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Photodegradation enhancement of Congo red aqueous solution using a mixture of $SnO_2 \cdot xH_2O$ gel/ZnO powder

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Abstract

The system tin oxide gel mixed with zinc oxide powder ($SnO_2 \cdot xH_2O$/ZnO powder) was investigated for Congo red removal from aqueous solution. The Congo red photodegradation increases when a gel of tin oxide is mixed with a small amount of zinc oxide powder (2.5% in mass). This activity increases more when tin oxide gel is mixed with smaller particles size of ZnO prepared by precipitation method. When the amount of zinc oxide is higher (25% in mass), Congo red is removed by adsorption process rather than by photodegradation. This adsorption is mainly due to zinc oxide powder. The adsorption reaction is more active when zinc oxide is mixed with tin oxide gel than when zinc oxide is used alone.

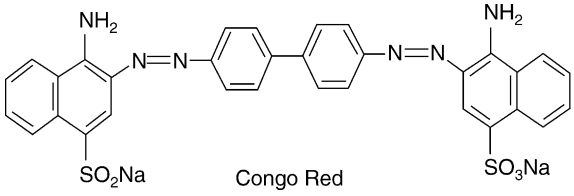
Keywords: Congo red removal; Tin oxide gel; Zinc oxide

1. Introduction

Dyes found in textile wastewater are serious pollutants and they should be removed. Heterogeneous photocatalysis degradation of organic pollutants in water using semiconductors, such as TiO_2 and ZnO, has attracted extensive attention of many researchers [1–5]. Such semiconductors can degrade most kinds of persistent organic pollutants such as detergents, dyes, pesticides and volatile organic compounds, under UV-irradiation. In a recent study, we found that the photocatalytic activity of the wet tin oxide gel ($SnO_2 \cdot xH_2O$) is higher than the gel dried at room temperature and much higher than the gel heated at 600 °C [6]. As the particle size increases, the photocatalytic activity decreases. A recent research study shows that a mixture of SnO_2/ZnO powder obtained after heating a precursor is more reactive for degradation of methyl orange than the SnO_2 powder alone [7,8]. Thus, the objective of this paper is to study the photocatalytic activity of the wet tin oxide gel when it is mixed with zinc oxide powder for degradation of Congo red aqueous solution.

2. Experimental

$SnO_2 \cdot xH_2O$ gel with nanosized particles was prepared according to the procedure recently reported [6]: the wet gel obtained can be dried at room temperature and used for purity and particles size analysis. Congo red is water soluble, yielding a red colloidal solution with high absorption bond in UV spectrum located around 500 nm. It has the following chemical structure.



Congo Red

The Congo red solution was prepared by dissolving Congo red powder ($C_{32}H_{24}N_6O_6S_2$ from BDH Chemical Ltd Poole England) in distilled water to obtain a solution 2.5×10^{-5} M concentration. The photocatalysis experiments were carried out in 100 mL beaker containing about 75 mL of Congo red aqueous solution (0.025 mM) and about 400 mg of SnO_2 (4 g/L) in the form of wet gel $SnO_2 \cdot xH_2O$ as photocatalyst. Zinc oxide powder (from BDH Chemical Ltd Poole England) was added

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to the gel with different amount. The irradiation was done with an 80-W UV lamp (OSRAM), which was placed close to the beaker. These experiments were followed by different spectroscopic techniques as powder X-ray diffraction (Philips 1710, diffractometer), UV spectroscopy (UV spectrometer Cary 50 Conc) and Transmission electron microscope (Jeol 1234).

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction patterns of as-prepared tin oxide. The X-ray diffraction pattern of pure crystallised tin oxide is also displayed for comparison. The as-prepared sample presents a pure tin oxide phase with broad diffraction peaks as a consequence of very fine particles. Transmission electron microscope (Fig. 1b) shows pure homogenous well-dispersed particles of about 2 nm.

Zinc oxide commercials (10 mg) was mixed with the wet gel ($SnO_2{\cdot}xH_2O$) and added to Congo red solution in 100 mL beaker. This mixture was exposed to UV radiation for 120 min. The solution was separated from the catalyst and analyzed by UV–vis spectroscopy. Fig. 2 shows the UV–vis spectrum of that solution (c) along with Congo red solution without catalyst (a) and Congo red with tin oxide gel alone exposed to UV radiation for 180 min (b). Tin oxide gel mixed with ZnO shows more reactivity although the exposed time used was only 120 min less than the used time for the gel alone (180 min).

