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Original Research Paper

Green and eco-friendly synthesis of cobalt-oxide nanoparticle: Characterization and photo-catalytic activity

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ABSTRACT

Cobalt-oxide nanoparticles (NPs) were fabricated using *Punica granatum* peel extract from cobalt nitrate hexahydrate at low temperature. The synthesized cobalt-oxide NPs were characterized using X-ray powder diffraction, scanning electron microscopy, energy-dispersive X-ray, Atomic force microscopy, Fourier transform infrared spectroscopy and UV-visible techniques. The cobalt-oxide NPs were in highly uniform shape and in the size range of 40–80 nm. Photo-catalytic activity (PCA) of the synthesized NPs was evaluated by degrading Remazol Brilliant Orange 3R (RBO 3R) dye and a degradation of 78.45% was achieved (150 mg/L) using 0.5 g cobalt-oxide NPs for 50 min irradiation time. In view of eco-benign, secure, cost-effective nature, the biosynthesis has gained much for NPs synthesis and present investigation revealed that *P. granatum* could be used for the synthesis of cobalt-oxide NPs for photo-catalytic applications.

1. Introduction

To date, researchers are focusing on the fabrication of NPs to tune the electronic, optical, catalytic and magnetic properties irrespective of bulk materials. The main aspects that are important in order to tune the properties are quantum effects and surface area [1]. Extensive research have been carried out to control the shape and size of NPs since size and shape have significant effect on physico-chemical properties [2,3].

Cobalt NPs have various applications due to their high resistance to corrosion as well as oxidation and have potential applications in everyday life [4]. Various physical and chemical methods have been used for the synthesis of cobalt NPs including; thermal decomposition, high temperature solution phase, reduction and hydrothermal micro emulsion etc [5–9]. However, biosynthesis of NPs is evolved into a significant offshoot of nanotechnology [10–20]. This technique is eco-friendly and cost effective versus conventional synthesis techniques, where high pressure, temperature, energy and chemical additive are used [1,21]. Therefore, there is a need to develop and utilize safe synthetic techniques, which must be environment friendly, nontoxic, efficient and low cost. In this contest, various researchers used biosynthesis technique for the fabrication of NPs [10,11,13,15,20,22–26]. Plant derived materials are used for the fabrication of NPs, which is eco-friendly and is credible alternatives to physical and chemical methods. The use of plant extract eliminates the laborious and complicated protocols of physico-chemical methods. Plant extract contains bioactive compounds such as tannins, phenolic acids, saponin and flavonoids [27–29]. These bioactive compounds can quench singlet oxygen, donate hydrogen and are good chelation agents. Because of their redox activities plant mediated synthesis of nanoparticles is more compatible than the physico-chemical methods. Plant extracts

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are non-toxic, easy to handle and can be processed using easy protocols [11,13,15,20,23–26,30–36].

P. granatum is a rich source of polyphenolic compounds, has extensive applications in various industrial process i.e., cosmetics, food and medicines etc. The major compounds (gallic acid, punicalagins A and B, Ellagic acid and gallotannins) in *P. granatum* could act as a reducing, stabilizing and capping agents [37]. The polyphenolic compounds could limit the particle growth and ruling out agglomeration of particles [38–40]. In recent years, the innovative cobalt catalytic properties attracted the attention of researchers due to non-precious cobalt source versus precious metals [41]. The cobalt exhibits a wide range of size-dependent structural, magnetic, electronic, and catalytic properties. Being a p-type anti-ferromagnetic semiconductor, it is a multi-functional material with various practical applications i.e., heterogeneous catalysis, energy storage, electro-chromic sensors, and anode materials in Li-ion rechargeable batteries [42–45].

The textile dyes are the one of major class of environmental pollutants [46] and most of the dyes are mutagenic and carcinogenic [47,48]. There are numerous conventional chemical and physical techniques such as chlorination, ozonation, adsorption, reverse osmosis, ultra-filtration, biodegradation and coagulation for the pollutants including textile dyes [49–64]. Nevertheless, the majority of these methods degrade dyes into harmless end product and secondary pollution issues are encountered. To date, the advance oxidation process is an efficient alternative for the treatment of toxic dyes and other organic compounds [3,65–69]. Radiation energy such as UV radiation is utilized in the process and treatment can be carried out under ambient conditions [50,70]. However, UV based processes are costly and solar light is viable alternative to UV radiation. In this regard, photo-catalyst active under light are needed, which is more promising then UV based processes. Nano scale cobalt particle have remarkable catalytic properties [71]. Particularly, owing to their large surface area, cobalt NPs displayed very high reactivity, which makes them appropriate for catalysis [72].

