SYNTHESIS AND CHARACTERIZATION OF HYBRID NANOCATALYST (AgNPs-Fe$_2$O$_3$) FOR CATALYTIC REMEDIATION OF HAZARDOUS 2,4-DINITROPHENOL

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ABSTRACT. Hybridized nanocatalysts (AgNPs-Fe$_2$O$_3$) were prepared with silver nitrate and ferric chloride in the presence of sodium borohydride. The synthesized nanocatalyst was calcined, milled, and sieved for further applications. The nanocatalyst was characterized using Fourier transform infrared spectroscopy (FTIR) for the identification of functional moieties involved in the synthesis of the nanocatalyst. The vibrations of Fe and Ag were found at 566, 790 and 892 cm^{-1}. The crystalline nature of the nanocatalyst was determined using X-ray diffraction (XRD) studies. The diffraction peaks for Ag and Fe can be seen at 2θ values of 30.42, 44.36, 62.45, 42.24 and 53.25. The morphology and elemental analysis of nanocatalysts were studied using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDAX). The particles are found to be spherical in shape. The signal for Ag and Fe can be found at 3.0 keV and 0.7, 6.3, 7.0 keV, respectively. The synthesized nanocatalyst was employed in the remediation of 2,4-dinitrophenol. The AgNPs-Fe$_2$O$_3$ nanocatalyst completely reduced (97%) the 2,4-dinitrophenol to 2,4-diaminophenol within 24 h.

KEY WORDS: Nanocatalyst, Chemical precipitation, Impregnation methodology, Milling, Sieving, Remediation

INTRODUCTION

Nanotechnology is a multi-disciplinary science that covers many areas of scientific techniques, like biomedical, pharmaceutical, agricultural, environmental, materials, general chemistry, general physics, electronics, data sciences and technology, etc [1, 2]. Nanoparticles are materials that shows individuality in size (generally varies from 1 to 100 nm), structure, physio-chemical, electric, magnetic, thermal, mechanical, catalytic, optical scattering properties and shape [3]. Magnetic nanoparticles like iron oxide nanoparticles are more successful under the influence of magnetic field and are often the core formers of nano-biomaterials [4, 5]. The properties of iron oxides nanoparticles are well known from ancient times, but in the recent past the nanometric scaled nanoparticles possess the starting point of vide variety of applications [6]. The magnetic properties of iron oxide nanoparticles are strongly influenced by the surface area of the particles [7, 8]. Different methods are employed to synthesize magnetic nanoparticles, they are chemical co-precipitation assisted by ultrasonics [9]; sol–gel combustion and coprecipitation [10];

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solvothermal, hydrothermal [11] and thermal decomposition [12]. Noble metal nanoparticles have been the subject of much intensive research due to their potential applications in microelectronics and so on. Silver (Ag) is a vital inorganic material that has an extensive application perspective in superconducting, catalysis, photosensitive components, etc [13]. Nanocatalysts, due to their unique properties such as high surface area, enhanced reactivity, and size-dependent catalytic activity, have shown promise in the degradation of various pollutants, including DNP. These catalysts can be composed of various materials such as metal nanoparticles (e.g., iron, palladium, platinum), metal oxides (e.g., titanium dioxide, iron oxide), or carbon-based materials (e.g., graphene, carbon nanotubes). The valuable properties of Fe_3O_4/Ag nanocomposites have attracted much interest in various applications [9]. These nanocomposites have the combined advantage of magnetic iron oxide (Fe_3O_4) along with the good catalytic and antibacterial activity provided by silver (Ag) [14]. The organic pollutants from industries, agricultural land, and spilled chemicals are polluting water hazardously which is a menace for human as well as aquatic organisms [15]. The photocatalytic breakdown approach is highly efficient in transforming organic pollutants, and its byproducts comprising water, carbon dioxide, and inorganic mineral ions [16]. 2,4-Dinitrophenol (DNP) is considered as a hazardous environmental contaminant around the world, has been widely used as a herbicide along with other herbicides like DNOC. DNP is widely used as explosives in many countries. DNP is a toxic compound that is often found as a pollutant in industrial wastewater, and its remediation is necessary to protect ecosystems and human health. DNP causes severe and acute effects in bone marrow, central nervous system and cardiovascular system. Several approaches are used to remove these pollutants, including membrane processes like nanofiltration, ultrafiltration, reverse osmosis, etc., however these approaches possess many of limitations, which includes high pressure, high membrane cost, and, most notably, chemical or microbial membrane obstructions, leading to decreased flow and prevents water from getting through the filter [17]. The present study deals with the preparation of hybridized nanocatalysts (AgNPs-Fe_2O_3) for catalytic remediation of hazardous 2,4-dinitrophenol.

