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Synthesis of Silica-Supported Preyssler Nanoparticles and their Applications for Azo Dyes Degradation

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Synthesis of Silica-Supported Preyssler Nanoparticles and their Applications for Azo Dyes Degradation

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Abstract
In the present work, Silica supported Preyssler nanoparticles were synthesized, characterized and for the first time, their photocatalytic activity in the photodegradation of methylene blue as an azo dye was investigated. Our results have shown that these nanoparticles can be used as efficient heterogeneous photocatalysts for this aim in the presence of oxidant. Also, we have explored the effect of nanocatalyst value on the degradation rate. It is found that increasing the catalyst amount results an increase in the photodegradation rate.

Keywords: Preyssler, silica-supported, Methylene Blue, Photodegradation

1. Introduction

The widespread disposal of industrial wastewater containing organic dyes into land and water bodies has led serious contaminations that represent a widespread environmental danger in many countries. The effluents containing dyes are highly coloured and cause major environmental problems. There are strict international environmental standards for treatment of these coloured wastes before disposal.

Among various types of dye, different cationic dyes including methylene blue (MeB) are used in dye, paint production and in wool dyeing [1]. MeB is also used in microbiology, surgery and diagnostics [2]. There are several methods to treat wastewaters for removing MeB. The most commonly used methods for dye removal are biological oxidation and chemical precipitation [1]. The chemical treatment processes are more effective methods [3]. Also, the photocatalytic degradation over solid supports such as heteropolyacids and TiO_2 are interesting propositions [4].

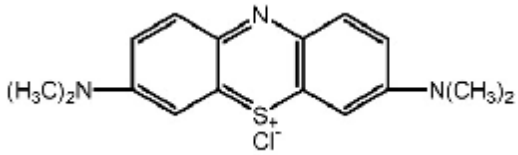

Figure 1. Structure of methylene blue (MeB) [5].

In recent years, heteropolyacids (HPAs) have been studied extensively as acid and redox catalysts and photocatalysts in many reactions [6]. HPAs belong to a large class of metal oxygen cluster anions and can be formed by a self-assembly processes. These catalysts are green and harmless to the environment with respect to non-corrosiveness, safety, quantity of waste, and separability.

Along green chemistry, there are several industrial processes utilizing HPA catalysts as oxidative and acid catalysts both in solid state and in solution [6]. However, it is needed to develop the application of these solid acids compounds as green catalysts in homogeneous

and heterogeneous catalysis reactions.

Preyssler acid, $H_{14}[NaP_5W_{30}O_{110}]$, as a type of HPA is a highly acidic catalyst with excellent catalytic activity in a variety of acid catalyzed and photocatalyzed reactions [7, 8].

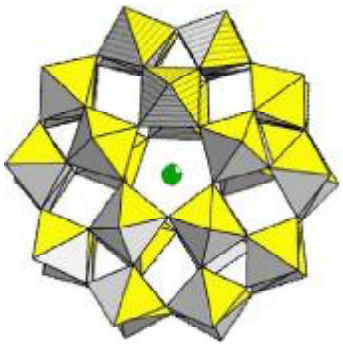

Figure 2. Preyssler's Anion Structure [9].

Recently, we have introduced silica supported Preyssler nanoparticles [6] and we have investigated their catalytic activity [10, 11]. In continuation of our work in the application of Preyssler and Preyssler nanoparticles catalysts, it was of great interest to investigate their application on azo dyes degradation. In this paper, for the first time, we have investigated the activity of silica supported nanoparticles in the MeB degradation under UV light irradiation using hydrogen peroxide as an oxidant.

2. Experimental

Methylene blue, hydrogen peroxide (35%) and all other chemicals were obtained from Merck Company and used as received. Preyssler acid was prepared according to the literatures [7] and Silica supported Preyssler nanoparticles were synthesized based on our earlier work [6].

In a typical reaction, 30 ml of MeB solution, H_2O_2, and Silica supported Preyssler nanoparticles were mixed in a quartz glass equipped with a magnetic stirrer. The mixture was purged with N_2 prior to irradiation. The solution was magnetically stirred in the dark for about 20 minutes. Then it was irradiated under a high pressure mercury vapor lamp (125 W) as UV light source at constant room temperature. At the given irradiation time intervals, liquid samples were taken from the mixture, and the absorbance of the MeB solution measured with a UV-Vis spectrophotometer.

The degree of MeB decolorization was calculated according to the equation:

$$C\% = \frac{A_0 - A}{A_0} \times 100$$

Where C: degree of decolorization, A_0: initial absorbance of the MeB solution, and A: absorbance of the MeB solution after photodegradation. The Silica supported Preyssler nanoparticles acts as a heterogeneous photocatalyst in this reaction and it was separated straightforward by filtration or low speed centrifugation.