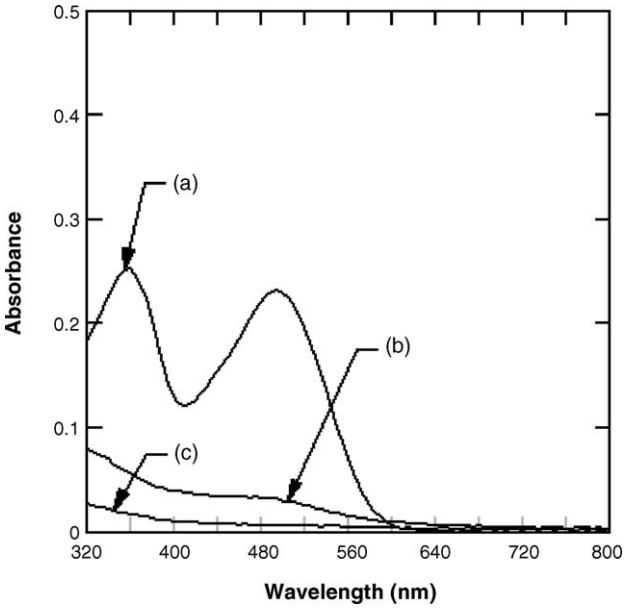
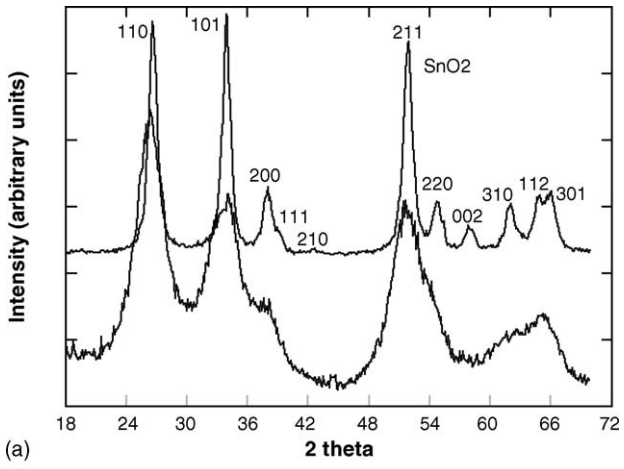


Fig. 2. (a) Congo red solution exposed to UV radiation (180 min). (b) Congo red solution with tin oxide gel and exposed to UV radiation (180 min). (c) Congo red solution With $SnO_2{\cdot}xH_2O$ gel/ZnO and exposed to UV radiation (120 min).



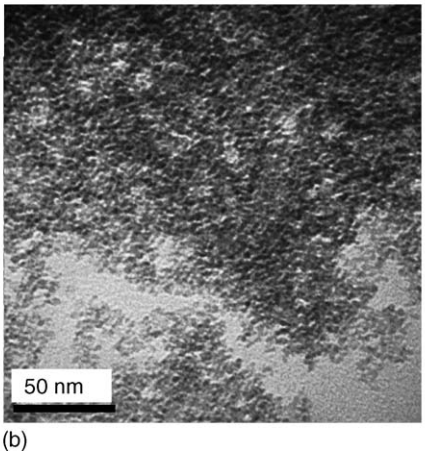


Fig. 1. (a) X-ray diffraction pattern of as-prepared tin oxide, along with pure crystalline SnO_2 sample. (b) Transmission electron microscope of as-prepared tin oxide.

Experiments with increasing amount of zinc oxide indicate fast removal of Congo red from solution. In Fig. 3, the removal of Congo red solution was followed by measuring the UV absorbance value of the highest spectrum band (at 500 nm) with increasing amount of ZnO powder. In all experiments, the time of reaction was fixed to 15 min. As the amount of ZnO increases, the intensity of the band at 500 nm decreases sharply and the red color intensity of solution decreases until colorless solution was obtained with 0.100 g ZnO.

This fast removal of Congo red is mainly due to increase of ZnO amount in the gel. To understand the effect of the gel on the mixture catalyst, two experiments were carried out: the first

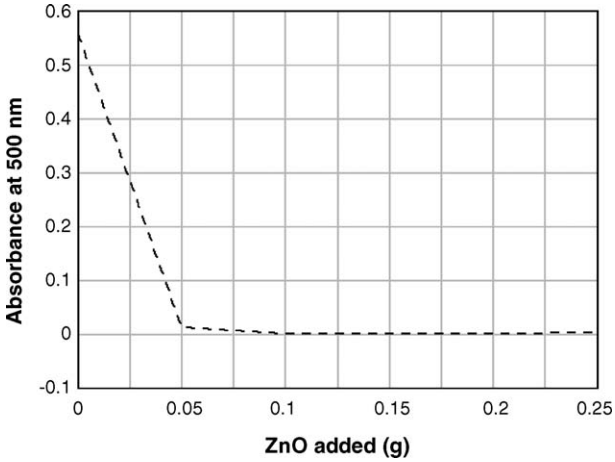


Fig. 3. Absorption band at 500 nm vs. amount of ZnO added (experiments were carried out during 15 min).