EXPERIMENTAL

Synthesis of iron oxide Fe_2O_3 nanoparticle

The nanocatalyst was synthesized by chemical precipitation method using sodium borohydide, according to Sun *et al.* [18] with slight modifications. Sodium borohydide (0.2 M) and ferric chloride hexahydrate (0.05 M) were blended for 30 min, and stirred in a magnetic stirring at 250 rpm. The prepared nanoparticles were strained and rinsed with distilled water and dilute ethanol.

Biosynthesis of silver nanoparticles

Biosynthesis of silver nanoparticle was achieved by following the procedure of Vanaja and Annadurai [19]. The plant extract was prepared by boiling the surface sterilized and finely chopped leaf of *Couroupita guianensis* (Aubl.) for 5 min at 60 °C. The filtered extract was stored at 4 °C for further process. To synthesis silver nanoparticles 1 mM silver nitrate solution was mixed with leaf extract and incubated for 10 min at room temperature. The change in colour to brown indicates the production of silver nanoparticles and characterized by UV-spectrophotometer (Perkin Elmer Lambda double beam UV-Spectrophotometer) in wavelength ranges of 340 to 740 nm.

Fabrication of hybrid nanocatalyst

For fabrication of hybrid AgNPs and Fe_2O_3 nanocatalyst, impregnation technique was employed Melo *et al.* [20]. Fe_2O_3 nanocatalyst and AgNPs were magnetically stirred for 90 min at room

temperature and calcination was carried out at 450 °C at a heating rate of 10 °C per min for duration of 4 hours. Milling and sieving was done to make the final granules to uniform size using.

Characterization of nanocatalyst

The functional moieties involved in the preparation of silver nanoparticles and hybrid nanocatalyst were determined by Fourier transform infra-red spectroscopy (FTIR). To determine the crystallinity X-ray diffraction (XRD) method was used (Bruker D2 Advance diffractometer). Scanning electron microscopy (SEM) was used to morphologically characterize the nanocatalysts (AgNPs-Fe$_2$O$_3$) using a JSM5800 (JEOL). The elemental analysis of the hybridized nanocatalyst was done by using an Energy Dispersive X-Ray-Spectrometer Quantax 200 with X Flash® 6130.

Catalytic activity of AgNPs-Fe$_2$O$_3$

NaBH$_4$ was used as reducing agent in reduction of aromatic 2,4-dinitrophenol (DNP) [21]. A typical reaction mixture contains 2.5 mL of 0.1 mM DNP and 0.6 ml of freshly prepared 0.1 M NaBH$_4$ in a quartz cuvette. 5 mg of hybrid AgNPs-Fe$_2$O$_3$ nanoparticles were added to reaction mixture to initiate the reduction process. UV-Vis spectroscopic technique was used to observe the conversion of 2,4-dinitrophenol (DNP) to 2,4-diaminophenol (DAP) in the wavelength range of 200-800 nm at room temperature. An external magnetic field was used to separate the hybrid AgNPs-Fe$_2$O$_3$ catalyst from the reaction mixture and washed with ethanol for reuse.

RESULTS AND DISCUSSION

Characterization of nanocatalyst

Fourier transform infra-red spectroscopy (FTIR)

The FTIR spectrum of iron oxide nanoparticles is depicted in the Figure 1. It displays several bands at 566, 790, 892, 1642, 2422 and 3151 cm^{-1}. The vibration bands (566, 790 and 892 cm^{-1}) may be assigned to Fe–O–Fe stretching vibration, O-H stretching and bending vibration are observed at 3151 cm^{-1} and 1642 cm^{-1}, respectively. The presence of Ag can be observed in the range of 566 cm^{-1} and Ag is present as O-Ag. The formation of Fe$_2$O$_3$ can be observed at the vibration bands at low frequencies regions. The formation of Fe$_2$O$_3$ is confirmed by the presence of two absorption bands of Fe-O-Fe stretching at 790 and 892 cm^{-1} [22].

