



# Silica nanoparticles assisted photodegradation of acridine orange in aqueous suspensions



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## ABSTRACT

Silica nanostructured materials are often used as catalyst support but their catalytic role has not been deeply investigated yet. In the present study, the photocatalytic degradation of acridine orange zinc chloride double salt (AO) has been studied using silica nanoparticles (NPs) as catalysts. NPs of different size (55 and 146 nm) were prepared by a sol–gel procedure and their surface was modified with amino groups to investigate the role of the chemical groups linked to the silica surface on the dye degradation. The silica nanomaterials were fully characterized by use of transmission electron microscopy (TEM), zeta potential measurements and UV–vis spectrophotometric methods.

The photodegradation experiments were carried out irradiating at 313 or 490 nm for 50 min the aqueous samples containing the dye and the silica NPs of 55 or 146 nm in diameter. The photocatalytic degradation of the dye was determined from the decrease of its fluorescence intensity. AO fluorescence intensity did not change when bare SiO<sub>2</sub> beads were used as catalysts, whereas an efficient decoloration (up to 58%) was achieved with amino functionalized NPs, with a photodegradation rate constant value of 0.136 m<sup>-1</sup>. The data collected from the degradation experiments demonstrated that the functional groups on the silica surface have a fundamental role in the efficiency of the degradation processes.

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## 1. Introduction

Wastewater discharged by dye manufacturing and textile finishing industries has become an environmental concern since it contains relevant concentrations of synthetic organic dyes, which are characterized by very high COD and TOC values as well as high colouring capacity [1].

Dye wastewater discharged from the textile industry can damage water resources. The presence of even small amounts of dye is highly visible and affects the optical properties of the water and consequently the photosynthetic activity of aquatic organisms and the solubility of gases. Besides, the textile dyes might have toxic and potentially carcinogenic effects [2].

Synthetic dyes are prepared to ensure high stability to light, temperature, acids, bases, oxidizing agents and microbial agents, as these are the desired properties of the dyed clothes. Therefore, it is difficult to treat wastewater and to remove dyes using

conventional techniques. Clean and cost-effective technologies for the degradation of organic pollutants have become an important industrial concern.

In the last decades, based on the development of nanostructured materials and the understanding of their optical and electronic properties, nanomaterial-assisted photocatalytic methods have been proposed. It has been shown that specific interactions occur in hybrid colloidal systems at the interface between the semiconductor nanocrystals and organic moieties adsorbed/coordinated on the semiconductor surface, and these interactions modify the photochemical/photophysical behaviour of the colloidal system [3]. In particular, much attention has been paid to the study of titanium and zinc oxide nanostructures and their impact on the photocatalytic degradation of organic pollutants [4–7]. These materials show important electronic properties that have attracted the interest of industry and researchers particularly aimed at the cost-effectiveness optimization of preparation methods [8]. Among others, titania and zinc oxide materials have wide band gaps (3.0–3.2 eV), which confer strong absorption capacity over a large portion of the UV solar spectrum. The investigation of the semiconductor properties of such materials improved

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understanding and description of the underlying photocatalytic mechanisms [9–16]. The principle of the semiconductor photocatalytic reaction is widely accepted [17]. Upon absorption of photons with energy larger than the band gap of the semiconductor, electrons are excited from the valence band to the conduction band, creating electron–hole pairs. These charge carriers migrate to the surface and react with water and oxygen generating radicals or intermediate species such as  $\text{OH}^\bullet$ ,  $\text{O}_2^{\bullet-}$ , and/or  $\text{O}_2$ , which decompose the organic chemicals adsorbed on the surface of the semiconductors [18].

Different engineering approaches have also been developed to narrow the material band gap and improve solar light absorption ([19] and references there in). One of the most widely investigated strategies is based on dye absorption. Under visible light illumination, the adsorbed dye is excited and subsequently electron injection or transfers (even through intermediate species) assisted by the semiconductor can occur. These processes lead to the formation of reactive radical species, such as hydroxyl radicals, able to degrade the molecules adsorbed on the particle surface.

Titanium dioxide, especially the anatase-phase nano-titania [20], is the photocatalyst with the best photocatalytic performances, but its use is too expensive for large scale water treatment. Different semiconductors, such as  $\text{SnO}_2$ ,  $\text{ZrO}_2$ , CdS and ZnO, have been tested as photocatalysts for the degradation of dyes [15–17,21–25]. In particular, Kansal and co-workers obtained methyl orange and rhodamine 6G aqueous solution photocatalytic decoloration efficiencies above 90% using ZnO [26].

Silica has a very wide band gap (nominally 8.9 eV) making this material transparent to vis radiations. For these properties, it has been used to entrap dyes and drugs in order to improve stability as well as delivery [27–29]. However, the presence of structural defects alongside the reduced crystallinity can decrease the band gap energy or enhance the material photoactivation capacities in the UV-region [30]. Silica has a quite reactive surface due to the presence of silanol groups, capable of adsorbing organic and inorganic species and this property can be enhanced when silica is shaped as colloidal particles [30–32]. Silica nanomaterials exhibit measurable photocatalytic activity under UV irradiation [30–34], lower costs as compared to  $\text{TiO}_2$  and ZnO and much lower environmental impact.