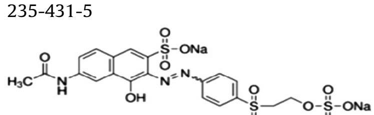
In view of importance of biosynthesis, nevertheless, the cobalt oxide NPs are synthesized using *P. granatum* extracts. Therefore, the principle objectives of current investigation were to synthesize the cobalt oxide NPs using *P. granatum* extracts. The synthesized cobalt oxide NPs was characterized using advance techniques and finally, PCA was evaluated by degrading RBO 3R dye under solar light irradiation.

2. Material and methods

2.1. Chemical and reagents

Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), (99%), RBO 3R (Table 1) were purchased from Sigma Aldrich chemical supplier company. For the preparation of solution, ultrapure water with a resistivity of 18.2 MΩ cm from Milli-Q system (Millipore) was used throughout this study.

Table 1
Physico-chemical properties of Remazol Brilliant Orange 3R dye (RBO 3R).

Purity	≥70%
Synonym	Remazol Brilliant Orange 3R
Empirical formula	$C_{20}H_{17}N_3Na_2O_{11}S_3$
Molecular weight	617.54
Colour index number	17757
EC number	235-431-5
Chemical structure	

2.2. Preparation of green reducing and stabilizing agent

The *P. granatum* peels were collected from the local market, Bahawalpur, Pakistan. Peels were sliced into pieces and washed with ultrapure water to remove impurities. *P. granatum* peels (20 g) and 150 mL waster was homogenized in an electrical grinder. Then mixture was heating at ~75 °C along with continuous stirring, cooled down and filtered. The filtrate (brown color) was collected and used for the synthesis of cobalt oxide NPs.

2.3. Synthesis of Cobalt-Oxide nanoparticles

For the fabrication of cobalt oxide NPs, freshly prepared peels extract (90 mL) was added to 1 M solution of cobalt nitrate hexahydrate, heated at ~ 70 °C till precipitates appeared and then, the temperature reduced to 60 °C and kept the solution at 60 °C for 90 min. The mixture was kept overnight at room temperature and then centrifuged at 14,000 rpm for 10 min. The precipitates were washed thrice with ultrapure water and absolute ethanol to remove un-reacted particles and impurities. The obtained precipitates were dried in an oven at 60 °C for 8–9 h [73], grinded and subjected characterization.

2.4. Characterization

The purity of the synthesized cobalt oxide NPs was confirmed by XRD analysis (Bruker, German), using Cu Kα radiation in the range of 2θ = 20–80° at a scanning rate of 5° min^{-1}. The element analysis was performed by Energy Dispersive X-Ray Spectroscopy (EDX) (JEOL, Japan). The structural morphology was examined by scanning electron microscopy (SEM) (Hitachi SX-650, Tokyo, Japan). To confirm the functional bio-molecules associated with the cobalt oxide NPs, FTIR analysis was carried out (Nexus 470, FTIR) in the range of 500–4000 cm^{-1} with resolution setting of 4 cm^{-1}. The UV–Vis absorption spectra was recorded on UV–Vis spectrophotometer (Perkin Elmer, USA). Moreover, the confirmation of the particle size and morphology of fabricated cobalt oxide NPs was carried out by atomic force microscopy (AFM).

2.5. Photo-catalytic activity procedure

The PCA of as-synthesised cobalt oxide NPs was evaluated by degrading RBO 3R. For PCA study, 0.5 mg of cobalt oxide NPs was mixed with 100 mL dye solution (150 mg/L). The suspension was kept in the dark for 30 min in order to ensure the adsorption–desorption equilibrium and then, irradiated to solar light generated by solar simulator (150 W Xe lamp having cutoff filter ($\lambda \geq 420$ nm). After stipulated time intervals (10, 20, 30, 50 min), the samples were drawn, filtered by Millipore filter and analyzed for dye residual concentration by UV-vis spectrophotometer (Perkin Elmer, USA) at 495 nm along with scanning from 190–900 nm. To evaluate the pure photolysis effect, blank experiment was also performed under similar conditions. Triplicate degradation experiments were run under ambient conditions (25 °C). The dye percentage degradation was estimated by employing the relation shown in Eq. (1).

$$\text{Decolorization} \quad (\%) = \left[\frac{(C_i - C_f)}{C_i}\right] \cdot 100 \qquad (1)$$

where C_i is the initial concentration of RBO 3R dye and C_f is the concentration of dye after photocatalytic degradation.