X-Ray diffraction (XRD)

Figure 2 shows X-ray diffraction (XRD) pattern of synthesized AgNPs-Fe$_2$O$_3$ nanocatalyst exhibiting five peaks at 2 theta values of 30.42, 44.36, and 62.45 which assigned to silver nanoparticles and 42.24 and 53.25 assigned to Fe$_2$O$_3$ nanoparticles. These peaks assigned to diffraction of the (001), (200), (220), (400), and (422) planes. Among the planes (400) and (422) indicates that spinel structured magnetite nanoparticles (JCPDS card no. 39-1346) [23]. Similarly, Shukla *et al.* [24] reported that oligo sachharide coated iron oxide nanoparticles. Due to the lack of the template the iron oxide particles are not adequately crystalline [25]. The average crystallite size of the nanocatalyst is found to be 17.20 nm.

Scanning electron microscope (SEM)

SEM analysis was used to observe the morphological characters of the chemically synthesized nanocatalyst (Ag-Fe$_2$O$_3$ NPs) oxide sample. The results observed from the Figure 3 clearly show

that the synthesised nanocatalyst have spherical shape. Most of the particles were aggregated and some are individual particles were observed from the SEM image. The grain size of synthesized nanocatalyst is found to be 171 nm. The aggregation between nanoparticles is occurred may be due to the effects of electrostatic attraction between the particles [26-28].
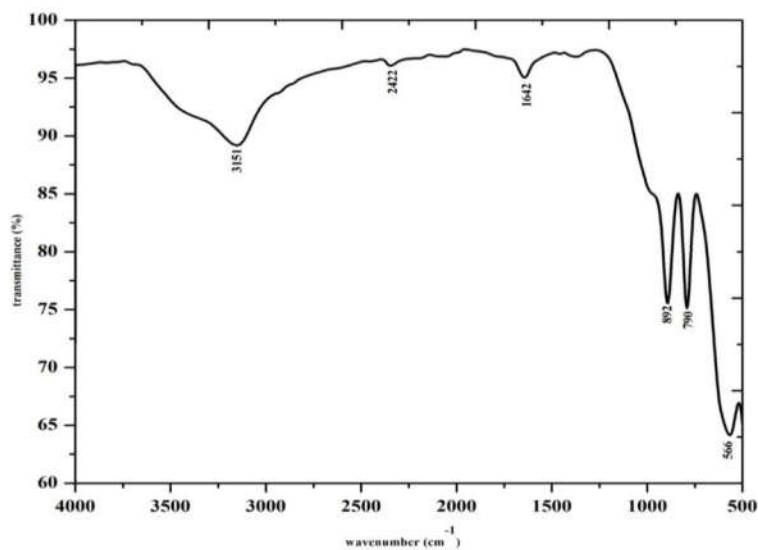

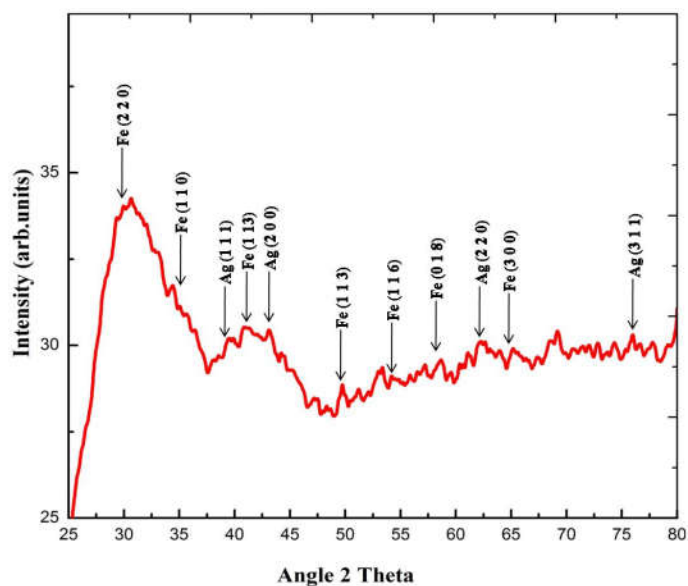Figure 1. FTIR spectrum of AgNPs-Fe$_2$O$_3$ nanocatalyst.