3. Results and Discussion

Silica-supported Preyssler nanostructures were obtained through a micro emulsion method. Infrared spectroscopy have shown that in $(H_{14}[NaP_5W_{30}O_{110}])/SiO_2$, the Preyssler is preserved in SiO_2 nanoparticles [10]. The heteropolyacid $H_{14}[NaP_5W_{30}O_{110}]$ in the SiO_2 nano particles was confirmed by infrared spectroscopy as shown in Figure 3. The asymmetric stretching frequency of the terminal oxygen is observed at 960 cm^{-1} and the

P-O asymmetric stretching frequency is noted at 1080 and 1165 cm^{-1}. The prominent P-O bands at 960, 1080, and 1165 cm^{-1} are consistent with a C_5V symmetry anion. These bands demonstrate that $H_{14}[NaP_5W_{30}O_{110}]$ is preserved in the HPA/SiO_2 nano particles. In addition, the protonated water of $H_{14}[NaP_5W_{30}O_{110}]$ also remained in the nano particles at 1730 cm^{-1}.

It could be confirmed that the heteropolyacid $H_{14}[NaP_5W_{30}O_{110}]$ was successfully immobilized into the SiO_2 nano particles since the heteropolyacid does not react with tetraethoxysilane or with water in the micro emulsion, but it can remain in the Silica nano particles without appreciable change of the structures (the Silica particles were not large enough to cause a scattering baseline).

Therefore, it is expected that Silica supported Preyssler nanoparticles show the catalytic and photocatalytic activity of the Preyssler. Interestingly, it was indicated that the morphology of this nanostructures strongly depend on the reaction conditions such as concentration and time. So that, by changing the water to sodium bis(2- ethylhexyl) sulfosuccinate molar ratio and reaction time, the size and morphology of ($H_{14}[NaP_5W_{30}O_{110}]$)/$SiO_2$ can be controlled [6]. For example, TEM investigations have shown that for a short time the tubular structure is prevailing (at a molar ratio = 3 and up to 30 h, Figure 4b), whereas the spherical shapes are dominated at longer times (molar ratio = 3 and 30 h, Figure 4a). Our results showed that higher molar ratios are unfavorable.

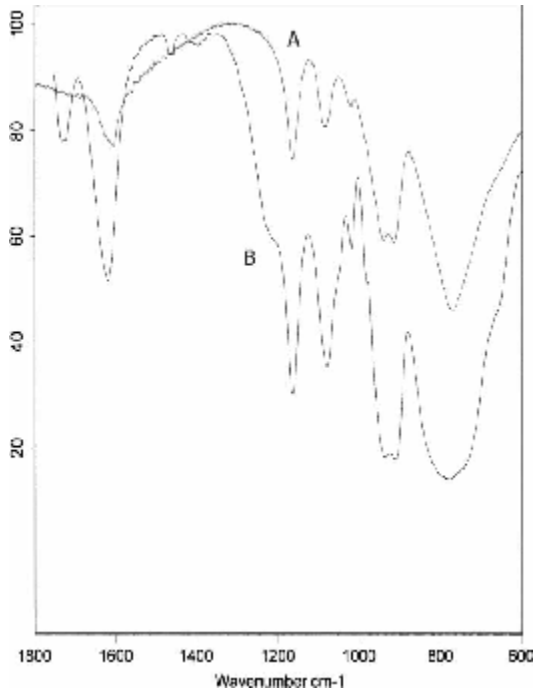

Figure 3. Infrared spectroscopy of Preyssler heteropolyacid in bulk form (B) and nano form (A)

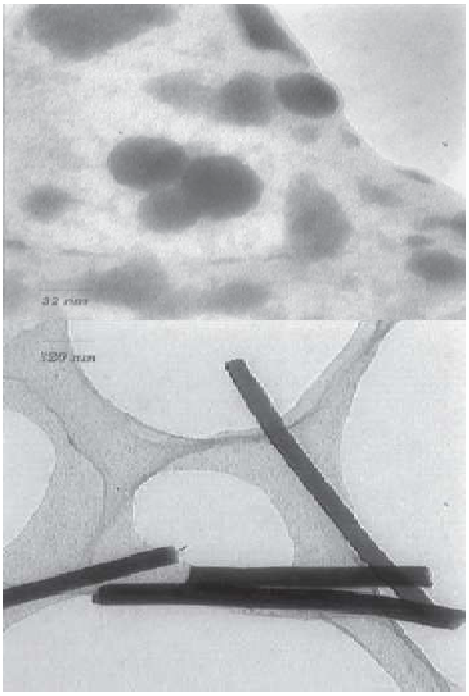

Figure 4. TEM images of the synthesized nanostructures (a) molar ratio=3, t= 30 h, and (b) molar ratio=3, t =18 h

The ratio of water to surfactant of 3:1 and the time of 30 h was selected as optimum conditions and the obtained ($H_{14}[NaP_5W_{30}O_{110}]$)/$SiO_2$ was used as photocatalyst for the degradation of MeB.