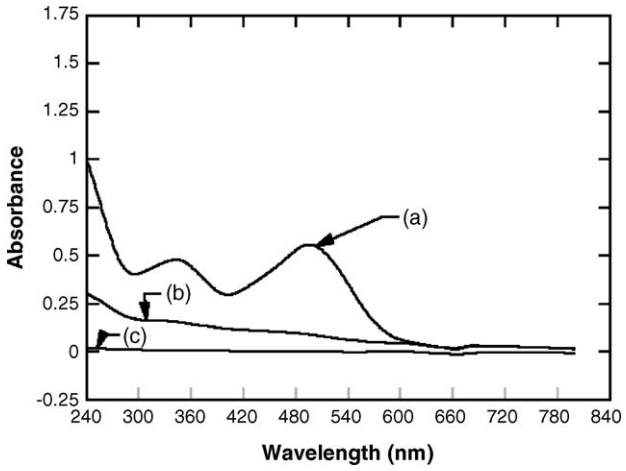


Fig. 4. UV spectra of Congo red solution (a) with tin oxide gel only (b) with 0.100 g ZnO only (c) with a mixture of tin oxide gel and 0.100 g zinc oxide.

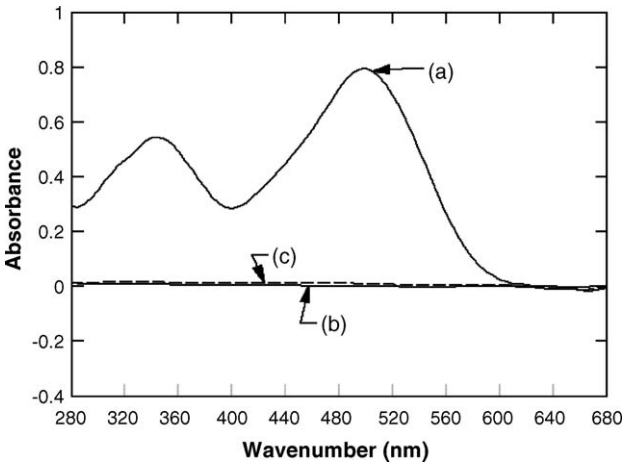


Fig. 6. UV spectra: (a) Congo red solution only; (b) SnO_2 gel with 0.100 g ZnO exposed to UV radiation (15 min); (c) SnO_2 gel with 0.100 g ZnO in the dark (15 min).

experiment using a mixture of the gel with 0.100 g of ZnO; in the second experiment only 0.100 g of ZnO was used alone. The two experiments were exposed to UV radiation for 15 min. We found that removal of Congo red is more active when zinc oxide is mixed with tin oxide gel than the zinc oxide used alone, this can be seen in Fig. 4.

To understand this observation, the mixture was analyzed by transmission electron microscope (Fig. 5). TEM micrographs show particles of ZnO, in general, less agglomerate when they are mixed with tin oxide gel compared to ZnO alone. This will increase zinc oxide surface area that increases its reaction. Probably it is a reason, which leads zinc oxide to be more reactive when it is mixed with the wet gel of tin oxide.

The mixture, wet $SnO_2{\cdot}xH_2O$ gel and ZnO powder, has a white color, with increasing amount of ZnO the mixture color, after photocatalytic reaction, become reddish, similar to Congo red color. Its red color intensity increases as the amount of ZnO increases. From previous experiment [6], the white SnO_2 gel did not show any change of color after Congo red photodegradation. May this suggest an adsorption process of Congo red on the mixture rather than a photocatalytic degradation process? If this suggestion is correct, a repeat experiment with the same conditions in the dark (without radiation source) will lead to the same result because the radiation energy will not affect this process. Fig. 6 depicts the results for removal of Congo red solution using a mixture of SnO_2 gel and 0.100 g ZnO exposed to UV radiation for15 min (curve b) and the same experiment without radiation (in dark, curve c). The two experiments show the same result. This suggests that Congo red is adsorbed in the mixture. This adsorption is mainly due to zinc oxide because the intensity of red color on the mixture increases with increases on ZnO amount.