Figure 2. XRD diffractogram of AgNPs-Fe$_2$O$_3$ nanocatalyst.
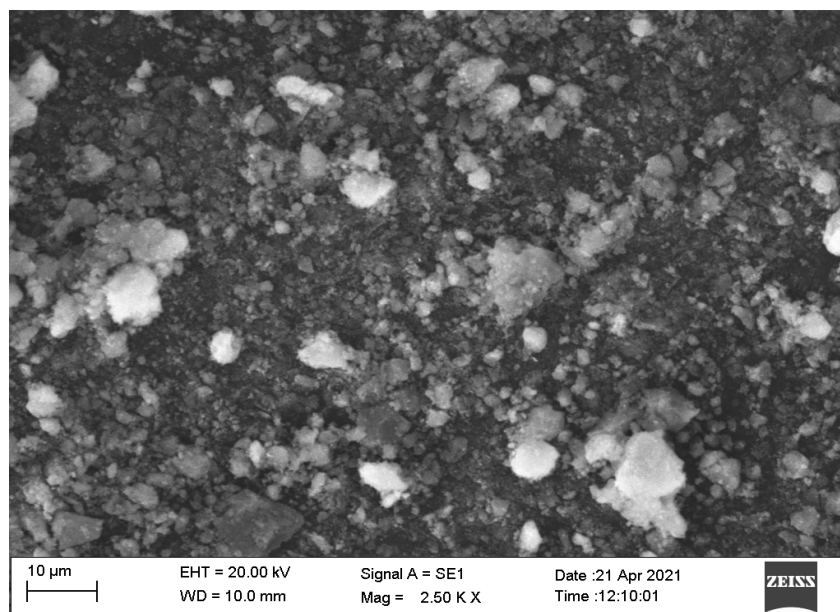
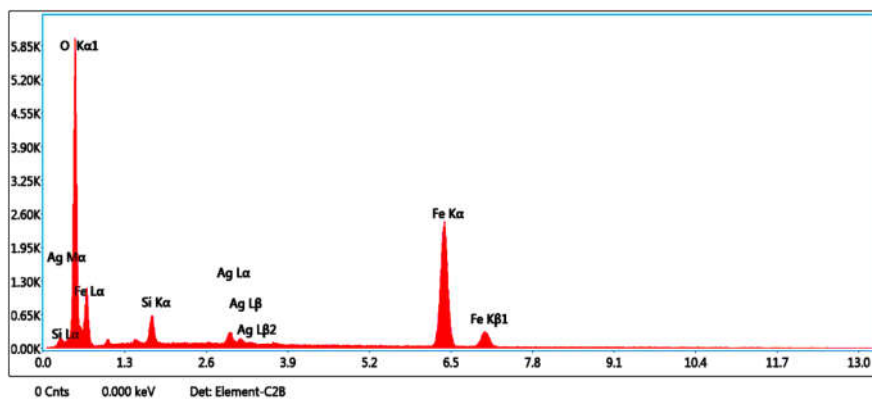Figure 3. SEM image of AgNPs-Fe$_2$O$_3$ nanocatalyst.

Figure 4. EDS of AgNPs-Fe$_2$O$_3$ nanocatalyst.

*Energy dispersive X-ray spectrometry (EDS)*

Energy dispersive X-ray (EDS) spectrometer confirms that formation of elemental silver and iron in the reaction solution (Figure 4). Identification of peaks for the major binding energies for silver metal was observed at 3keV, while the peaks around 0.7, 6.3 and 7.0 keV are determined for the binding energies of Fe [29]. A strong signal was observed from the binding energy at 0.5 keV indicates the presence of O. This is confirmed that silver and iron oxide bonded together and formed bimetallic nanoparticles. EDS spectra also confirmed that presence of 3.7% of Ag, 56.3% of Fe and 36.1% of oxides are shown in Table 1. Weak signal was received at the binding energies around 0.2 and 1.8 keV of Si, this impurity may be during calcinations or other handling process.

Table 1. Elemental composition of AgNPs-Fe$_2$O$_3$ nanocatalyst by EDS.

