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Liquid phase synthesis of pectin–cadmium sulfide nanocomposite and its photocatalytic and antibacterial activity

Vinod Kumar Gupta [a,*], Deepak Pathania [b], Mohammad Asif [c], Gaurav Sharma [b]

[a] Department of Chemistry, Indian Institute of Technology Rookree, Roorkee 247667, India
[b] Department of Chemistry, Shoolini University, Solan, Himachal Pradesh 173212, India
[c] Department of Chemical Engineering, King Saud University, Riyad, Saudi Arabia

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ABSTRACT

We report the synthesis of pectin–cadmium sulfide nanocomposite (Pc/CSNC) in aqueous phase at 60 °C using pectin as the coupling negotiator. The nanocomposite was characterized by using techniques such as X-ray powdered diffraction (XRD), transmission electron spectroscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). TEM results indicated that the average size of particles in Pc/CSNC was in the range from 4 nm to 10 nm. These results were consistent with the results obtained from XRD data. Pc/CSNC was explored for the photocatalytic degradation of methylene blue (MB) dye from waste water in the presence of sunlight and sodium lamp source. Photocatalytic degradation of methylene blue dye was recorded to be higher under visible light irradiation (95.5%) as compared to that under sodium lamp source (88.9%) after 6 h of irradiation. Pc/CSNC offered excellent antibacterial activity against *Escherichia coli* bacteria culture.

1. Introduction

Interest in nano-sized objects has increased recently due to their unique physical, chemical, electrical and optical properties in comparison to their bulk counterparts. Synthesis of semiconductors of groups II–VI in a nanopowder form is currently an area of intense scientific interest due to their vital applications in optoelectronics, photonics, biomedical and light emitting devices [1–3]. CdS is one such semiconductor with a direct band gap of 2.42 eV at 300 K. It's applications for optoelectronics, being used in photosensitive and photovoltaic devices, solar cells, transistors, light emitting diodes, photo catalysis and photoluminescence sensors are already established by various studies [4–7]. CdS nanomaterials have been used as bioorganic detector of proteins or DNA [8]. CdS nanoparticles with accurate surface modification have recorded enhanced luminescence properties [9,10].

Recently, hybrid organic–inorganic nano-composites have gained much attention due to their credibility to offer synergistic feature of polymeric material with those of inorganic constituents. They offer the dual advantages of the inorganic material like rigidity, thermal stability, etc. and those of organic polymer like flexibility, dielectric, ductility, and processability. In polymer based nano-composites the small size of the fillers results in dramatic increase in interfacial area as compared to their traditional composites. This interfacial area creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings [11–13]. The surfaces of inorganic particles are usually hydrophilic, while those of polymers are usually hydrophobic. Therefore, the surfaces of inorganic particles need to be modified or pretreated by using some coupling agents in order to promote the compatibility between polymeric phase and inorganic phase and to maintain unique morphology [14]. Polymers are exceptional host materials for nanoparticles of metals and semiconductor [15]. Hybrid materials have high specific stiffness and strength, high toughness, corrosion resistance, low density and thermal insulation [16–18]. Pectin is a natural, non-toxic and amorphous carbohydrate present in cell walls of all plant tissues and functions as an intercellular and intracellular cementing material. Pectin has been commonly used in the food industry on account of its gelling, stabilizing thickening and emulsifying properties and also due to its excellent eco-friendly biodegradable applications [19–21]. Pectin macromolecules are able to bind with some organic or inorganic substances through molecular interactions.

Dyes are discharged into water system from the effluents of industries like textile, paper, printing, plastics and leather. Many of these dyes are toxic, non-biodegradable, carcinogenic and mutagenic to aquatic life and human being [22,23]. Thus, the presence of even small amount of dye in water is of high concern. A number of techniques have been used for the removal of dyes from water system [24–28]. Nowadays bio-adsorbent based materials have gained importance due to their low-cost, easy processability, high-volume application, renewable nature and possibility of recycling.

* Corresponding author. Tel.: +91 1332285801; fax: +91 1332273560.
E-mail addresses: vinodfcy@gmail.com, vinodfcy@iitr.ac.in (V.K. Gupta).

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Although adsorption has been a widely used method for dye treatment, but it results in secondary pollution due to transfers of dye from aqueous to solid phase. On the other hand, advanced oxidation process initiated by photocatalytic degradation can offer a better solution for decolorization, breakdown and mineralization of dyes [29]. Since photocatalytic reaction takes place on the surface of the semiconductors, morphology and surface alteration have a strong influence on the photocatalytic effect [30]. The semiconductor nanoparticles, when irritated with light, produce an electron–hole pair, with an electron in the conduction band and hole in the valence band. Photocatalytic process results in oxidation–reduction and finally the degradation of a wide variety of organic pollutants through their interaction with photo generated holes or reactive oxygen species, such as $^{\bullet}OH^{-}$ and $^{\bullet}O^{2-}$ radicals. The developments of nanoparticles with antimicrobial activity are of considerable interest due to microbial contamination in food industry. Nanoparticles have been reported to have effective antibacterial properties against Gram-positive and Gram-negative bacteria [31].

Our group has been working on the synthesis and application of polymer based nanocomposites. Recently, CuS–pectin, CdO–BSA, CdS–BSA, etc. nanocomposites have been synthesized and are having diverse applications [32]. To the best of our knowledge, no study has been attempted on the synthesis of Pc/CSNC nanocomposite with photocatalytic and antibacterial activity.

