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Green synthesis of $ZnAl_2O_4$ nanoparticles for the degradation of methyl orange dye under visible light

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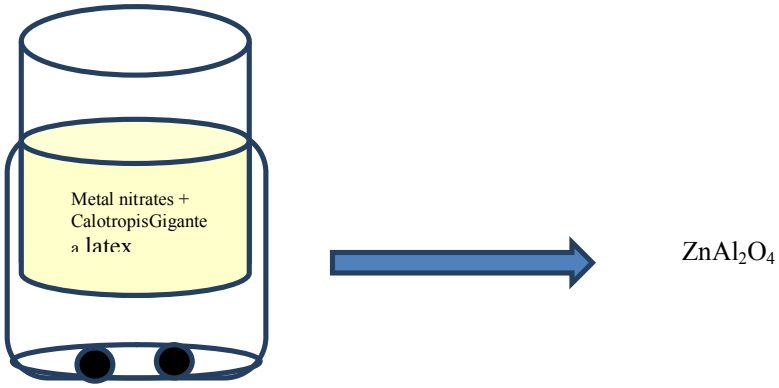
Abstract : In the present work, synthesis of zinc aluminate using Calotropis gigantea milk as gelling agent was investigated. Calotropis gigantean milk simplifies the process, provides an alternative simple, cheap and fast method of synthesis of $ZnAl_2O_4$ nanoparticles. The as-synthesized $ZnAl_2O_4$ nanoparticles were characterized by X-ray diffraction (XRD) studies, Fourier transform infrared spectroscopy (FT-IR) studies and high resolution scanning electron microscopy (HR-SEM)

The XRD results confirmed the formation of the cubic phase $ZnAl_2O_4$. The formation of pure Zinc aluminate phase was confirmed by FT-IR. The size and morphology of $ZnAl_2O_4$ nanoparticles was confirmed by HR-SEM and their possible formation mechanisms were also proposed. $ZnAl_2O_4$ prepared by this method was investigated for the degradation of methyl orange under solar radiation to evaluate its photocatalytic activity.

Keywords: Zinc Aluminate nanoparticle, Calotropis gigantea, Photocatalyst, Methyl orange dye.



Magnetic Stirrer

Introduction

Significant efforts have been made to synthesize semiconductors and apply as a photo catalyst to remedy the environmental pollution has gained much attention [1]. $ZnAl_2O_4$ a normal spinel oxide, is also a semiconductor due to its wide band gap (3.8eV) [2]. Desirable optical properties of $ZnAl_2O_4$ have drawn the attention of the researchers to use as photo catalyst. In order to enhance the photo catalytic properties of $ZnAl_2O_4$ nanoparticle various methods have been reported such as, hydrothermal [4], citrate [5], sol-gel [6],

combustion [7], pyrolysis[8], co-precipitation [9] etc. All the above mentioned methods require expensive chemicals, release of toxic intermediates etc. So there is a need for an alternative method which has advantageous such as low cost, environmentally benign, shorter reaction time, free from toxic chemicals etc [10]. Recently, plant extracts have been used as reducing, stabilising and gelling agent for the synthesis of nanoparticles. Literature reports on the various plant extracts explored for the synthesis of nanoparticles are Ixora coccinea [11], Ocimum sanctum [12], aloe vera[13],Opuntia dilenii haw[10],etc.

Generally, Calotropis gigantean is a latex bearing plant belonging to Asclepiadanceae family and it is use to cure a variety of diseases. It is a common waste land weed, frequently found in india. White milky latex is present in the inner part of the whole Calotropis gigantean plant. The latex contains calotropin, calactin, uscharin, trypsin, voruscharin, syriogenin etc[14]. Calotropis gigantean milk latex provides a simple, green and efficient method of synthesis of nanomaterials Leaf extract of calotropis gigantean have used as reducing agent for the synthesis of nanomaterials [15].The choice of Calotropis gigantean milk latex for the synthesis of nanoparticles was a non-polluting, environment friendly reducing and gelling agent.

The catalytic property of $ZnAl_2O_4$ nanoparticles depends on the distribution of cations in the spinel structure. Photocatalytic degradation of organic dyes by $ZnAl_2O_4$ nanoparticles was widely investigated. Though there are numerous reports on UV photocatalytic activity, Visible light photocatalytic efficiency was not explored much.

In the current work, we report photocatalytic activity of $ZnAl_2O_4$ nanoparticles, prepared by a green method, for sun light driven degradation of aqueous MO dye.

Experimental

Synthesis of $ZnAl_2O_4$ nanoparticles

$Zn(NO_3)_2$ (99%, SR Chemicals, India) and $Al(NO_3)_3$(98%, SR Chemicals, India) were dissolved in deionized water and then mixed in the molar ratio of 1:2. To the solution,10ml of Calotropis gigantean milk latex was added under constant stirring at room temperature until a sol was obtained. Then the sol was dried at 100 °C for 3 h to obtain precursor. The precursor was then sintered at 600 °C for 2 h in a muffle furnace and the sample obtained was characterised.

Characterisation

The obtained powder was characterized by powder X-ray diffraction method using Cu$K\alpha$ radiation Bruker (D8 Advance) X-ray diffractometer. Morphological studies were carried out by Scanning Electron Microscopy (FEI Quanta FEG 200). FT-IR measurement was executed using KBr disc technique (FT-IR spectrometer- Thermo NicolateCompany Avatar 330).