Element	Weight %	Atomic %	Error %	K ratio
O K	36.1	65.7	6.7	0.2000
SiK	3.8	4.0	7.6	0.0223
AgL	3.7	1.0	10.0	0.0311
FeK	56.3	29.3	2.1	0.5096

Catalytic activity of AgNPs-Fe$_2$O$_3$

Photocatalytic reduction using AgNPs-Fe$_2$O$_3$ nanocatalyst was demonstrated by using 2,4-dinitrophenol. The colour of the solution transformed from yellow to colourless. The reduction of 2,4-dinitrophenol was performed in the visible region as a function of different time intervals between 10 min and 24 hours. The absorption spectrum was recorded in the range from 200 nm to 600 nm. The image showed the decreased peaks for 2,4-dinitrophenol at different contact times. Initially, the absorption peaks at 315 nm showed maximum intensity and it gradually decreased with increase of reduction time that indicates the photocatalytic degradation reaction has taken place. The gradual decreasing in the intensity at 315 nm was continued up to 24 hours. After 24 hours, the reaction was completed and indicates that conversion of 2,4-dinitrophenol to 2,4-diaminophenol (Figure 5).
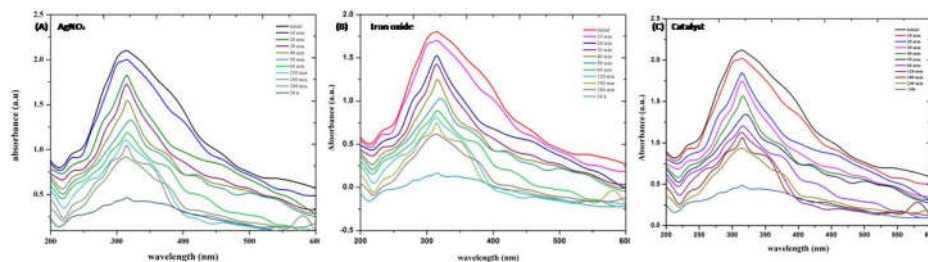
Figure 5. Catalytic reduction of 2,4-dinitrophenol by AgNO$_3$, iron oxide and AgNPs-Fe$_2$O$_3$ nanocatalyst.
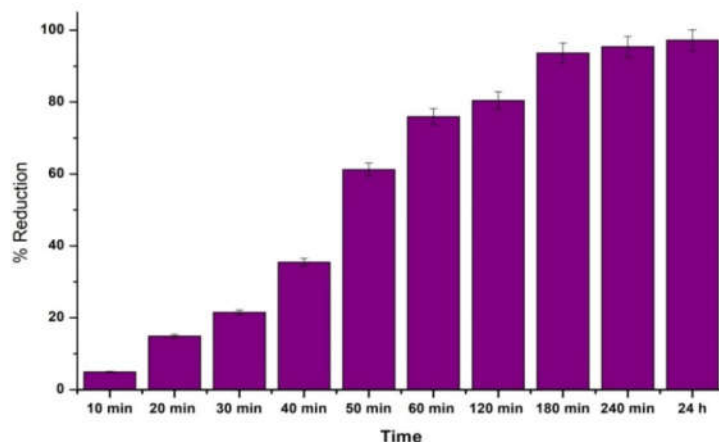
Figure 6. Percentage reduction of 2,4-dinitrophenol by AgNPs-Fe$_2$O$_3$ nanocatalyst.

The percentage degradation efficiency of AgNPs-Fe$_2$O$_3$ nanocatalyst was calculated as 97% at 24 h (Figure 6). The degradation percentage increased as increasing the exposure time of 2,4-dinitrophenol and AgNPs-Fe$_2$O$_3$ nanocatalyst complex in sunlight (Figure 6). Absorbance peak for 2,4-dinitrophenol was centered at 315 nm in visible region which diminished and finally disappeared while increasing the reaction time, which indicates that the 2,4-dinitrophenol had been catalytically reduced. Similarly, Hasan *et al.* [30] reported that PAN-g-Alg@Ag-based nanocatalysts for the reduction of toxic dinitrophenol with a degradation potency of 94% within a 50-min period.

CONCLUSION

AgNPs-Fe$_2$O$_3$ nanocatalyst was effectively synthesised utilizing chemical precipitation method and was used to the remove the lethal nitro compound (2,4-dinitrophenol). The formation of metallic ferrites was confirmed by FTIR and XRD analyses and their allied characteristic behavior. The AgNPs-Fe$_2$O$_3$ nanocatalyst showed the excellent catalytic reduction of 2,4-dinitrophenol. The AgNPs-Fe$_2$O$_3$ nanocatalyst completely reduced (97%) the 2,4-dinitrophenol with in 24 h. The AgNPs-Fe$_2$O$_3$ nanocatalyst is a capable catalyst predominantly for remediation of wastewater in environment. This catalyst is effective in remediation of noxious nitro derivatives and other major organic pollutants.

ACKNOWLEDGEMENTS

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