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Effect of Operational Parameters on Photodegradation of Methylene Blue on ZnS Nanoparticles Prepared in Presence of an Ionic Liquid as a Highly Efficient Photocatalyst

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In the present study, photocatalytic degradation of methylene blue (MB) on ZnS nanoparticles, prepared in aqueous solution of a room-temperature ionic liquid (RTIL), was studied and the results were compared with commercial ZnS. Influence of various operational parameters such as calcination temperature, catalyst weight, pH of solution, and initial concentration of MB on the photodegradation reaction was investigated to achieve maximum degradation efficiency. The optimum value of pH and catalyst dose was found to be 9.5 and 0.6 g l^{-1}. It was demonstrated that the photodegradation of MB follows a pseudo first-order kinetic. At optimized conditions, the rate constant of the reaction on ZnS nanoparticles prepared in aqueous solution of the RTIL is about five and four times greater than the prepared sample in water and commercial ZnS, respectively.

Keywords: ZnS, Photocatalysis, Room-temperature ionic liquid, Methylene blue, Nanoparticle

INTRODUCTION

Many industries such as textile and printing are using dyes and pigments and thus producing colored waste effluents. Disposal of these wastes into water causes environmental problems [1,2]. The removal of these compounds from wastewaters is of a great important, because many dyes and their degradation products are toxic and carcinogenic, posing a serious hazard to the environment [3]. Photocatalysis can provide solutions for many of the environmental problems facing the world because it provides a simple way to use light to induce degradations [4]. For this reason, scientific interest on photocatalytic degradation of organic pollutions has quickly grown in recent years [5,6]. This method is generally based on generation of OH radicals which attack organic pollutants leading to progressive degradation and subsequently complete mineralization [7,8].

The initial step of photocatalysis processes is absorption of photons with the wavelength adequate to match energy levels of the photoactive materials. In the case of semiconductors, illumination induces electron promotion from valence to conduction band if the energy of the photons exceeds the band width. Most of these electron-hole pairs recombine, releasing the absorbed energy. A small percentage of these pairs migrate to the surface of photocatalyst where they can be captured by adsorbed molecules to start the catalytic reactions [4]. An important method for producing highly active heterogeneous photocatalysts is to suppress recombination of photogenerated electrons and holes so as to maximize the number of photogenerated electron-hole pairs that can participate in surface chemical reactions [9-11].

Room-temperature ionic liquids (RTILs) have been widely studied as a new kind of reaction media owing to their unique physicochemical properties [12]. RTILs have recently

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received a great deal of attention as potential new media for preparation of various nanomaterials [13-17]. RTILs generally have high-cost relative to conventional solvents. Moreover, RTILs with PF_6^- and BF_4^- ions are known to decompose in the presence of water and as a result, toxic and corrosive species are formed [18,19]. For these reasons, we have applied a halide-free and low-cost RTIL with alkyl sulfate anions in preparation of some nanomaterials with improved properties [20-23]. The RTILs with alkyl sulfate anions are halide-free and relatively hydrolysis-stable compounds [24].

Nanoparticles of ZnS have mainly prepared in 1-butyl-3-methylimidazolium tetrafluoroborate as a halide containing RTIL [25-29]. However, to the best of our knowledge, there is not any report about effect of RTILs on photocatalytic activity of the prepared samples. Very recently, in a preliminary study, we have prepared ZnS nanoparticles in aqueous solutions of 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM] [$EtSO_4$]) [22]. The results demonstrate that photocatalytic activity of the ZnS nanoparticles prepared in presence of the RTIL has been improved.

In the present paper, ZnS nanoparticles were prepared in aqueous solutions of [EMIM] [$EtSO_4$] and the influence of various parameters such as calcination temperature, catalyst weight, pH of solution and initial concentration of methylene blue (MB) on photocatalytic degradation of the dye was studied to achieve maximum degradation efficiency. Moreover, photocatalytic activity of the prepared nanoparticles was compared with ZnS nanoparticles prepared in water and commercial ZnS.

