Research Article

Antioxidant, Antimicrobial, and Photocatalytic Potential of Cobalt Fluoride (CoF₂) Nanoparticles

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Herein, CoF₂ nanoparticles (NPs) are prepared by simple coprecipitation method and are characterized by various techniques, i.e., XRD, SEM/EDX, FTIR, and UV/Vis, for their structure identification. As-prepared nanostructures were used as photocatalyst, as antioxidant, and as antimicrobial agent. The degradation studies of the prepared samples were carried out for specific time for the degradation of methylene blue (MLB) dye under a UV/visible spectrophotometer to determine decolorization and change in concentration of MLB with respect to time. The antibacterial activity against *Escherichia coli* (*E. coli*) and *Bacillus subtilis* (*B. subtilis*) was measured by well diffusion and serial dilution method to determine their efficiency against these two bacteria, through a dose-dependent method. The antibacterial activity was further confirmed against the experimental bacteria through calculation of minimum inhibition concentration (MIC). The antioxidant activity (radical scavenging activity) of the prepared CoF₂ NPs was also assessed.

1. Introduction

The utilization of matter at the nanoscale (1-100 nm), i.e., atomic, molecular, or supramolecular, for commercial and industrial applications is related to nanotechnology. Quantum confinement and size are the important aspects of the nanomaterials for the development of devices and commercial products [1, 2]. Nanotechnology includes a variety of fields, and on the basis of size, nanomaterials have diverse applications including energy storage, surface chemistry, semiconductor, catalysis, organic chemistry, engineering, biology, thin layer, and self-assemblies [3–5]. Various types of semiconductor oxide and sulphide like TiO₂, SnO₂, Fe₂O₃, ZnO, WO₃, Cds, Ws₂, ZnS, and MoS₂ have been used widely for the degradation of organic pollutants; however, they have poor activity without the addition of cocatalyst due to the rapid recombination of electron and hole pair before they migrate to the surface for reaction [6–8].
fluorides (like zirconium, aluminum, rare-earth metals, and hafnium) have commercial application in isotopic separation and metallurgy and in the preparation of optical and ceramic materials; however, recently, their used has been increased in the field of biosensing, catalysis, as cathode materials for LIBs, super capacitors, and photonicics [9–12]. In the past, researchers have used CoF₂ as promising anode material for LIBs. Fu et al. for the first time use CoF₂ as anode material for LIBs [13]. MnF₂ and CaF₂ were used as antimicrobial agents for gram-positive and gram-negative bacteria to find their efficiency [14, 15]. Similarly, Zapala et al. used niflumic acid synthesized with different transition metal complexes for determination of their catalytic and antibacterial activity [16]. Xi et al. used fluorides as disinfectant for the treatment of bacteria [17]. Gajendiran et al. synthesized cobalt ferrite and treat as antimicrobial agent which shows good results against gram-positive bacteria [18]. Arun and Li et al. prepared cobalt and cobalt ferrite NPs and used them as photocatalyst for the degradation of organic dyes like MLB dye and showed efficient results against these dyes as catalyst [19, 20]. Yan et al. used bimetallic fluorides as efficient oxygen reduction catalyst in the defect-enriched carbon nanofibers [21]. Li et al. used cobalt- and fluoride-based photocatalyst for the high-performance evolution of oxygen [22–24]. However, no literature data on CoF₂ is available as catalyst for the degradation of MLB and as antimicrobial agent and used as photocatalyst for the first time with high efficiency by decolorizing and degraded MLB. The novelty of the prepared CoF₂ nanostructures lies in their application, i.e., catalytic and antimicrobial results which were carried out for the first time and not reported in the literature yet.

2. Experimental

2.1. Materials. Cobalt nitrate tetrahydrate, deionized (DI) water, ammonium fluoride, ethanol, etc. were purchased from Sigma-Aldrich and used for the preparation of CoF₂ NPs.

2.2. Synthesis of CoF₂ NPs by Coprecipitation Method. CoF₂ NPs were prepared by dissolving 0.582 g of cobalt nitrate tetrahydrate and 0.182 g of ammonium fluoride in two separate beakers in 4 mL of DI water. The two solutions were then mixed in 30 mL of ethanol in a beaker and stirred for 20 minutes. Immediately, pink color precipitate will appear for CoF₂ NPs; centrifuge and filter the precipitate and dry in an oven for two hours and characterize on various techniques for their structure confirmation and identification. The prepared CoF₂ NPs were then used as catalyst for the degradation of MLB dye as antioxidant and as microbial agent for the treatment of gram-positive and gram-negative bacteria.

