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Nanocrystalline ferrite (MFe_2O_4, M=Ni, Cu, Mn and Sr) photocatalysts synthesized by homogeneous Co-precipitation technique

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ABSTRACT

Pertaining to the diverse environment, application of ferrites (MFe_2O_4 = Ni, Cu, Mn and Sr) in scientific and industrial categories, it is vital to optimize its properties and hence a facile homogeneous co-precipitation route was used to formulate MFe_2O_4 nanoparticles in order to study its morphological, optical and magnetic perspective. The enviable phase pure spinel nanoparticles were deliberated by X-Ray Diffractometer (XRD), Fourier Transform Infrared (FTIR), Laser Raman, Transmission Electron Microscopy (TEM), Brunauer–Emmett–Teller adsorption-desorption isotherm (BET) and Vibrating Sample Magnetometer. XRD depicts the phase formation, crystallite size, lattice parameter and the speck size was calculated by Scherrer formula. The FTIR spectrum reveals the absorption bands between 4000–400 cm^{-1} whereas the Raman spectrum is extended for the photon modes of asymmetric and symmetric stretching vibrations. The morphological and particle distribution was studied using TEM. Surface analysis was performed using the Isothermal BET technique for the as-synthesized nanoparticles. UV-visible analysis reveals the significance of optical property in application of Photo-Fenton activity. Using Kubelka-Munk plot, bandgap was found for as-synthesized samples. The synthesized MFe_2O_4 photo catalyst was studied for its significance in photo-Fenton activity of Methylene blue (MB) dye degradation. The synthesized photo catalyst was reused for 5 cycles and it was evident that it had no significant loss, which makes it an adroit candidate in industrial distillation.

1. Introduction

The surfacing of toxic waste in the water bodies has enthused coerce for the embryonic new-fangled technologies. Organic dye derivatives orginates amid the unremittingly breathing pollutant from manufacturing waste due to their wide use in textile industries [1,2]. Organic pollutant connotes an a significant category of Persistent Organic Pollutants (POPs) unconstrained hooked on the milieu chiefly from the textile and pesticide industries and it is pointed by authorities worldwide, owing to their low biodegradability and towering toxicity. The inhibitory in effects of these microbial activity comprise are being reported for the concentrations outsized to 500 ppm, and organic dyes reveal bio toxicity even at low concentrations [3,4]. In folks, endocrinal developmental, neurologic, immunologic adverse health, behavioral and reproductive possessions

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have been correlated due to the organic wastes. Ecological concerns have led to the wide-ranging delve to secure and effective, amputation of perilous crude compounds from water bodies. A superlative squander handling route ought to absolutely mineralize the noxious genus present in the desecrate stream devoid of leaving behind a dangerous residue in a lucrative approach. Abundant module of abatement route counting to physico-chemical treatments, thermal and biological have been urbanized in the most recent times for the detoxification of organic dyes in water bodies. Advanced Oxidation Process (AOP's), a advanced skill, reduces the deliberation of organic pollutants from ppm to ppb. The ascendancy of Photo-Fenton route in water treatment is owed to several rewards above the customary techniques, such as non formation of oxidation of pollutants in the ppb range, quick oxidation, polycyclic products etc. [5]. The ferrites in nano range have honored Photo-Fenton activity than in bulk nature. These ferrite nanomaterials have a relevant facet of tapered band gap in the visible region. This type of optical property allows ferrites to be efficiently utilized the solar spectrum in the photocatalytic activity such as degradation of different organic pollutants using decomposition of H_2O_2 and oxidative dehydrogenation of hydrocarbons. It was reported that ferrite nanocatalyst are removable and reused even after several cycles which makes it a significant contender in industrial application purpose. As a prominent members of ferrites, MFe_2O_4 (M = Ni, Cu, Sr and Mn) have captivated research the community by its revitalizing ferromagnetic nature. MFe_2O_4 have an inverse spinel phase formation with the Fe^{3+}cations distributed between the sites, Ni^{2+}, Sr^{2+}, Cu^{2+} and Mn^{2+} cations being located in octahedral sites and the magnetic ordering in the inverse spinel structure of MFe_2O_4 is ferromagnetic in nature [6]. Researchers have adopted several routes to synthesize MFe_2O_4 nanoparticles such as co-precipitation, hydrothermal, solvothermal and microemulsion [7–10]. In this paper, MFe_2O_4(M = Ni, Cu, Sr and Mn) nanoparticle was as-synthesized by a facile low temperature co-precipitation route, due to its ample significance such as control over the particle size, homogeneous and free from impurities. The as-synthesized nanomaterial was characterized to study their properties. In the present application, Methylene Blue was used as a mock-up dye and the photocatalytic behaviour in the presence as-synthesized nano catalyst was studied.

