

Photocatalytic Degradation of Toxic Methyl Red Dye Using Silica Nanoparticles Synthesized from Rice Husk Ash

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Abstract

Herein we reported the preparation and potential application of SiO₂ NPs (SiO₂ NPs) for the photocatalytic degradation of methyl red dye in aqueous medium. These are synthesized from rice husk ash (RHA) which was collected from rice mill near Shankaraghatta (Shimoga, Karnataka). Silica was present in large quantity in RHA, hence it can be extracted by an alkaline precipitation method was developed to produce pure silica xerogel. From XRD and FT-IR analysis revealed the amorphous nature of SiO₂ NPs along with the presence of siloxane group. TEM image confirms the formation of SiO₂ NPs at 10 to 20 nm range. Furthermore the stabilization and formation of SiO₂ NPs was confirmed by SEM/EDAX and TEM analysis. The photo catalytic activity of prepared pure SiO₂ NPs towards remediation of dyes like Methyl red (MR) dye has been tested.

Keywords: Rice husk ash; Silica nanoparticles; Methyl red dye; Degradation

Introduction

Dyes are one of the most hazardous contaminants in aquatic environment because majority of the used dyes are azo reactive dyes which one or several azo (-N = N-) groups associated with substituted aromatic structures [1]. These are used in industries like textiles, leather, paper, ceramics, and food-processing technologies. The released wastewater from these causes the carcinogenic and mutagenic diseases to human health and environment. Furthermore these show the deleterious effect of the colour in the receiving water bodies and environment [2]. Owing to their toxicity and contamination, the efficient degradation of these azo dyes has become a challenging task in recent years.

Methyl Red (MR) is a commonly used monoazo dye in laboratory assays, textiles and other commercial products. It was well known that methyl red dye has been used in paper printing and textile dyeing [3]. However, it may cause eye and skin sensitization and digestive tract irritation if inhaled or swallowed [4]. It is, therefore, essential to remove the dye from wastewater and inevitable to investigate new alternatives for the adequate treatment of these azo based dyes.

Different types of methods are employed for remediation of these toxicants via physical and chemical processes. The chemical methods involve chlorination and ozonation, while the physical methods consist of reverse osmosis, flocculation, membrane filtration process and degradation [5]. Among these methods degradation is one of the most investigated methods for remediation of dye in aqueous medium due to its ease of operation as compared with reported methods [6].

Rice husk is an agricultural waste material abundantly available in rice-producing countries [7-12]. These are the natural sheaths that form on rice grains during their growth [13]. Moreover RHA is a cheap source of amorphous silica. It is generated by burning rice husk, an agricultural by product. It is used as a fuel for generation of energy mainly in rice milling plants [14]. A large quantity of RHA is generated as waste material from rice mill. RHA is also generated from industries like brick making, distilleries, furnaces, gasifiers, and power plants, where rice husk is used as a fuel. Usually, the ash is dumped in the open, which causes air and water pollution by blowing wind. Thus

it is a great challenge to dispose of RHA or to utilize it economically for other useful purposes. RHA contains mainly silica and that silica may be used for a variety of purposes. Silica of the ash may be either amorphous or crystalline or mixture of both, depending on the burning temperature. The ashes obtained after slow combustion of husk at low temperatures contain amorphous silica, whereas ash formed at higher temperatures contains mostly crystalline silica. Amorphous SiO₂ NPs play a pivotal role in wide number of applications, because these are having unique features such larger surface area than that of other particles and materials, high efficiency towards catalytic reactions involves adsorption and degradation of toxic elements and dyes in aqueous medium.

Although SiO₂ NPs are essentially inert for many reactions, it shows noticeable activity towards photocatalytic degradation of dyes in aqueous medium. Moreover pure silica was proven to promote photocatalytic reactions such as the photo-oxidation of CO and the photometathesis of propene. Additionally, silica-based photocatalysts, such as silica-alumina, silica-supported zirconia, silica-supported magnesia, and silica-alumina-titania, exhibit activity under UV irradiation at room temperature. The photoactive sites were formed on the surface of silica (SiO₂) prepared by an extraction method by using rice husk ash [15-18].

In precedent work, the main objective was preparation of SiO₂ NPs from RHA and their formation was completely studied and confirmed by FT-IR, SEM/EDXA and TEM analysis. Furthermore these SiO₂ NPs are used as effective reductant for photocatalytic degradation of methyl orange dye in aqueous medium.