2.3. Preparation and Extraction Procedure of MLB Dye for Degradation Studies. Take 3 mg of CoF₂ catalyst powder in three separate 1-Chem glass vials and add 10 μL of MLB (10 ppm solution) to each vial; seal the vial, vortex, and shake for 1 minute to promote contact between the sample powder and MLB solution. The substrate will be adsorbed on the surface of catalyst, and after 0 min, 10 min, 30 min, 60 min, and 120 min extracted with 2 mL of isopropanol alcohol (IPA), filter through a 0.45 μm PTFE syringe filter and analyze on a UV/visible spectrophotometer for their degradation studies. The reaction and extraction procedure was used for the rest of sample preparation and degradation studies. To find the efficiency of synthesized CoF₂ NPs, the amount of catalyst and methylene was kept fixed for all the samples and only varying the time duration.

2.4. Antimicrobial Activity of Cobalt Fluoride NPs. The prepared CoF₂ NPs were examined for their antibacterial activity against *Escherichia coli* (*E. coli*) and *Bacillus subtilis* (*B. subtilis*), by well diffusion and serial dilution method [25, 26] to determine their efficiency against these two bacteria, through a dose-dependent method. In this method, in 1 mL of deionized water, 2 mg of cobalt fluoride was dissolved and sonicate this solution for 30 min. The bacteria under test were purchased from CGMCC (China General Microbial Culture Collection Center). Incubate the bacterial culture containing LB media in a 4 mL tube. Keep the tube at 37°C to achieve the 0.5 standard of McFarland (1×10^8 CFU/mL). Transfer 100 μL of this turbid culture into a Petri dish containing agar media, and disperse bacterial culture in the Petri dish by small beads. Make 4 wells of 6 mm in the Petri dish by metal borer. Add 60 μL to 4 mm well containing different concentrations of 0.25 mg/mL, 0.5 mg/mL, 1.0 mg/mL, and 2.0 mg/mL. Place the Petri dish for 48 h for incubation at 37°C, and calculate the inhibition zone in the unit of millimeter. The antibacterial activity was further confirmed against the experimental bacteria through calculation of minimum inhibition concentration (MIC).

2.5. Minimum Inhibition Concentration (MIC). The minimum concentration at which no visible growth of the tested bacteria occurs is used as indicator to confirm and verify the inhibition of bacteria. CoF₂ NPs and needles of different concentrations (i.e., 7.5, 15, 30, and 60 μg/mL) were added to 4.0 mL LB media broth in four different tubes, and also, 60 μL of culture bacteria to each tube was added. Place these tubes at 37°C for 48 h for incubation and then observe and note the growth of bacteria in each tube.

2.6. Antioxidant Activity. The antioxidant activity (radical scavenging activity) of the prepared CoF₂ NPs and needles was performed as reported in literature [27, 28]. Dissolve different concentrations (0.031, 0.062, 0.125, 0.25, 0.5, and 1.0 mg/mL) of CoF₂ NPs and needles in methanol and add 0.5 mL of 1 mM of DPPH to each tube containing different concentrations and incubate in the dark for 30 min at room temperature. After that, measure the absorbance of both control and sample by UV-Visible Cary 50 at wavelength 517 nm by taking methanol as blank and vitamin C as control blank and calculate their scavenging ability through the following equation.
%Scavenging activity (inhibition) = \frac{A_c - A^*}{A_c} \times 100. \quad (1)

$A_c$ is the absorbance of the control.
$A^*$ is the absorbance of the tested sample.

3. Results and Discussion

3.1. Physicochemical Characterization. To find the crystal structure and composition of synthesized CoF$_2$ NPs, XRD techniques were used. The X-ray diffraction studies of the synthesized CoF$_2$ NPs matched with JCPDS card number 01-072-1179, which shows purity and tetragonal structure for CoF$_2$ NPs. After drying in oven at 110°C, the crystallinity of the synthesized material improved as evident from the XRD spectrum (Figure 1). The particle size of the prepared cobalt fluoride NPs was calculated by the Scherrer equation which is 36.45 nm after drying.

To find the morphology and shape of the synthesized CoF$_2$ NPs, SEM was employed. SEM studies of the prepared NPs show flake-type morphology, and the particles agglomerate instead of dispersion as shown in Figure 2. EDX was performed to determine the elemental composition of CoF$_2$ NPs. EDX studies of NPs are shown in Figure 3, and it exhibits that the synthesized material contains only Co, F, and oxygen with no impurities.

FTIR studies were used to further confirm the prepared CoF$_2$ NPs. FTIR spectrum of the synthesized material shows its frequency range between 400 cm$^{-1}$ and 4000 cm$^{-1}$. FTIR spectrum of the prepared material shows that the broad peak of the hydroxyl group for water disappears after drying as shown in Figure 4 which indicate that the material is pure. Other stretching frequencies for CoF$_2$ NPs appear at 538 cm$^{-1}$, 1212 cm$^{-1}$, 1363 cm$^{-1}$, and 1747 cm$^{-1}$, which are due to C-H, C-O, and C-F stretching.

