are present in almost all aspects of our everyday life and their application is continuously growing. They are widely used for traditional applications, textile and non-textile dyeing, and as functional dyes and optical brighteners. [61, 62]. These hazardous substances can infiltrate into ground and drinking water through the soil leading to a great hazard to human health. As one of the most reactive rare earth oxides, ceria (CeO₂) is abundant, nontoxic, and inexpensive. Furthermore, CeO₂ is a semiconducting material that absorbs light in UV and slightly in the visible region and therefore can be used in heterogeneous photocatalysis [62, 63].

MB is commonly used as a redox indicator in analytical chemistry. MB exhibit 3 absorption peaks at 264, 291 and 664 nm. In biology, MB is used as a dye for large number of different staining procedures such as Wright's stain and Jenner's stain [61]. MB can also be used to investigate DNA and RNA under a microscope or in a gel, and this is what prompted us to choose MB as a model dye for photocatalytic degradation in this work.

The photocatalytic activities of different sizes of CeO₂ NPs were assessed by following the degradation of MB dye in an aqueous solution at room temperature under UV-irradiation, at 664 nm. CeO₂ is a semiconducting material and the onset of the absorption will be at a wavelength below 420 nm and thus irradiation by a light with a wavelength less than 420 nm is suitable for the transfer of electrons from the valence band to conduction band creating holes, h⁺, and electrons, e⁻ pairs which are responsible for photodegradation reactions.

The change in absorption of aqueous MB solution (3*10⁻⁵ M) during the photodegradation reaction at different time intervals in the absence and presence of CeO₂ nanoparticles are shown in Fig.8. It was observed that the absorption intensity of MB under UV irradiation in the absence of CeO₂ NPs, decreased slowly,

Fig. 6. FT-IR spectra of CeO₂ NPs synthesized in the presence of (T2) and (T5).

Fig. 7. Raman spectra of CeO₂ NPs prepared in the presence of Tween 20 (a) and Tween 80 (b).

Scheme 1: Mechanism of degradation of MB by CeO₂ NPs synthesized in the presence of Tween 20 and Tween 80.

whereas, in the presence of CeO₂ NPs, decreases gradually with the raise in irradiation time, due to the destruction of benzene rings and the hetero-polyaromatic linkage [64]. The mechanism of Photocatalytic activity of CeO₂ NPs is presented in Scheme 1.

The significant adsorption reactions have been taken place on the CeO₂ NPs and photo-generated e⁻-h⁺ pairs provide effective pathways for the oxidation (from the holes) and reduction (from the electrons) reactions to degrade the MB molecules. The photoelectrons scavenge the molecular oxygen and produce superoxide radicals by the following reactions [65]:

On the other hand, another reactive intermediate which is responsible for the degradation is hydroxyl radical (OH·), which can be generated from the water by the holes [66, 67]. The powerful oxidizing agent hydroxyl radicals degrade most of MB by the following reactions;

Fig. 8 shows a typical UV-vis spectral curves of MB dye during the photodegradation at different time intervals at pH= 10.5. MB shows a main absorption peak at 664 nm in visible region. The rate of decolourization was recorded with respect to the change in intensity of absorption peaks at 664 nm for MB. The absorption peaks, corresponding to dye, diminished with time which indicated that the dyes had been degraded. As depicted in Fig. 9, the rate of MB photocatalytic degradation increases gradually with time reaching the efficiency values of 78.5 %, 84 % and 65.5% after only 2 hs of irradiation for CeO₂ NPs prepared, respectively, in the presence of T1, T2 and T3 at pH=10.5. On the other hand, the

photocatalytic degradation efficiencies was 78.5, 42.0, and 35.3% for T4, T5 and T6, respectively.

