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Photocatalytical Elimination Of Alizarin Red By Chitosan-CdS Composite Nanoparticles

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ABSTRACT

Chitosan-CdS composite nanoparticles were prepared by reverse microemulsion reactions. The alizarin red was degraded rapidly by chitosan-CdS composite nanoparticles in a short time. 98.1% of the alizarin red disappeared at 30min when the concentration is 20mg/L. The absorption peak became weak rapidly and disappeared finally at maximum absorption wavelength 261nm during the photocatalytical elimination process of alizarin red, and the new absorption peaks appeared at 223nm and 228nm respectively, which showed new products formed. The elimination of alizarin red was pH-dependent, more efficient at acidic condition than at neutral and alkaline. The photocatalytical elimination efficiency of chitosan-CdS composite nanoparticles was increased by 24.2% and 28.4% respectively at 2min and 30min compared with common CdS. The hypothetical mechanism of photocatalysis was put forward preliminarily: The primary step was the sorption of chitosan-CdS composite nanoparticles, which stimulated the photocatalytical elimination of alizarin red.

KEYWORDS

Chitosan-CdS composite nanoparticles;
Photocatalytical elimination;
Alizarin red;
Mechanism.

INTRODUCTION

Photocatalytical degradation of organic pollutants by semiconductor is receiving increasing interests. Among the semiconductors, cadmium sulphide (CdS) is one of the most active photocatalyst, which can absorb light in the visible part of the energy spectrum and therefore may be driven efficiently by so-

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lar energy[1]. According to the report of literature[2], high photostable CdS nanoparticles modified with alkyl group were prepared by an improved microemulsion technique using hexanethiol ($C_6H_{13}SH$) as cosurfactant. The surface-modified layer should not be oxidized in the photocatalytic process, moreover, an enhancement of the photocatalytic activity has been clearly observed to photodegrade 4-chlorophenol under UV light. Chitosan has been widely used in the treatment of wastewaters[3, 4] and reported to prevent the coagulation of inorganic nanoparticles[5]. Here, we present photocatalytical elimination of alizarin red, one model substance for complex aromatic compounds, by CdS nanoparticles modified with chitosan (chitosan-CdS).

EXPERIMENTAL

Preparation of microemulsion of $CdCl_2$ and chitosan salt

Triton X-100
Cyclohexane
n-Hexanol
Solution of $CdCl_2$ and chitosan salt
→ a,b → Microemulsion of $CdCl_2$ and Chitosan salt

Preparation of microemulsion of $(NH_2)_2CS$ and chitosan salt

Triton X-100
Cyclohexane
n-Hexanol
Solution of $(NH_2)_2CS$ and chitosan salt
→ a,b → Microemulsion of $(NH_2)_2CS$ and Chitosan salt

Preparation of chitosan-CdS composite nano particles

a) Mixed in a definite proportion; b) Stirring; c) Addition of NaOH solution at 60°C; d) Incubation at 30°C for 24h; e) Centrifugation; f) Washing with EtOH and H_2O; g) Freeze-dry

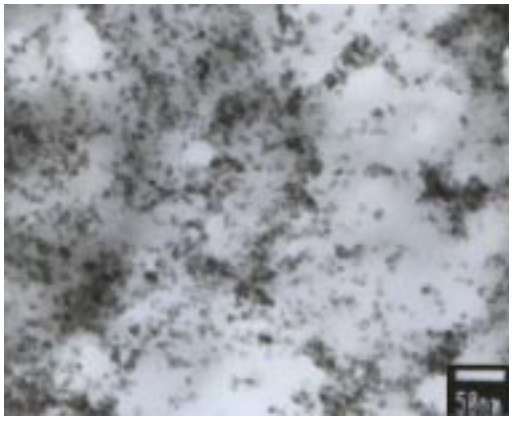

Figure 1: SEM photograph of chitosan-CdS composite nanoparticles

Methods

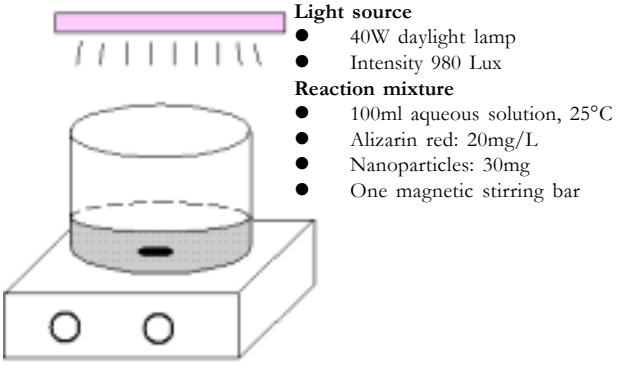

Figure 2: Experimental setup (The whole setup is shaded in order to avoid other light sources)

RESULTS AND DISCUSSION

The influence of illumination and dark reaction on decolor of alizarin red

The results (Figure 3) showed chitosan-CdS composite nanoparticles have the effect of photocatalytical elimination and sorption on alizarin red, and the latter accelerated photocatalytical elimination at a great degree. In dark reaction, the efficiency of adsorption reached 41.9% and 64.0% respectively at 2min and 30min. In daylight lamp, the efficiency of elimination reached 54.8% and 98.1% respectively at 2min and 30min.