UV/visible spectroscopic analysis was performed between 200 and 800 nm to find the wavelength absorption and optical band gap of the synthesized CoF$_2$ NPs through Kubelka-Munk function. The band gap for CoF$_2$ NPs was calculated to be 2.79 eV as shown in Figures 5 and 6, before and after drying. Catalytic properties of the prepared CoF$_2$ NPs depend mainly upon their microstructure, particle size, and surface morphology. XRD studies of the prepared CoF$_2$ NPs show that after drying the crystallinity of the material improved; also, particles size decreases which increase the surface area, and thus, the catalytic behavior of the CoF$_2$ NPs increases. Moreover, band gap calculation of the CoF$_2$ NPs also shows that after drying the crystallite size decreases which decrease the band gap, and thus, their catalytic effect increases as shown in Figure 6 from their band gap calculation through the Kubelka-Munk function.

3.2. Degradation Studies of MLB Dye. Degradation studies of MLB solution (10 ppm) were carried out with the help of UV/visible spectrophotometer (Cary 50) to determine the efficiency of CoF$_2$ photocatalyst with respect to time and their decolorization rate. Initially, 3.0 mg of CoF$_2$ catalyst powder is in three separate I-Chem glass vials, and add 10 μL of MLB (10 ppm solution) to each vial, seal the vial, vertex, and shake for 1 minute to promote contact between the sample powder and MLB solution. The substrate will be adsorbed on the surface of catalyst, and after 0 min, 30 min, 90 min, and 120 min extracted with 2 mL of isopropyl alcohol (IPA), filter through a 0.45 μm PTFE syringe filter and analyze on a UV/visible spectrophotometer for their degradation studies. The same reaction and extraction procedure was used for the rest of sample preparation and degradation studies. To find the efficiency of synthesized CoF$_2$
NPs, the amount of catalyst and methylene was kept fixed for all the samples and only varying the time duration. UV/visible data of the CoF$_2$ NPs shows that after 0 min no degradation and decolorization occur; after 30 min, 40%; after 60 min, 50% degradation; after 90 min, 70% degradation and decolorization appear in all the samples; and after 120 mint, 90-94% of the samples were degraded with the decrease in concentration with respect to time as indicated from their UV/visible graph (Figure 7).

3.3. Antioxidant Activity. The scavenging activity of CoF$_2$ NPs is shown in Figure 8. By getting electron or hydrogen
from the donor atom, 1-diphenyl-2-picrylhydrazyl (DPPH) radical is reduced [29, 30]. It shows high efficiency at concentration of 1 ppm (1 mg/mL). For CoF₂ NPs, the IC₅₀ was higher than 1 μg/mL. The mechanisms of antioxidant activity of CoF₂ NPs were unknown; however, it depends upon the transfer of electron from oxygen to nitrogen atom of DPPH and the electronic transition occurs at 517 nm for n → π* transition.

3.4. Antibacterial Activity. The antibacterial activity of CoF₂ NPs was tested against gram-positive B. subtilis and gram-negative E. coli bacteria (Figure 9). The results showed the inhibition of both bacteria at different concentrations of 2, 1, and 0.5 and 0.25, 0.5, 1.0, and 2.0 mg/mL of CoF₂ NPs. These NPs show higher inhibition against B. subtilis as compared to E. coli at different concentrations. The zone of inhibition (ZOI) for B. subtilis was 17 mm at concentration of 1 mg/mL. However, E. coli were less susceptible to NPs. The exact mechanism of action of CoF₂ NPs on these bacteria is unknown; however, through oxidative stress, it ruptures the cell membrane by damaging the bacterial lipid layer, DNA, and inhibits bacterial growth. Fluoride act as anticaries, by increasing acidification, reducing bacterial growth, and enhancing permeability of proton through membrane by ATPases [31–33].

4. Conclusion

CoF₂ NPs were prepared through the coprecipitation method and characterized by various techniques, i.e., XRD, SEM/EDX, FTIR, and UV/Vis, to conform their structure. Further catalytic efficiency of CoF₂ NPs was checked against MLB dye for the first time. The UV/visible studies of the synthesized catalyst show that MLB degraded after some time by decolorizing the IPA solution, and also, the concentration of dye decreases with passage of time. Thus, it is concluded that CoF₂ can be used as an efficient catalyst for the degradation of organic dyes (MLB). The prepared CoF₂ NPs show effective antibacterial and antioxidant results against gram-positive and gram-negative bacteria, i.e., Escherichia coli (E. coli) and Bacillus subtilis (B. subtilis), for the first time by rupturing their lipid membrane through oxidative stress and acidification.

Data Availability

All the available data are incorporated in the MS.

Conflicts of Interest

The authors declared that they have no conflict of interest.

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