3.2.1. Effect of pH

It is well known that the degradation rate in a photocatalytic system is pH dependent because the adsorption capacity of dyes on the photo catalyst is an important factor. An increase in the number of target molecules adsorbed onto a catalyst causes an increase in the rate of degradation [68]. We studied the effect of pH on the photocatalytic activity of CeO₂ nanoparticles (1.0 g/L) during the MB degradation process with an initial concentration of 10 mg/L MB for the three pHs, 4.0, 7.0, 10.5 (Fig 10). Sample solution pH was adjusted by adding suitable amounts of HCl or NaOH of 0.1 mol/L concentration.

The rate of MB photocatalytic degradation increases gradually with increasing pH reaching the efficiency values of 13.2 %, 7.4 % and 84 % after 2 hours of UV irradiation for CeO₂ NPs prepared, respectively, in the presence of T2 at different pH values (Fig.10 a). The same behaviour was in case of T4 but the efficiency values were 7.9 %, 6.1 % and 78.5 % (Fig 10 b), respectively.

The higher the pH of the solution, the higher the concentration of hydroxyl ions (OH⁻) for reaction with the holes (h⁺) and for the formation of reactive hydroxyl radicals (OH·). Also, the adsorption of positively charged dye molecules (MB⁺) occurred strongly in the basic solution because of the negative charge of the catalyst surface. The Nano sized CeO₂ samples produced in the presence of tween 20 show higher photocatalytic activity than CeO₂ NPs produced in the presence of tween 80 and this may be attributed to the smaller particle sizes which produced in case of using tween 20. The results show that the maximum degradation efficiency was obtained at a pH of 10.5 which coincides with earlier work [66] and that pH was used for further studies.

3.2.2. Kinetic Study

Fig. 11 illustrates the kinetics of degradation of MB dye in

Fig. 8. Photocatalytic performance of MB in the presence of T1, T2 and T3 (a) and T4, T5 and T6 (b) under UV irradiation at different times intervals (pH 10.5).

Fig. 9. Degradation efficiency of MB dye (3×10^{-5} M) catalyzed by CeO₂ NPs prepared in the presence of tween 20 (a) and tween 80 (b) at pH=10.5.

Fig. 10. Degradation efficiency of MB dye (3×10^{-5} M) catalyzed by T2 (a) and T5 (b) at different pH 4.0, 7.0 and 10.5.

Fig. 11. Plot of $\ln(C_0/C_t)$ versus time for photocatalytic degradation experiment of MB by CeO₂ NPs at pH=10.5 (Insets: Kinetics analysis for MB dyes degradation).

Fig. 12. Antibacterial (a) and antifungal (b) as inhibition zones (mm) of prepared CeO₂ NPs.

Table 3: Antibacterial and antifungal activity of the as-synthesized CeO₂ NPs.

	Inhibition Zone (mm)							
	Bacteria Strains					Fungai Strains		
	s. aureus	S. epidermidis	S. pyogene	K. Pneumoniae	E. coli	A. fumigatus	C. albicans	G. candidum
T1	18.2±0.33	15.3±0.12	13.2±0.39	17.4±0.39	19.7±0.37	19.2±0.28	18.4±0.32	20.3±0.25
T2	20.3±0.21	19.2±0.29	17.1±0.42	19.6±0.19	20.8±0.42	20.4±0.34	19.2±0.52	22.4±0.31
T3	0	0	0	0	0	10.6±0.29	8.4±0.18	9.1±0.35
T4	16.9±0.28	16.1±0.37	14.1±0.12	17.2±0.17	19.2±0.62	18.3±0.11	15.4±0.23	19.3±0.27
T5	16.8±0.28	14.1±0.39	12.5±0.41	16.8±0.24	18.6±0.19	13.4±0.24	11.7±0.62	15.6±0.16
T6	15.2±0.34	16.4±0.25	11.7±0.63	13.1±0.10	16.2±0.16	15.6±0.10	14.1±0.20	16.4±0.12
Ampicillin	28.9±0.14	25.4±0.18	26.4±0.34	-	-	-	-	-
Gentamycin	-	-	-	26.3±0.15	25.3±0.18	-	-	-
Amphotericin B	-	-	-	-	-	23.7±0.10	21.9±0.12	26.4±0.20