Our observation have shown that without catalyst, the reaction is very slow and in the absence of hydrogen peroxide as an oxidant, the reaction will not progress. Figure 5 shows the UV/Vis spectra of the solution of MeB (2.5×10^{-5} M), silica supported Preyssler

nanoparticles (0.06 g) and H_2O_2 at different stages of treatment. It can be seen that Preyssler nanoparticles catalyzed the MeB degradation reaction efficiently under UV irradiation in about 50 min.

The effect of silica supported Preyssler nanoparticles amount on the rate of MeB photodegradation was investigated by changing the initial amount of catalyst from 0.02 to 0.08 g, keeping the initial concentration of MeB and amount of H_2O_2 constant at 2.5×10^{-5} M and 2 mL, respectively. Figure 6 shows that photodegradation rate of MeB increases by increasing the amount of silica supported Preyssler nanoparticles.

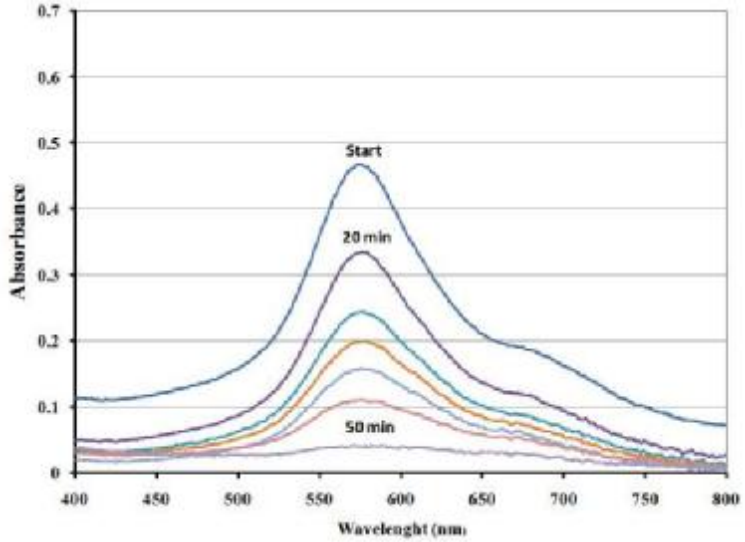

Figure 5. UV-Vis spectra of MeB degradation in the presence of silica supported nanopreyssler ([MeB] = 2.5×10^{-5} M and Preyssler nanoparticles = 0.06 g, H_2O_2=2 mL)

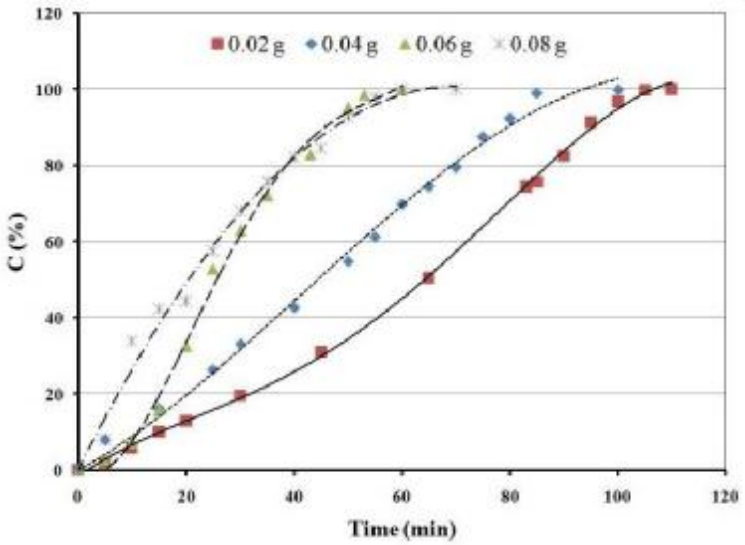

Figure 6. The effect of silica supported nanopreyssler on the rate of decolourization ([MeB]=2.5×10^{-5} M and H_2O_2=2 mL)

Conclusions

In the present work, the Silica supported Preyssler nanoparticles were synthesized, characterized and for the first time, they were used as a heterogeneous photocatalyst in the photodegradation of methylene blue as an azo dye. Our results have shown that these nanoparticles can be used as an efficient photocatalyst for this aim. Also, we have shown

that increasing the photocatalyst would increase the degradation rate.

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