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Materials and Methods

Materials

The rice husk can be taken from near rice mill and convert to rice husk ash. Whatman No. 41 ashless filter paper and double distilled water was used throughout in this study. The percentage of dye removal from aqueous medium was estimated from its optical density at $\lambda_{\text{max}}=522$ nm using UV-Vis spectrophotometer.

Preparation of pure SiO₂ NPs from RHA

We have followed the procedure reported by Kamath et al. in the year 1998 [18]. Sixty ml portions (60 mL) of 1N NaOH were added to the washed RHA samples and boiled in closed 250 ml Erlenmeyer flask for 1 h with constant stirring to dissolve the silica and produce a sodium silicate solution. Then the solution was filtered through Whatman No. 41 ash less filter paper, while the carbon residue was washed twice with 100 ml of boiling water. The filtrates and washings are allowed to cool at room temperature by adjusting the pH 7, later titrate this against 1N HCl with constant stirring. Due to the precipitation, silica gels are formed, that is allowed to ageing for 18 h. Then doubled distilled water (100 mL) was added to silica gels to make slurry. These gels are transferred into a beaker, which is kept it into hot air oven at 80°C for drying. After, these NPs are washed twice and repeat the drying process to get pure SiO₂ NPs. These samples are kept in a vacuum desiccator, stored up to 45 days.

The X-ray diffraction pattern (XRD) of the samples were recorded using D2 phaser XRD (Bruker AXS GmbH, Germany) with Ni-filtered Cu K_α radiation, $\lambda=1.5417$ nm. Infrared spectrum of the samples was recorded by KBr pellet method using IR analyzer (FT-IR8600PC, Shimadzu Corporation, Japan).

Photo catalytic degradation of MR dye from SiO₂ NPs prepared from RHA

In a typical stoichiometric case, freshly prepared pure SiO₂ NPs (1.0 gm) was added to MR dye solution (0.05 mM, 100 mL) and stirred magnetically. In order to establish the adsorption equilibrium between the MR dye and the photocatalyst, the resulting solution was stirred in the presence of sunlight for 2 h; the reaction mixture was withdrawn periodically by using a syringe tube and then centrifuges (REMI, R-8C BL Bench Top Centrifuge) to separate the suspended silica nanoparticles. The decrease in the MR dye concentration was estimated from its optical density. The decrease in the dye concentration due to reaction between SiO₂ NPs and MR dye was expressed in terms of % reduction as a function of time.

Results and Discussion

Formation of SiO₂ NPs from RHA

Synthesis of the SiO₂ NPs using RHA is a green synthesis method. These NPs are amorphous in nature within the range of 10 to 30 nm. The surface area of the amorphous nanoparticles is very high so the reactivity of the nanoparticles is also high. Amorphous SiO₂ NPs can be prepared by using rice husk ash via sodium hydroxide is a precipitating agent. Rice husk silica is converted into NaSiO₂, as a xerogel then it is heated at 80°C to form SiO₂ NPs and it is again washed and dried. Dried pure SiO₂ NPs are characterized by using FT-IR, XRD, SEM/EDAX and TEM analysis.

XRD and FT-IR analysis of SiO₂ NPs

Formation of pure SiO₂ NPs was confirmed by XRD analysis as

shown in Figure 1. The broad X-ray diffraction pattern of RHA silica indicates a typical form for amorphous solids, furthermore confirmed the absence of any ordered crystalline structure. A broad peak ($2\theta=22^\circ$, (101)) confirmed the amorphous nature of the silica [19]. The sharp smaller peaks indicate the presence of sodium chloride that was formed during the silica precipitation.

FT-IR spectra of freshly prepared pure SiO₂ NPs are shown in Figure 2. These shows absorption bands arising from asymmetric vibration (Si-O and Si-OH) are 1090 cm⁻¹, 950 cm⁻¹ and symmetric vibration (Si-O) at 793 cm⁻¹ respectively [20]. The absorption bands between 800 and 1260 cm⁻¹ have been described as a superimposition of various SiO₂ peaks due to residual organic groups. Water shows an intense characteristic absorption band at 3486 cm⁻¹ assigned to O-H stretching in H-bonded water. Moreover this band can be cross checked through the 1640 cm⁻¹ band due to scissor bending vibration of molecular water.