Photocatalytic activity

In this study, methyl orange dye (MO) was used as a model dye to study the photocatalytic activity of green synthesized $ZnAl_2O_4$ nanoparticles under sun light irradiation. The photocatalytic experiments under sunlight were carried out in a transparent vessel (beaker) during the mid-day of April at Chennai. The photocatalytic degradation of Methyl orange dye (molecular weight = 327.33g mol–1;) was studied in dye concentration of 600 mg L^{-1}. The $ZnAl_2O_4$ nanoparticle was added to 100 ml of MO dye solution and stirred in the dark for 30 minutes to reach the adsorption−desorption equilibrium, after which it was irradiated with sun light for different durations. After the exposure with the sunlight, the photocatalyst was removed and the concentration of MO dye in aqueous solution was analysed by UV-Vis spectroscopy. The following equation was used to calculate the % removal efficiency of dyes.

$$\% \text{ Removal} = (C_o - C_i / C_o)$$

Where C_o is the initial absorbance of MO dye solution before the addition of photocatalyst and C_i is the absorbance of MO dye solution after the addition of photocatalyst and exposure to sunlight at various time intervals.

Results and discussion

Structure and morphology

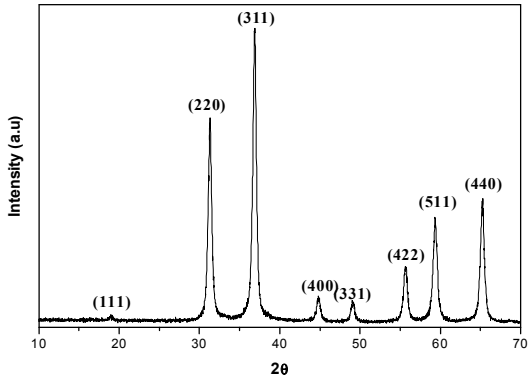


Fig.1.Powder Xray diffraction pattern of $ZnAl_2O_4$ nanoparticles

The XRD pattern for $ZnAl_2O_4$ is shown in Figure 1. All the peaks are indexed based on the JCPDS No. 82-1043. The XRD pattern indicates the pure phase formation. The average crystallite size of spinel $ZnAl_2O_4$ sample was calculated by using Debye–Scherer formula

$$D = \frac{0.89\lambda}{\beta \cos\theta}$$

where'D' is the average crystallite size, 'λ' the X-ray wavelength, 'θ'the Bragg diffraction angle and '□', the full width at half maximum (FWHM). The average crystallite size was found to be 16.61 nm. The surface morphology of the sample was investigated by Scanning electron microscopy. The SEM image of $ZnAl_2O_4$ shows the particles are porous in nature and agglomerated (Fig.2).

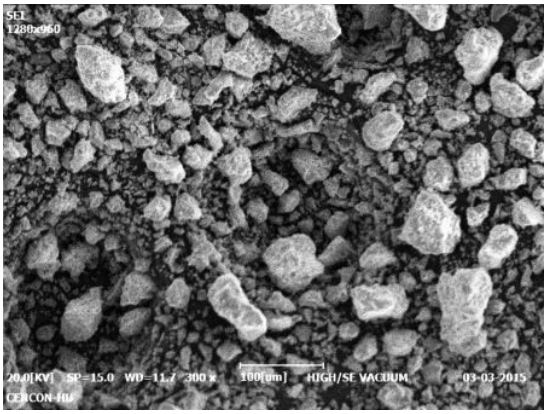


Fig.2. SEM image of $ZnAl_2O_4$ nanoparticles

Photocatalytic studies

Photocatalytic studies have been carried out by sunlight irradiation of aqueous solution of 100ml of 600mg/l MO dye with $ZnAl_2O_4$ nanoparticles. The effect of adsorbent dosage (0.01 to 0.1 g) on 100 ml of dye solution was studied for 120min time duration and the results are shown in Fig.3. MO dye molecules adsorbed on $ZnAl_2O_4$ nanostructures react with the highly reactive hydroxyl radicals (•OH) and superoxide radicals ($\bullet O_2^-$) leading to their degradation. On increasing the adsorbent dosage the degradation efficiency increases and maximum efficiency of 70% was attained for 0.1 g of the catalyst.

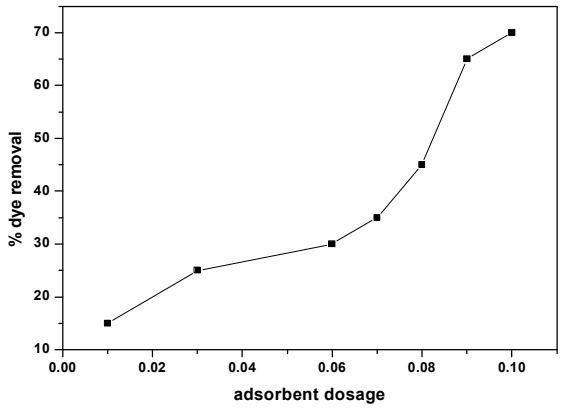


Fig.3. Effect of adsorbent dosage on the degradation of methyl orange dye

Conclusion

In summary, $ZnAl_2O_4$ nanoparticle was synthesized by a green method using Calotropis gigantean milk as a gelling and reducing agent. The formation of $ZnAl_2O_4$ nanophase was confirmed by XRD results. The synthesized nano zinc aluminate was used as a photocatalyst for the degradation of methyl orange dye in aqueous solution. Hence simple, rapid bio-synthetic green method using Calotropis gigantean milk was developed to synthesize nano $ZnAl_2O_4$ with better catalytic properties.

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