presence of T1-T6 using initial concentration of 10 mg/L under the optimized conditions. The results show that the photocatalytic decolourization of the dyes in aqueous CeO_2 can be described by the first order kinetic model, $\ln(C_0/C) = kt$, where C_0 is the initial concentration and C is the concentration at any time, t . The semi-logarithmic plots of the concentration data gave straight lines. The correlation constants (R^2) for the fitted lines were calculated to be 0.985, 0.990, 0.973, 0.936, 0.917 and 0.954 while the rate constants were calculated to be 0.0122 min⁻¹, 0.0137 min⁻¹, 0.009 min⁻¹, 0.009 min⁻¹, 0.004 min⁻¹ and 0.003 min⁻¹ for T1, T2, T3, T4, T5 and T6, respectively (Fig. 10 insets).

3.3. Antimicrobial studies of the prepared CeO_2 nanoparticles

Due to the redox nature of CeO_2 whereby the oxidation state switches between Ce^{3+} and Ce^{4+} depending on the external environment, CeO_2 NPs have been studied recently for their antimicrobial activity, [70, 71]. The prepared CeO_2 NPs samples were tested for their inhibitory effects on the growth of bacteria, *S. aureus*, *S. epidermidis* and *S. pyogenes* (G^+) and *K. pneumoniae* and *E. coli* (G^-) and fungi, *A. fumigatus*, *C. albicans* and *G. candidum* because such organisms can achieve resistance to antibiotics through morphological and biochemical modification [72]. The antibacterial and antifungal activities of the synthesized materials are listed in Table 3 and represented graphically in Fig. 12.

The differences in the reactivity of the prepared nanoparticles toward the bacteria and fungi may be because of the difference in morphology of these particles or the greater ratio of surface area to mass that occurs as the particle size decreases. The smaller particles tend to agglomerate to an extent which may lead to different binding features. Also, particles with rough surfaces or with irregular shapes have corners and edges that can be biologically and chemically reactive [73]. The sample T3 showed no activity toward bacteria while showed weak activity toward fungi. The samples T1 and T2 showed high activity toward fungi but showed moderate activity toward bacteria and the results of fungicidal screening showed that T1 and T2 samples have the highest growth inhibition which was very close to standard amphotericin B. The bactericidal screening results showed that the activity of T2 sample is greater than that of T1 toward both gram-positive and gram-negative bacteria. All the samples T4, T5 and T6 have exhibited a moderate activity toward fungi and bacteria except T4 which has a high inhibitory growth effect on fungi and T6 which showed a weak activity toward gram-negative bacteria.

Conclusion

In summary, the present work describes a simple method to synthesize pure CeO_2 NPs by a wet chemical method. CeO_2 NPs were prepared in presence of different concentration of the non-ionic surfactants tweens 20 and 80 of different HLB values to improve and control the size of CeO_2 NPs. The formation of CeO_2 NPs was confirmed by UV spectra, FT-IR, Raman, XRD, and TEM studies. This technique is interesting not only for the relatively short treatment time relative to the low power and temperature used but also the possibility of controlling the morphological and

structural properties. tween 20 with higher HLB value has been found to be more effective in producing smaller sizes of CeO_2 NPs. The nanoparticles were used for degrading aqueous methylene blue solution with UV light illumination with low power intensity (6 watt). The Nano sized CeO_2 samples produced in the presence of tween 20 show higher photocatalytic activity than CeO_2 NPs produced in the presence of tween 80 and this may be attributed to the smaller particle sizes which produced in case of using tween 20. As-prepared CeO_2 NPs was also tested for their antimicrobial activity towards some Gram-positive, Gram-negative bacteria and fungi strains. CeO_2 NPs exhibited good antimicrobial effect.

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