Removal of MR dye from SiO₂ NPs

The concentration of MR dye removal was estimated from its optical density at $\lambda_{\text{max}}=522$ nm using UV-Vis spectrophotometer. The decrease in MR dye concentration due to reaction between SiO₂ NPs was expressed here in terms of % reduction as a function of time as shown in Figure 3. MR dye degradation was observed before and after exposure to the sun light for different intervals of time. While in the presence of SiO₂ NPs as a photo catalyst, the intensity of the peak was found to decrease with increasing irradiation time due to photo catalytic activity of SiO₂ NPs. There was about 50% degradation in first 20 min, later increased up to 80% in 60 min was observed. The maximum degradation takes place in the first hour but in the second hour slow degradation can be seen in Figure 4. Moreover 95% degradation was observed at the end of 120 min.

Efficiency of SiO₂ NPs under UV irradiation

SiO₂ NPs were found to be photo excited under, which was attributed to the charge transfer from the bonding orbital of Si-O to the 2p nonbonding orbital of non-bridging oxygen. When a photon of

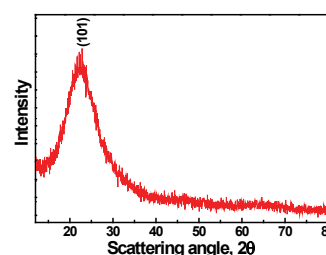


Figure 1: X-ray diffraction spectra of pure silica nanoparticles.

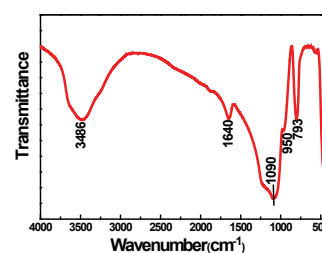


Figure 2: FT-IR spectra of pure silica nanoparticles.

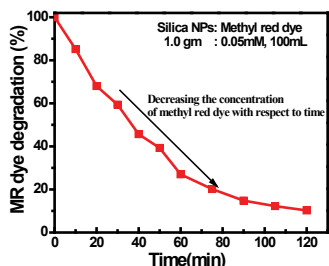


Figure 3: Removal of MR dye using amorphous silica Nps (silica Nps: 1.0 g, MR dye: 0.05 mM, reaction time: 120 min).

UV light strikes the SiO₂ surface, an electron from its valence band (vb) jumps to the conduction band (cb) leaving behind a positively charged hole (h⁺_{vb}). The negative charge is increased in the conduction band (e⁻_{cb}) and photocatalytic active centres are formed on the surface of SiO₂ NPs, SiO₂ + hv → e⁻_{cb} + h⁺_{vb}. The valence band holes react with the chemisorbed H₂O molecules to form reactive species such as ·OH radicals, which subsequently react with dye molecules to cause their complete degradation. The major role of the deposited surface particles is the consumption of electrons and passing of those electrons to H⁺ ions or to O₂. The retardation of electron-hole recombination will increase the photo catalytic efficiency as well as accelerate the hydroxyl radical formation which will enhance the rate of MR dye degradation [21].

SEM/EDAX and TEM analysis

The SEM images of the pure SiO₂ NPs have been shown in Figure 4. These particles are formed approximately in the range 12 nm and furthermore these are not having definite shape and size. Hence, it can be conclude that nanoparticles are amorphous in nature.

These SiO₂ NPs are having high specific surface area i.e., 68 m²/g, which is due to the presence of small size of the SiO₂ NPs and shows high efficiency towards the photo catalytic reactions. However EDX analysis confirmed the formation of pure SiO₂ NPs which contain only silica and oxygen along with some impurities like sodium in low concentration. The particle size and morphology of the catalysts were assessed by transmission electron microscopy (TEM).

Figure 5 shows the TEM results of amorphous SiO₂ NPs synthesized using RHA. As shown in Figure, nanoparticles are amorphous in nature which was formed that is consistent with FE-SEM images in density, morphology and dimension. Moreover TEM image confirms the formation of SiO₂ NPs at 10 to 20 nm range. Overall, the TEM results reveal the formation of silica nps is amorphous in nature. The results are good agreement with previous literature [22].