Microemulsion of $CdCl_2$ and chitosan salt
Microemulsion of $(NH_2)_2CS$ and chitosan salt
→ c, d, e → Raw product → f, g

Pure chitosan-CdS nanoparticals with good decentralization (SEM photograph showed in Figure 1)

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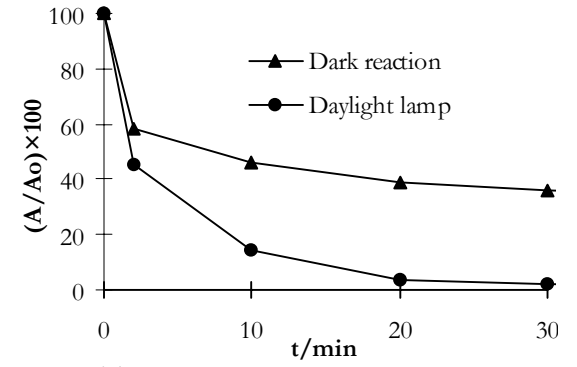

Figure 3: The influence of illumination and dark reaction on decolor of alizarin red

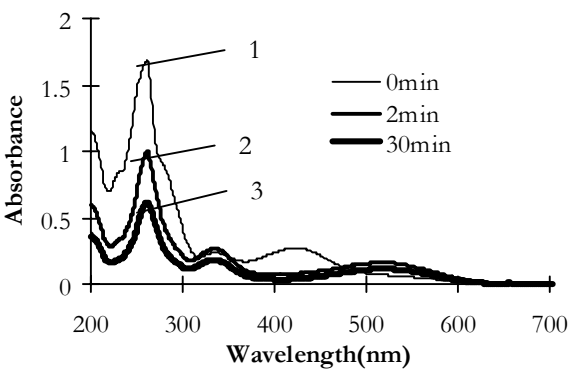

Figure 4: UV-Vis-spectra of the supernatant of the reaction mixture at reaction time of 0, 2, and 30min in dark reaction. Peak 1: 261nm; Peak 2: 261nm; Peak 3: 261nm

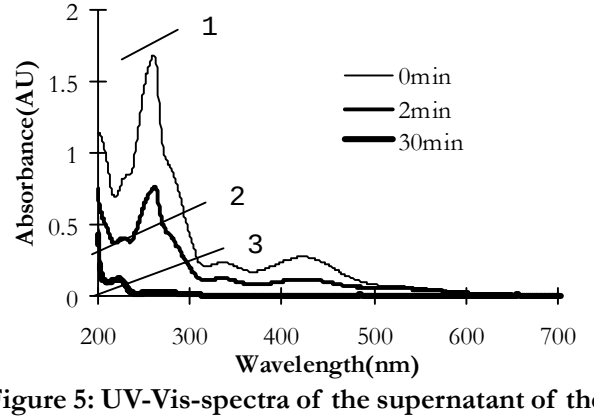

Figure 5: UV-Vis-spectra of the supernatant of the reaction mixture at reaction time of 0, 2, and 30min. Peak 1: 261 nm; Peak 2: 228 nm; Peak 3: 223nm

In dark reaction, UV-Vis-spectra (Figure 4) showed that alizarin red didn't disappear during adsorption.

In daylight lamp, UV-Vis-spectra (Figure 5) showed that alizarin red disappeared (Peak 1) during the photocatalytical elimination and small amounts of new products formed (Peak 2 and 3).

The influence of pH on the elimination of alizarin red

The elimination of alizarin red was pH-dependent, more efficient at acidic condition than at neutral and alkaline(Figure 6).

The control experiments of chitosan-CdS composite nanoparticles and CdS

The results(Figure 7) showed chitosan-CdS composite nanoparticles were more efficient in eliminating alizarin red than CdS alone with the same dosage. At 2min and 30min, the efficiency of elimination reached 54.8% and 98.1% respectively for chitosan-CdS composite nanoparticles, however, the efficiency