MATERIALS AND METHODS

Materials

Zinc acetate ($Zn(CH_3COO)_2.2H_2O$ extra pure), thioacetamide (TAA, CH_3CSNH_2 GR for analysis), commercial ZnS and absolute ethanol were obtained from Merck, and employed without further purification. The ionic liquid was 1-ethyl-3-methylimidazolium ethylsulfate, [EMIM] [$EtSO_4$], and synthesized according to the literature [30]. Nanoparticles of ZnS were prepared in presence of the RTIL and water according our previously reported method [22]. Double distilled water was used for the experiments.

Apparatus

Reaction kinetics was investigated spectrophotometrically using a Unico 2100 spectrophotometer. UV-Vis absorption spectra were recorded on a Shimadzu 1600 PC apparatus.

Photocatalysis Experiments

Photocatalysis experiments were performed in a cylindrical pyrex reactor with a capacity of about 400 ml. The reactor provided with water circulation arrangement to maintain the temperature at 25 °C. The solution was magnetically stirred and continuously aerated by a pump to provide oxygen and complete mixing of the reaction solution. A UV Osram lamp with 125 W was used as UV source. The lamp was fitted on the top of the reactor. Prior to illumination, a suspension containing a desired value of the nanoparticle and 250 ml of MB solution (with desired concentration) was stirred continuously in the dark for 30 min, to attain adsorption equilibrium. Samples were taken from the reactor at regular intervals and centrifuged to remove the photocatalyst before analysis by spectrophotometer at 664 nm corresponding to maximum absorption wavelength (λ_{max}) of MB.

RESULTS AND DISCUSSION

Photocatalytic degradation of MB on the nanoparticles was studied spectrophotometrically in a batch reactor. Plots of absorbance *vs*. wavelength for photodegradation of MB on ZnS nanoparticles (prepared in presence of the RTIL) obtained at various irradiation times are demonstrated in Fig. 1 ([*MB*] = 2.20×10^{-5} M, catalyst weight = 0.1 g). It is clear that 664 nm is an appropriate wavelength for investigating the reaction kinetics.

Dependence of photocatalytic reaction rate on concentration of the organic pollutants is generally described by the following kinetic model [31]:

$$rate = -\frac{d[MB]}{dt} = \frac{kK[MB]}{1+K[MB]} \quad (1)$$

where k is first-order rate constant of the reaction and K is adsorption constant of the pollutant on the photocatalyst. Also, [*MB*] is concentration of MB (M) at any time; t is the irradiation time. Equation (1) can be simplified to a pseudo first-order equation [31]:

$$\ln\frac{[MB]_o}{[MB]} = \ln\frac{A_0}{A} = kKt = k_{obs}t \quad (2)$$

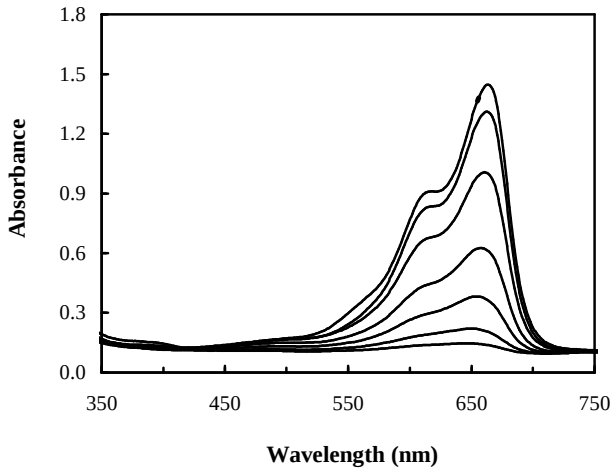

Fig. 1. Absorption spectra in various times for degradation of MB at 25 ºC on ZnS nanoparticles prepared in aqueous solution of the RTIL.