Conclusion

We have successfully achieved the preparation of pure SiO₂ NPs and confirmed the formation of SiO₂ NPs by XRD, FT-IR, SEM/EDAX and TEM analysis. Moreover prepared SiO₂ NPs are having high specific

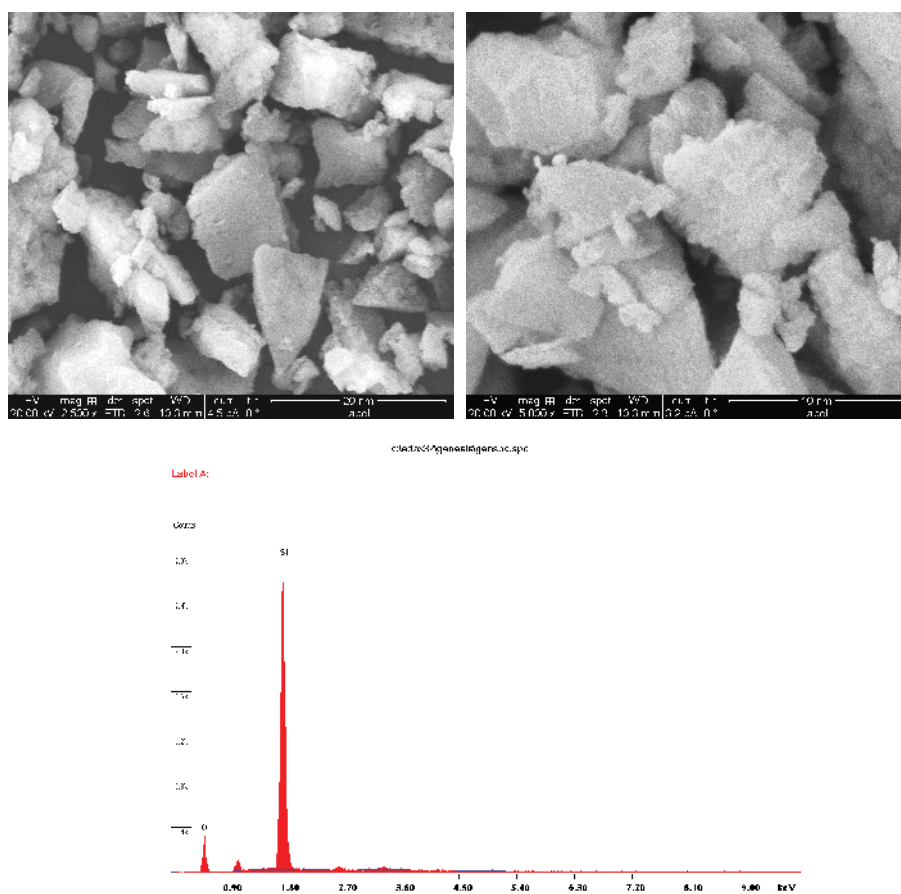


Figure 4: SEM with EDX analysis shows the surface morphology of pure silica Nps synthesized from RHA.

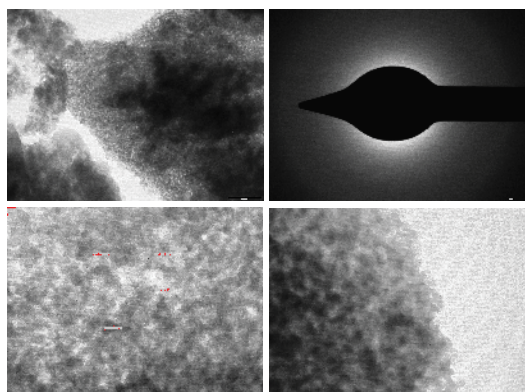


Figure 5: TEM analysis of pure silica Nps synthesized from RHA under ambient conditions.

surface area and highly active in the presence of sunlight. Hence due to this, degradation of MR dye was very rapid in the presence of sunlight. The removal of MR dye can be achieved rapidly through photo catalytic degradation process by SiO_2 NPs from aqueous medium. The removal of MR dye concentration was estimated from its optical density at $\lambda_{\text{max}}=522$ nm using UV-Vis spectrophotometer. The decrease in MR dye concentration due to reaction between SiO_2 NPs was expressed here in terms of % reduction as a function of time.

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