2. Experimental

2.1. Preparation of MFe_2O_4(M = Ni, Cu, Sr and Mn) nanocatalyst

Nanosized MFe_2O_4 particles were as-synthesized by a slick co-precipitation route. The chemicals were used without further purification. Nickel nitrate ($Ni(NO_3)_2$), copper nitrate ($Cu(NO_3)_2$), manganese nitrate ($Mn(NO_3)_2$), Strontim nitrate ($Sr(NO_3)_2$) and ferric nitrate ($Fe(NO_3)_2$) was taken in a stoichiometric ratio of 1:2, and dissolved separately in 50 ml of distilled water in order attain homogeneous mixture. Then, 2 M of NaOH was added as a mineralizer to attain pH 8 and the pH was maintained throughout the synthesis process. The solution was continuously stirred at 80 °C for 3 h as a result brown precipitate was formed. The brown precipitate thus obtained was magnetically washed twice with double distilled water and once with ethanol inorder to remove impurities and nitrates, the resultant by-product was dried overnight at 70 °C in an oven. Then the dried nanopowder was grounded and calcinated at 500 °C for 3 h in a muffle furnace, as a result nanocrystalline MFe_2O_4(M = Ni, Cu, Sr and Mn) nanoparticles were obtained.

2.2. Photocatalytic activity

Photocatalytic activity for MFe_2O_4 nanoparticles was examined by measuring the percentage of degradation of MB in the aqueous solution using nano catalyst under visible light irradiation of mercury light source. In this experiment 100 mg of as-synthesized catalyst was dispersed in 100 ml of 10 mg/l of MB dye solution. Before irradiating the solution to light, the aqueous solution with nanocatalyst was kept in dark for adsorption −desorption reaction for 30 mins, then the aqueous solution with nanocatalyst was exposed to light after the adding up 4 ml of 30% H_2O_2. At every given interval, 3 ml of aliquots was taken and centrifuged to obtain the catalyst and reuse the nanocatalyst. The percentage of degradation of MB was examined by UV–vis spectrophotometer.

3. Results and discussion

3.1. XRD analysis of MFe_2O_4(M = Ni, Cu, Sr and Mn) nanoparticles

XRD analysis has many significant applications like quantitative phase analysis, qualitative phase analysis, determination of crystallite size and the fortitude of unit cell parameter. Fig. 1 depicts the diffraction pattern of synthesized MFe_2O_4 (M = Ni, Cu, Sr and Mn) nanoparticle as-synthesized by coprecipitation route. The diffraction pattern shows the presence of cubic spinel phase formation, which is indicated by the reflection peaks (220), (311), (400), (422), (511) and (440). This six diffraction peaks were obtained at 2θ = 23.38, 30.35, 35.62, 43.45, 52.36 and 60.19°. There was no secondary phase formation which confirms the single phase spinel formation. Crystallite size was calculated from the diffraction prominent peak corresponding to the plane (311) of MFe_2O_4 nanoparticles using Scherrer formula,

$$\Phi = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$