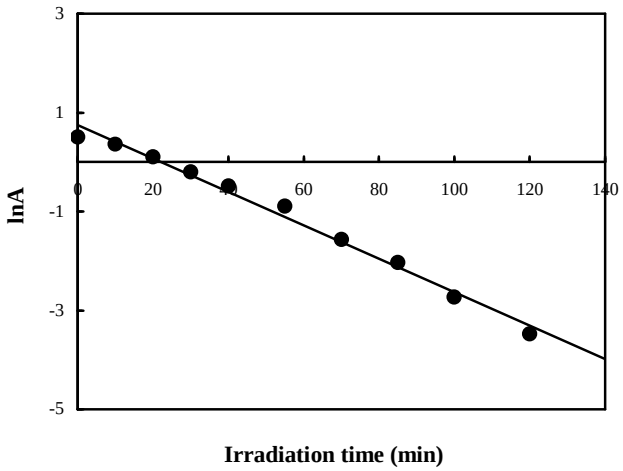

Fig. 2. Plot of ln*A* (absorbance) *vs*. irradiation time for degradation of MB on ZnS nanoparticles prepared in aqueous solution of the RTIL ([*MB*] = 2.55×10^{-5}, catalyst weight = 0.10 g, calcination temperature = 200 ºC).

in which k_{obs} is the observed first-order rate constant of the photodegradation reaction. In order to examine whether the reaction rate could be congruent with a pseudo first-order reaction under different conditions, plots of ln*A* (logarithm of absorbance) *vs*. irradiation time, were considered. For example, Fig. 2 demonstrates plot of ln*A vs*. irradiation time for photodegradation of MB on ZnS nanoparticles prepared in aqueous solution of the RTIL, where [*MB*] = 2.55×10^{-5}, catalyst weight = 0.10 g, calcination temperature = 200 ºC. As can be seen, a well linear correlation existed between ln*A* and irradiation time.

Influence of various parameters including (i) calcinations temperature, (ii) catalyst weight, (iii) pH of solution and (iv) initial MB concentration on photocatalytic degradation of MB was carried out in order to obtain maximum degradation efficiency.

Effect of Calcination Temperature

Generally, photocatalytic activity depends on calcinations temperature of the photocatalysts. Dependence of MB absorbance on irradiation time on ZnS nanoparticles prepared in presence of the RTIL calcined at various temperatures is shown in Fig. 3. As can be seen, with calcination of the nanoparticles, the degradation of MB decreases. Figure 4 shows dependence of the observed first-order rate constant of

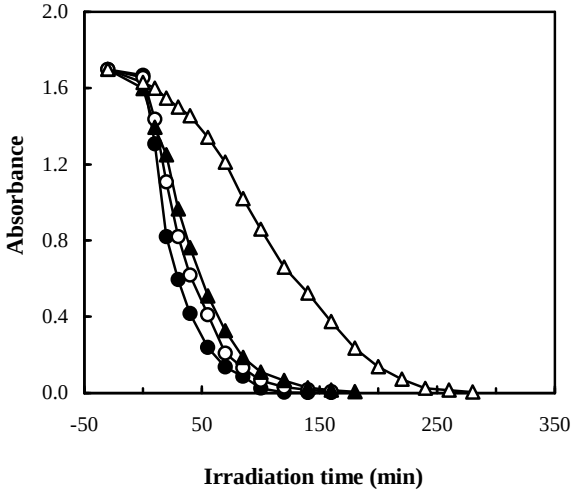

Fig. 3. Plot of absorbance *vs*. irradiation time for degradation of MB on ZnS nanoparticles prepared in aqueous solution of the RTIL calcined at various temperatures ([*MB*] = 2.55×10^{-5}, catalyst weight = 0.10 g). (◆) No calcinations, (◇) 200 ºC, (▲) 300 ºC, (△) 400 ºC.