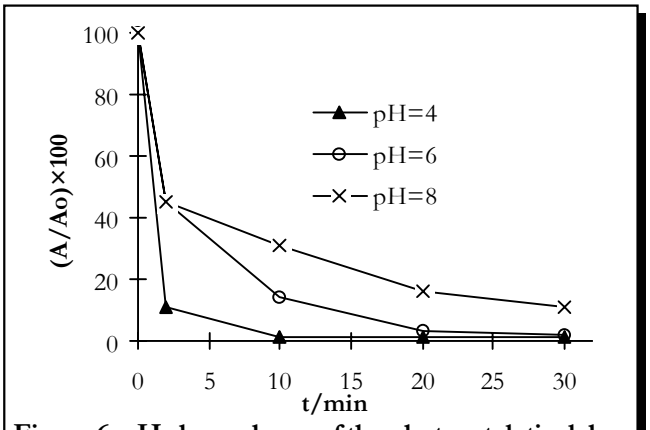

Figure 6: pH-dependence of the photocatalytical degradation of alizarin red by composite nanoparticles

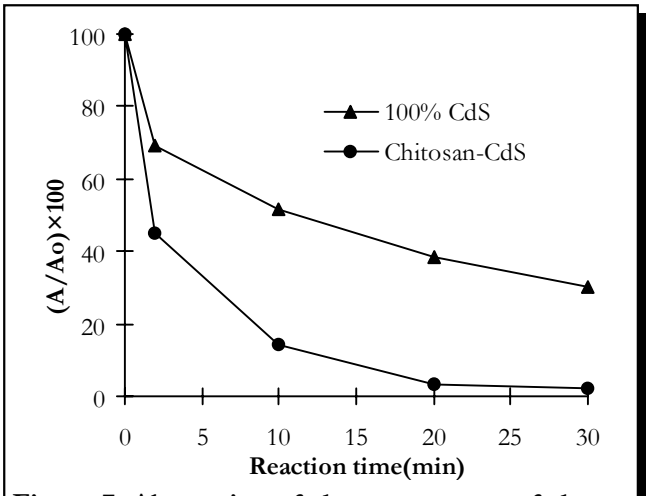

Figure 7: Absorption of the supernatant of the reaction mixture in the presence of CdS and chitosan-CdS composite nanoparticles

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only reached 30.6% and 69.7% respectively for CdS.

Hypothetical mechanism of the photocatalysis

The chemical structures of chitosan and alizarin red are shown in figure 8.

1st Step: Adsorption of alizarin red on the composite nanoparticles by the chitosan constituent.

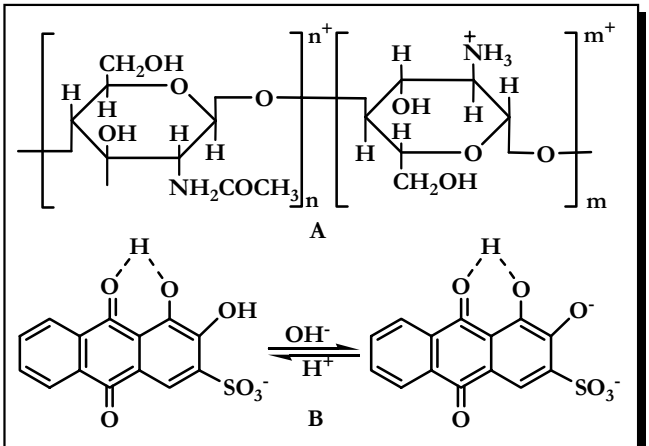
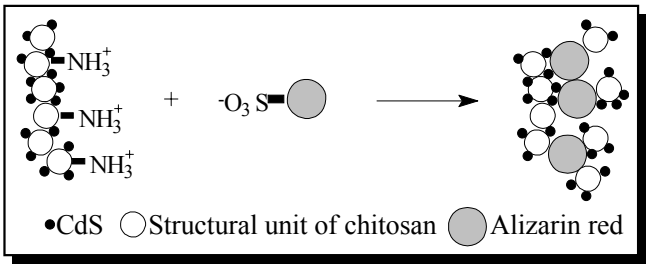


Figure 8: Chemical structures of chitosan (A) and alizarin red (B) at acidic and alkaline conditions

2nd Step: Formation of •OH radicals by light.



3rd Step: Oxidation of alizarin red by •OH radicals.

$$CdS \xrightarrow{h\ddot{O}} CdS(h^+) + CdS(e^-)$$

$$CdS(h^+) + H_2O_{adsorbed} \longrightarrow CdS + \bullet OH + H^+$$

$$\text{Alizarin red} + \bullet OH \longrightarrow \text{Degradation products}$$

CONCLUSIONS

1) Alizarin red was degraded rapidly by chitosan-CdS composite nanoparticles in a short time, and the new absorption peaks appeared at 223nm and 228nm respectively, which showed new products formed.
2) The elimination of alizarin red was pH-dependent, more efficient at acidic condition than at neutral and alkaline.
3) The chitosan-CdS composite nanoparticles had higher elimination degree than CdS alone.
4) The hypothetical mechanism of photocatalysis was put forward preliminarily: The primary step was the sorption of chitosan-CdS composite nanoparticles, which stimulated the elimination of alizarin red.

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