Also Congo red was removed quickly from the solution with increasing amount of zinc oxide, which is the property of adsorption reaction. When zinc oxide is used in small amount (10 mg), there is no change of color after Congo red degradation, which is normal as its quantity is low, compared to the amount of tin oxide gel. In order to study the effect of radiation on the mixture where small amount of ZnO is used, two experiments with Congo red solution mixed with the wet gel SnO_2 and 10 mg of ZnO were carried out. The first experiment was exposed to UV radiation for 80 min (Fig. 7c), the second experiment was carried out in the dark, also for 80 min, (Fig. 7b). For more clarity, UV spectrum of Congo red solution was reported (Fig. 7a). It can be seen that the decomposition of Congo red is efficient by using UV radiation. The experiment in the dark leads only to a sleight removal of Congo red solution, which probably is the consequence of adsorption of some amount of Congo red on the present zinc

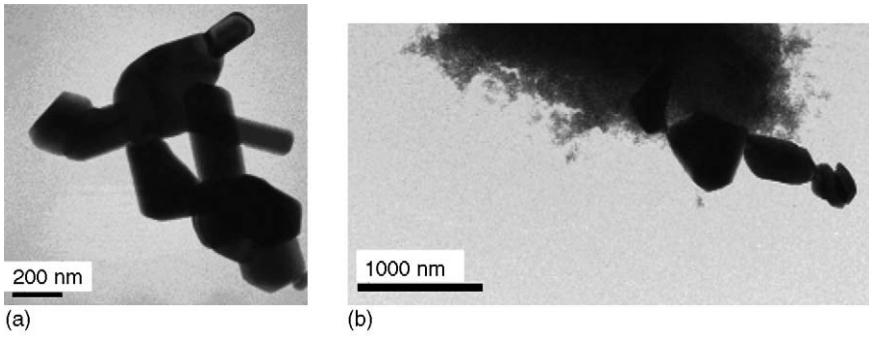


Fig. 5. TEM micrographs of (a) ZnO particles alone, (b) ZnO particles mixed with SnO_2 gel.

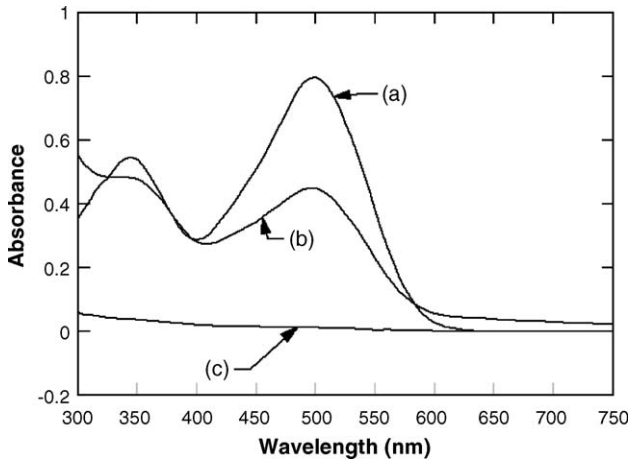


Fig. 7. UV spectra: (a) Congo red solution; (b) SnO_2 gel and 10 mg of ZnO in the dark (80 min); (c) SnO_2 gel and 10 mg of ZnO exposed to UV radiation (80 min).

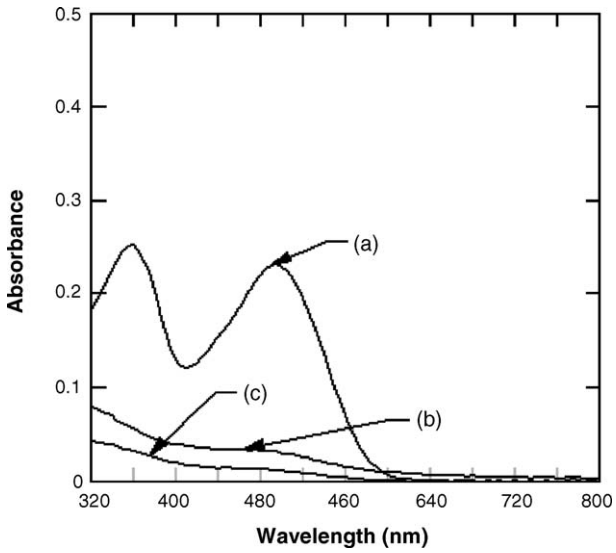


Fig. 9. UV spectra: (a) Congo red solution exposed to UV radiation (180 min); (b) with SnO_2 gel and exposed to UV radiation (180 min); (c) with SnO_2 gel/ZnO prepared and exposed to UV radiation (80 min).

oxide surface. This experiment indicates that with small amount of ZnO, UV radiation is necessary to achieve decomposition of Congo red solution, contrary when the amount of ZnO is higher. Because the photocatalytic or adsorption process takes place in the surface of the catalyst. Surface area, which has relation with the particle size, should be important. Usually, as the particle size decreases, the surface area increases and more active surface area is available for reaction [9]. Soft chemistry techniques as precipitation method can lead to materials with small particle size. Thus, zinc oxide was prepared by precipitation method.