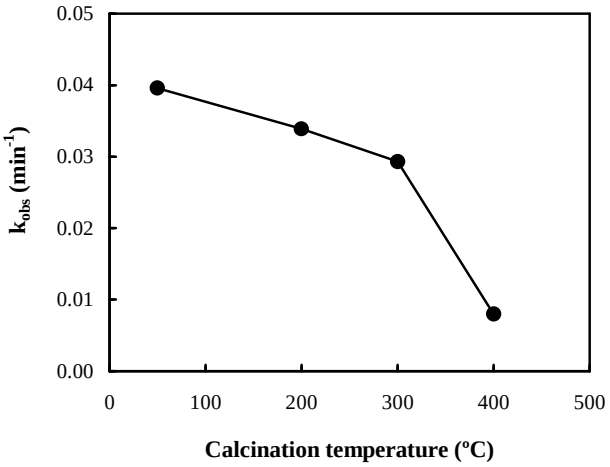

Fig. 4. Plot of observed first-order rate constant of the photodegradation reaction *vs*. calcination temperature.

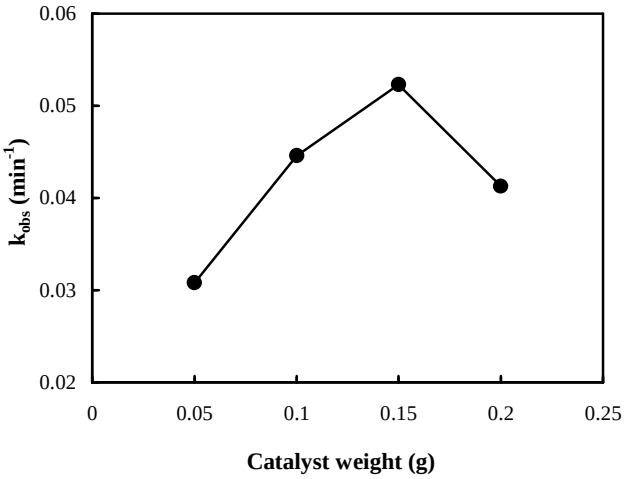

Fig. 5. Plot of observed first-order rate constant of the photodegradation reaction *vs*. the catalyst weight.

the reaction on calcination temperature. It is clear that the reaction rate constant decreases with the calcinations temperature (Fig. 4) which can be attributed to aggregation of the ZnS nanoparticles at higher temperatures. Similar results have been reported for various photocatalysts [32,33].

Effect of the Catalyst Weight

Rate constant for photocatalytic degradation of pollutants is generally related to the catalyst weight [34,35]. Hence, a series of experiments were carried out to find the optimum amount of the catalyst by varying the photocatalyst weight between 0.05 and 0.20 g. Figure 5 shows the plot of reaction rate constant *vs*. the weight of the photocatalyst. As can be seen, the degradation rate constant of the reaction increases with increasing weight of the photocatalyst and then decreases. Indeed, maximum value was achieved at 0.15 g of the photocatalyst, which might be due to two competitive processes [35]. In general, the greater amount of photocatalyst, the higher the reaction rates should be, due to the fact that active sites of the photocatalyst are increased. However, more photocatalyst would also induce greater aggregation of the photocatalyst, making a significant fraction of the catalyst to be inaccessible to either adsorbing the dye or absorbing the radiation. Then, the reaction rate constant decreases after an optimum value for the photocatalyst weight.

Effect of Solution pH

It is well known that pH of solutions influences adsorption and dissociation of substrate, photocatalyst surface charge, oxidation potential of the valence band and other physicochemical properties of the system [36]. Thus, the solution pH is an important variable in aqueous phase mediated photocatalytic reactions. For this reason, influence of pH on the photocatalytic degradation of MB was studied in the pH range of 2-11 using the optimum catalyst weight. The pH of solutions was adjusted by adding appropriate amounts of NaOH or HCl solutions. Figure 6 shows plots of absorbance *vs*. irradiation time for the degradation of MB at various pH. Moreover, plot of the observed first-order rate constants for the degradation of MB as a function of pH is shown in Fig. 7.