In this regard, silica nano-phases have been synthesized and employed to oxidize dyes. Badr and Mahmoud used silica nanoparticles and silica coated silver and gold NPs as photocatalysts for the degradation of methyl orange dye under xenon lamp excitation [35]. They observed that silica coated Ag and Au NPs show enhanced photocatalytic degradation compared to silica NPs and this is due to the reduction of the electron–hole recombination process, which favours the formation of  $\text{OH}^\bullet$  radicals.

In the present study, in order to explore the photocatalytic properties of silica colloids, the degradation efficiency of acridine orange zinc chloride double salt (AO) is determined in the presence of silica NPs. NPs of different size are prepared by a sol–gel method [36–38], characterized [27–29] and the effect of surface chemistry on the dye photodegradation is evaluated upon surface functionalization with amino groups [39–41]. The photoactivity of the samples is determined and compared by monitoring the fluorescence intensity decrease of AO after UV or vis monochromatic irradiation.

## 2. Materials and methods

### 2.1. Materials

Hexanol, cyclohexanol, Triton X-100, 3-aminopropyltriethoxysilane (APTES), Acridine Orange hemi (zinc chloride) salt (AO), acetone and aqueous ammonia solu-

tion (28–30%  $\text{NH}_3$  basis) were purchased from Sigma–Aldrich (Sigma–Aldrich, St. Louis, MO, USA) and used without further purification. Tetraethoxysilane (TEOS) and ethanol were obtained from Fluka (Milwaukee, WI, USA). Analytical grade water was used for the preparation of the solutions.

### 2.2. Preparation of the photocatalysts

#### 2.2.1. Preparation of silica nanoparticles through the microemulsion method

The NPs were prepared using a microemulsion method [37] in order to better control the growth process. The W/O microemulsion was prepared by mixing cyclohexane (75 mL), TX-100 (17.7 mL), hexanol (18 mL) and water (5.4 mL) under vigorous stirring. Then the hydrolysis and condensation reaction was initiated by adding 1 mL of TEOS and 0.7 mL of ammonia solution (28–30%) to the microemulsion and stirring for 24 h. The NPs were precipitated with acetone (40 mL), followed by centrifugation and washing with ethanol and water several times to remove the residual surfactant. Then the NPs (SNP1 sample) were dried in a water bath at 80 °C.

#### 2.2.2. Preparation of silica nanoparticles through the Stöber method

The NPs were prepared using the method developed by Stöber [38]. 0.5 mL of water, 23 mL of ethanol, 0.8 mL of ammonia solution (28–30%) and 1 mL of TEOS were stirred for 24 h. After the reaction was completed, the NPs (SNP2 sample) were centrifuged, washed three times with ethanol and dried in a water bath at 80 °C.

#### 2.2.3. Preparation of amine-functionalized silica nanoparticles

To functionalize the surface of silica NPs, APTES was dissolved in an ethanol:distilled water mixture (10:1) upon stirring for 6 h. The silica NPs (SNP1 or SNP2) were then added into the mixture and stirred at room temperature for 24 h. The sample was separated by centrifugation and washed twice with ethanol and once with water to remove the possible un-grafted APTES. The resulting powder was dried at room temperature. The functionalization of 1 mg of SNP1 or SNP2 was achieved using 561  $\mu\text{L}$  and 1.48 mL of the ethanol:water:APTES mixture (10:1:1) [39].

### 2.3. Photocatalyst characterization

The morphology of SNP1 and SNP2 samples was investigated by transmission electron microscopy (TEM) using a Philips model 208 microscope working at 80 kV of beam acceleration.

The average sizes of NPs were measured by statistical analysis of TEM images using ImageJ software (National Institutes of Health, USA). The particle size data were based on the image analysis of more than 300 particles.

The zeta-potential data of NPs in water and ethanol suspensions (SNP1, SNP2, SNP1-APTES, SNP2-APTES) were determined by NICOMP 380 ZLS equipped with a HeNe Laser source at 632.8 nm (Particle Sizing System, Inc., Santa Barbara, CA, USA).

#### 2.4. UV–vis absorption and fluorescence spectra of photocatalyst suspensions and dye solutions

Absorption spectra of the solid samples were recorded by a Cary 4000 (Varian Inc., Palo Alto, California, USA) spectrophotometer, equipped with a 150 mm integration sphere and a barium sulphate tablet as reference. The spectra were processed with the Kubelka–Munk equation in order to make possible the comparison.

Absorption spectra of the colloidal suspensions of the silica NPs and the dye were recorded with a PerkinElmer Lambda 800 spectrophotometer (Massachusetts, USA)

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