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Photocatalytic degradation of methyl orange and Congo red using C,N,S-tridoped SnO₂ nanoparticles

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ABSTRACT

In this study, the photocatalytic degradation of methyl orange and Congo red dye was investigated in aqueous solution using C,N,S-tridoped SnO2 nanoparticles as a nano photocatalyst. The degradation was carried out under different conditions including the photocatalyst amount, initial concentration and pH of the solution. The results indicated that the degradation of methyl orange and Congo red was strongly influenced by these parameters. The best conditions for the degradation of methyl orange and Congo red were obtained. The optimum value of photocatalyst amount used was 0.4 g/L. It was found that the photodegradation efficiency increase with increasing the initial concentration of methyl orange and Congo red. The optimum pH of the system used is 6.5.

Keywords: Photocatalytic degradation; Dye; SnO₂ Nanoparticles; Photocatalyst

INTRODUCTION

Waste dye disposal practices involve a number of conventional techniques, such as sewer and incineration. Despite the widespread utilization of these techniques, they do not to remove dye from contaminated waters. Waste dyes are disposed into water through sewer or direct disposal. Such practices could be hazardous and cause serious water contamination. Large band gap semiconducting particles are being investigated as catalysts for photodegradation of drugs and organic contaminants in water [1-3].

Nanometer range semiconducting materials have been a subject of intense study for last several years due to their size dependent physical and chemical properties below a critical size characteristic of the material. Newly, the interest in the physical properties of semiconducting metal oxide, such as SnO_2 , TiO_2 and ZnO, has significantly increased due to their potential applications, in special when they are intentionally doped with magnetic elements [4,5].

Wide energy-band-gap semiconductors have attracted a great deal of interest because of their potential applications in next-generation electronic and optoelectronic devices, such as field-effect transistors, organic bistable memory devices (OBDs), light-emitting diodes (LEDs), and solar cells [6–10]. Among the various kinds of wide energy-band-gap semiconductor nanoparticles. SnO₂ semiconductors have been particularly interesting due to their excellent optical

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and electrical properties, as well as their high chemical stability [11–13]. SnO₂ nanoparticles have been formed using several methods of sol-gel process, pulsed laser ablation, spray pyrolysis, CVD, and thermal evaporation [14–18].

In this work, we synthesized C,N,Stridoped SnO_2 nanoparticles by chemical precipitation method and their application for photo-degradation of methyl orange and Congo red was investigated.

EXPERIMENTAL

Materials

The chemical reagents used included Tin (IV) chloride pentahydrate (Sigma), Thiourea (Aldrich), ammonia solution (Merck) and distillated water. Congo red (CR) and Methyl Orange (MO) were purchased from LABCHEM.

Preparation of C,N,S-tridoped SnO₂ nanoparticles

N,S,C-SnO₂ powders were prepared using a precipitation method [19]. The thiourea was mixed with Tin (IV) chloride pentahydrate in 500 ml distillated water to form a 0.25 M aqueous solution. Then, the solution was stirred for 3 h. Following complete dissolution, the solution was treated with an ammonia solution (25%) until the solution pH reached to 7. The resulting solution was stirred for another 2 h. Precipitated products were separated from the solution by centrifugation, and dried at 100°C for 24 h. The obtained products were ground and calcined at an elevated temperature for 3 h with a heating rate of 5°C/min.

Characterization

The XRD patterns found on a X-ray diffractometer (type HZG41B-PC). The morphology of surface was tested using SEM (JSM 6701F—6701). The particle size of the nano powders was measured

using Transmission Electron Microscope (TEM) (Zeiss EM-900).

Assessment of the photo catalytic experiment

Photo catalytic degradation of dyes was used to evaluate the photo catalytic activity of synthesized C,N,S-tridoped SnO₂ nano powders. First, the different concentration solutions of dyes were prepared in deionized water and then 50 ml of prepared solution are transferred in two purely clean containers. Several amount of photocatalyst were added to containers. Solutions were placed at a distance of 30 cm from UV lamp with power of 30 W for a time interval of 60 minutes. The solutions were continuously stirred over the whole of time. Samples were taken from both solution and were filtered and centrifuged for 20 minutes to remove all nanoparticles completely. Finally, clear transparent solutions were obtained. Afterwards, samples were taken from obtained solutions and put in the double beam spectrophotometer to measure the absorbance of remained dye.