In the present work, Pc/CSNC nanocomposites were synthesized in aqueous phase at a temperature of 60 °C. Pc/CSNC was characterized by XRD, FTIR, TEM, TGA, etc. The nanocomposites were further evaluated for their photocatalytic degradation ability of methylene blue dye in the presence of sodium lamp source and sunlight radiation. Pc/CSNC was explored for antibacterial activity against Gram-negative *Escherichia coli* bacteria culture.

2. Experimental

2.1. Chemicals

All chemicals used in this study were of analytical grade. Pectin, $CdSO_4$, Na_2S and methylene blue (MB) were purchased from Sigma-Aldrich Company (India) and used as received. All the solutions were prepared in double distilled water.

2.2. Instrumentation

The phase composition of the CdS nanocomposite was determined by using X-ray diffractometer (Panalytical S X. Pert Pro) using CuKα radiation. Their morphology was studied with a transmission electron microscope (Hitachi TEM System). Thermal analysis was determined with Mettler Toledo (DSC-851E). Fourier transforms infrared spectroscopy analysis was done by using infrared spectrophotometer (Perkin-Elmer Spectrum 400). The concentration of dye was determined by using UV–visible spectrophotometer (Systronics 117).

2.3. Synthesis of Pectin–CdS nanocomposite (Pc/CSNC)

Pectin–cadmium sulfide nanocomposites (Pc/CSNC) were synthesized in aqueous phase at 60 °C using co-precipitation method followed by direct encapsulation with pectin. In a typical synthesis, different solutions of 0.1 M $CdSO_4$, 0.1 M Na_2S and pectin (0.20 g in 20 mL water) were prepared. 20 mL of pectin was added in 50 mL of 0.1 M $CdSO_4$ at room temperature with continuous stirring for 20 min. 100 mL of 0.1 M Na_2S was added dropwise to the above mixture with continuous stirring. The resulting mixture was stirred at magnetic stirrer for 3 h at 60 °C to obtain orange colored solution. The resulting solution was centrifuged at the rate of 10,000 rpm for 15 min on cooling. The precipitates obtained were cooled followed by washing several times with methanol and distilled water to remove the impurities. Finally the precipitates were dried in oven at 50 °C for 24 h.

2.4. Photocatalytic activity

The photocatalytic activity of the Pc/CSNC was evaluated for the degradation of methylene blue dye in the presence of solar light and sodium lamp radiation sources. In this process, 0.25 g Pc/CSNC was dispersed in 100 mL of 1×10^{-4} M methylene blue dye solution and stirred in the dark for 30 min. Then suspensions were exposed to solar light and sodium lamp radiation with constant stirring. 5 mL of solution was withdrawn at regular intervals and centrifuged to remove the catalyst particles. The concentration of MB in the solution was determined at 653 nm by UV–visible spectrophotometer. All the experiments were undertaken in triplicate with errors below 5% and average values were reported. The decolorization efficiency of MB dye was calculated by using the following equation:

$$\% \text{ degradation} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_o is the initial concentration and C_t is the instant concentration of the sample. The kinetics of dye degradation was described by pseudo first-order kinetics. The rate constant (k) was calculated by using Eq. (2).

$$k = 2.303 \times \text{slope} \quad (2)$$

where the slope was obtained from the plot of ln(c) versus t.

2.5. Antibacterial properties of Pc/CSNC

In this method, a colony was picked from the overnight Nutrient Agar plate culture of *E. coli* and was inoculated into 10 mL Nutrient Broth (NB) in a universal container and incubated at 37 °C under shaking condition of 100 rpm for 24 h. The culture was diluted to 10^{-5} CFU/mL (colony forming unit per mL) with NB according to MacFarland standard (Dual, 1963). 10 mL of the dilute culture was added into 190 mL NB in different conical flasks. Nanocomposites of different amounts (50 μg/mL and 100 μg/mL) were added into the above flasks. The flasks were incubated to 100 rpm at 37 °C for 24 h. 3 mL fraction of each sample was analyzed for optical density after every hour using spectrophotometer at 620 nm. A positive control was also analyzed simultaneously. The well diffusion method was also used to investigate the antibacterial activity of Pc/CSNC. The samples were prepared between in dimethyl sulphoxide (DMSO) in the range between 50 and 100 μg/mL. 15–20 mL of molten agar medium was poured into the sterilized petri dish and inoculated with 0.3 mL suspension of *E. coli* by spread plate method. Using sterile borex, three wells were made. The wells were filled with 100 and 50 μg/mL solution of Pc/CSNC. The petri dish was sealed with paraffin and incubated at 37 °C. The petri dish was examined for zone of inhibition after 48 h.

2.6. Fourier transform infrared spectroscopy (FTIR)

FTIR spectrum of Pc/CSNC was recorded by using KBr disk method. 10 mg of Pc/CSNC was thoroughly mixed with 100 mg of KBr, powdered and a disk was formed by applying the pressure. FTIR spectrum of Pc/CSNC was recorded between 400 and 4000°cm^{-1}.

2.7. X-ray studies

The X-ray diffraction pattern of Pc/CSNC was recorded by X-ray diffractometer using CuKα radiation. The spectrum was recorded between 10° to 80° at 2θ.

2.8. Scanning electron microscopy (SEM)

Scanning electron microphotographs of Pc/CSNC were recorded at different magnifications using scanning electron microscope.