A concentrate aqueous solution of zinc nitrate was stirred until all zinc nitrate was dissolved. When ammonium hydroxide was added, immediately a white precipitate appeared. In order to remove nitrate and ammonium ions present in the solution, the white precipitate was washed with distilled water several times. Then it was allowed to dry at room temperature. The powder X-ray diffraction pattern obtained depicts a semi-amorphous phase. After annealing at 300 °C a pure zinc oxide powder was obtained. Fig. 8 depicts its powder X-ray diffraction pattern. The X-ray diffraction peaks are broad compared to X-ray powder diffraction peaks of commercial zinc oxide, which could be a consequence of small particles size. About 10 mg of this prepared zinc oxide was added to the wet tin oxide gel and stirred for few minutes, then a solution of Congo red was added to this mixture. The same experimental conditions were maintained as with commercial zinc oxide. It is found that nearly the same result of Congo red degradation can be obtained with prepared

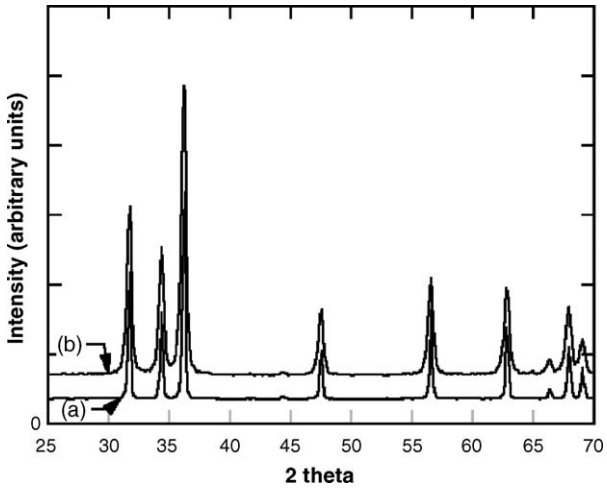


Fig. 8. Powder X-ray diffraction pattern of: (a) ZnO commercial; (b) ZnO prepared.

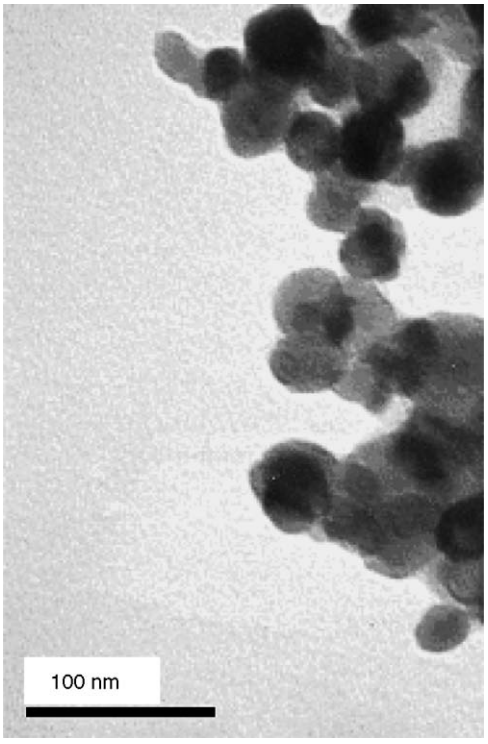


Fig. 10. TEM micrographs of ZnO prepared.

zinc oxide only after 80 min (Fig. 9) instead of 120 min with ZnO commercial (Fig. 2). In order to gain a better understanding, transmission electron microscope analyses on ZnO prepared was carried out. Fig. 10 shows ZnO prepared composed of small particles with spherical shape, the particle size is around 25 nm much smaller compared with commercial zinc oxide (around 200 nm). This is consistent with broad powder x-ray diffraction peaks. With smaller particles more active surface area is present which leads to more active reaction, probably this is the cause that makes zinc oxide prepared more active.

4. Conclusions

SnO_2 gel mixed with small quantity of ZnO increases its photocatalytic activity, which provides faster removal of Congo red solution. This activity is much higher when ZnO was prepared with smaller particles size. When SnO_2 gel is mixed with higher amount of ZnO, the process becomes more adsorption than photocatalysis.

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