As can be seen, the degradation of MB sharply increases up to pH 7, then slows down and decreases at pH higher than 9.5. Since the pH of zero point charge for ZnS is about 7 [37], then at pH values lower than 7, ZnS surface is positively charged and thus repulsive forces between the photocatalyst and MB with its cationic charge lead to a decrease in dye adsorption and photodegradation rate. Furthermore, similar to ZnO, ZnS nanoparticles are readily dissolved in acidic solutions [38]:

$$ZnS + 2H^{+} \longrightarrow Zn^{2+} + H_2S \quad (3)$$

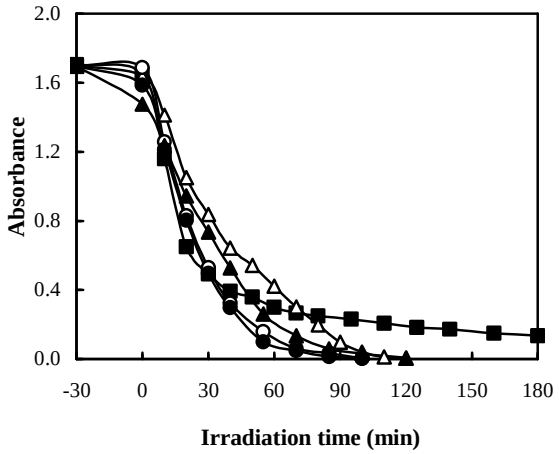

Fig. 6. Plot of absorbance *vs*. irradiation time for degradation of MB on ZnS nanoparticles prepared in aqueous solution of the RTIL at various pH ([*MB*] = 2.55 × 10^{-5}, catalyst weight = 0.15 g). (■) pH= 2, (△) pH = 5, (◇) pH = 7, (◆) pH = 9.5, (▲) pH = 11.

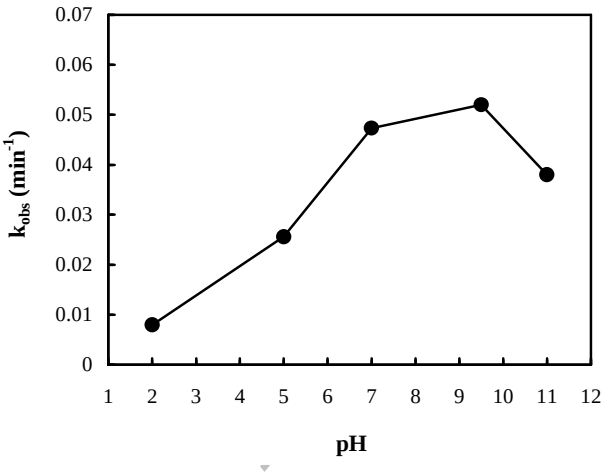

Fig. 7. Plot of observed first-order rate constant of the photodegradation reaction *vs*. solution pH.

Therefore, the photocatalyst has low stability in acidic solutions, and the photocatalytic reaction rate is sharply decreased with decreasing pH of the solution. In alkaline solutions, ZnS surface is negatively charged because of adsorbed OH^- ions. In this media, electrostatic interactions between MB with cationic charge and ZnS with anionic charge would favor adsorption of the dye, so photodegradation efficiency will be favored by increasing pH of solution. Also, the presence of large quantities of OH^- ions on the photocatalyst surface favors the formation of OH radical, which is accepted as the primary oxidizing species responsible for photodegradation [39]. However, with further increasing pH of solution, repulsion of hydroxide ions by the negatively charged photocatalyst surface can lead to a reduction in OH radical formation and hence, a decrease in photodegradation efficiency can be occurred.

Effect of Initial MB Concentration

The effect of pollutant concentration is an important parameter in wastewater treatment [40,41]. The photocatalytic degradation of MB at different initial concentrations in the range 7.0 × 10^{-6}-3.0 × 10^{-5} M was investigated under the optimized conditions (catalyst weight = 0.15 g, pH = 9.5). Figure 8 demonstrates dependence of the rate constant on concentration of MB. It is clear that the photodegradation of MB decreases with increasing concentration of the dye. By increasing the concentration of MB, more dye molecules are adsorbed at the catalyst surface, resulting in occupation of the catalyst active sites and consequently decreasing the OH radicals generated at the photocatalyst surface. Hence, the rate of photodegradation reaction, which related to the OH radicals [39], decreases with increasing the concentration of MB. Moreover, the large amount of the adsorbed MB is thought to inhibit the reaction between the dye molecules and photogenerated holes or the hydroxyl radicals [42]. Increasing absorption or scattering of the light at high concentrations of the dye molecules in solution also decrease the photons reaching the catalyst surface, thus decreasing the photodegradation rate of MB [42].