RESULT AND DISCUSSIONS *Photocatalyst characterization* X-ray diffraction (XRD)

The Fig. 1 shows the XRD pattern of C,N,S-tridoped SnO_2 nanoparticles. As seen, the diffraction peaks are well appointed to sample has a tetragonal crystalline phase (ICDD card No. 41-1445). The average particles size of samples are found to be 29 nm for C,N,S-tridoped SnO₂ nanoparticles.



Scanning electron microscopy (SEM)

Figs. 2 show the SEM images of C,N,Stridoped SnO_2 nanoparticles, showing products consist of nanoparticles structures. The average diameter of the sample was below 50 nm. As seen Fig. 2, the synthesized nanoparticles have aggregation to form spherical particles.



Fig. 2. SEM image of C,N,S-tridoped SnO₂ nanoparticles.

Transmission Electron Microscope (TEM)

The Fig. 3 shows the TEM micrograph of C,N,S-tridoped SnO_2 . Based on observations, the sample was monodispersed particles with spherical shape and size blow 50 nm with a permanent dispensation. Moreover, the TEM image shows that sample is nanometer scale, which is follow with the results obtained from the XRD patterns.



Fig. 3. TEM image of C,N,S-tridoped SnO₂ nanoparticle.

Photo catalytic Degradation Effect of the amount of C,N,S-tridoped SnO₂

Experiments carried out with several amount of C,N,S-tridoped SnO₂ are shown 4. Be observed that the in Fig. photodegradation valus enhance with an C,N,S-tridoped enhanced in SnO₂ concentration up to 0.4 g/L. This observation can be described in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension. The total active surface area increases with increasing catalyst dosage. At the same time, due to an increase in the turbidity of the suspension, there is a decrease in UV light penetration as a result of increased effect scattering and hence the photoactivated volume of suspension decreases [20].



Fig. 4. Effect of the amount of C,N,S-tridoped SnO₂ on the photodegradation efficiency Conditions: dye concentration=50 mg/L, pH= 6.5, V=50 mL.

Initial dye concentration effect

The influence of initial dye concentration on degradation was examined in the range of 25-100 mg/L with 0.4 g/L catalyst loading. The representative concentrationtime profiles were shown in Fig. 5. The rate of photodegradation of the dye decreased at higher concentrations. With increasing the amounts of dyes, the more of dye molecules will be adsorbed on the surface of the photocatalyst and the active sites of the catalysts will be reduced. Therefore, with increasing occupied space of catalyst surface, the generation of hydroxyl radicals will be decreased. Also, increasing concentration of dye can lead to decreasing the number of photons that is arrived to the surface of catalysts. The more light is absorbed by molecules of dye and the excition of photocatalyst particles by photons will be reduced. Thus, photodegradation efficiency diminished [21].



Fig. 5. Effect of initial dye concentration on the photodegradation efficiency Conditions: photocatalyst=0.4 g/L, pH= 6.5, V=50 mL.

pH of solution effect

Photodegradation of drug was studied in amplitude pH of 3.9-9.5 in the presence of C,N,S-tridoped SnO₂ catalyst (0.4 g/L). In all cases, the maximum degradation efficiency was obtained in acidic pH 6.5 for dyes. In the presence of C,N,S-tridoped SnO_2 and in pH 6.5, degradation efficiency was high. The interpretation of pH solution effects on the photocatalytic processes is very difficult task because of its multiple roles such as electrostatic interactions semiconductor between the surface, solvent molecules, substrate and charged radicals formed during the reaction process [22, 23].



Fig. 6. Effect of the pH on the photodegradation efficiency Conditions: dye concentration=50 mg/L, photocatalyst=0.4 g/L, V=50 mL.

The pH influences the characteristics of photocatalyst surface charge. the Therefore, pH of the solution is a significant parameter in performing the reaction on the surface of semiconductor acidic particles. In solutions photodegradation amount was more than that in basic solutions. This is because photodecomposition of C,N,S-tridoped SnO₂ takes place in acidic and neutral solutions.

CONCLUSIONS

C,N,S-tridoped SnO₂ nanoparticles synthesized by powders were the precipitation method from thiourea and tin (IV) chloride pentahydrate. XRD results show that average of particles size is in the range from 29 to 32 nm. TEM images of C,N,S-tridoped SnO₂ nano powders shows that the particle agglomerated with an average diameter < 50 nm. Other techniques, including SEM was employed characterize all of the synthesized materials. The photo catalytic properties of these nano structures cause decomposition of the CR and MO in presence of UV light irradiation. Results show, doping of SnO₂ nanoparticles with C, N and S, improve the photo catalytic SnO_2 . The optimal properties of degradation conditions of CR and MO are: 0.4 g/L catalyst, pH 6.5 and dye concentration 50 mg/L.

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