Comparison of Photocatalytic Activity of the Nanoparticles with Commercial ZnS

In order to demonstrate effect of the RTIL on photocatalytic activity of ZnS nanoparticles, the photodegradation experiments were carried out by the prepared ZnS in water and aqueous solution of the RTIL along with commercial ZnS at the optimized conditions of catalyst weight = 0.15 g, pH = 9.5 and [*MB*] = 2.55 × 10^{-5} M, and the results are shown in Fig. 9. It is clear that the degradation of

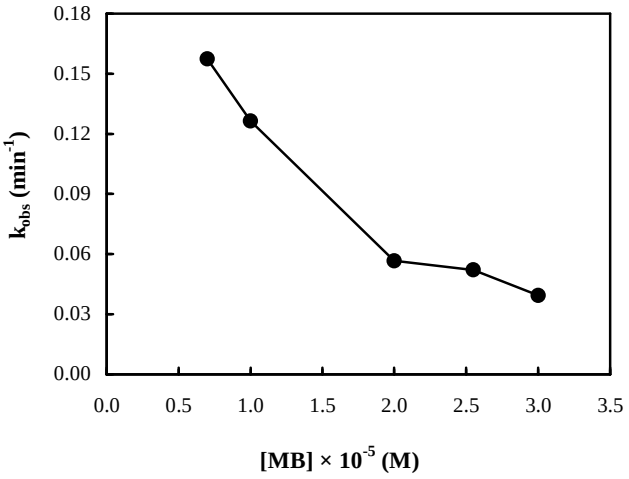

Fig. 8. Plot of observed first-order rate constant of the photodegradation reaction *vs*. concentration of MB.

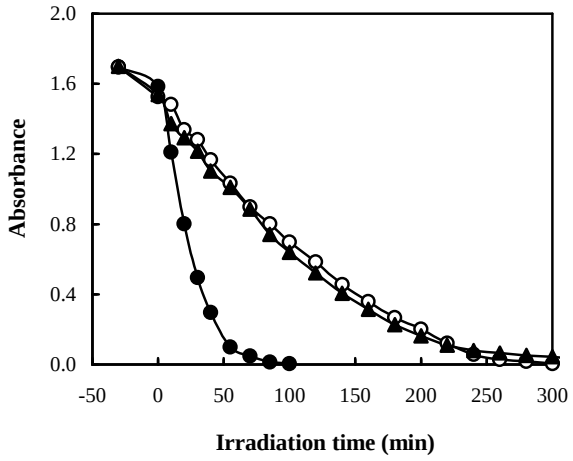

Fig. 9. Photodegradation of MB by the prepared ZnS in water and aqueous solution of the RTIL along with commercial ZnS at optimized conditions (catalyst weight = 0.15 g, pH = 9.5 and [*MB*] = 2.55 × 10^{-5} M). (◆) Prepared in water + RTIL, (◇) Prepared in water, (▲) commercial.

MB on ZnS nanoparticles prepared in presence of RTIL occurs at about 100 min which is remarkably shorter than the corresponding times for the other samples. The observed first-order rate constants of the reactions on ZnS nanoparticles prepared in aqueous solution of the RTIL, water and commercial ZnS are 52.0 × 10^{-3}, 10.7 × 10^{-3} and 12.6 × 10^{-3} min^{-1}, respectively. Hence, the rate constant of the reaction on ZnS nanoparticles in presence of the RTIL is about five times of the one prepared in water and four times of the commercial ZnS.

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کارگاه‌های آموزشی مرکز اطلاعات علمی

آموزش نرم‌افزار Word برای پژوهشگران

روش تحقیق کمی

آموزش مهارت‌های کاربردی در تدوین و چاپ مقالات ISI