Zinc Sulfide Prepared through ZnO Sulfuration: Characterization and Photocatalytic Activity

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P-nitrophenol (PNP) is a toxic organic pollutant and it is difficult to remove from wastewater by means of conventional treatment processes. Therefore, effective and low cost alternative water treatment technologies are required. In the last years there has been a growing interest in advanced oxidation processes involving semiconductor mediated photocatalysis because the process mineralizes many toxic organic pollutants to carbon dioxide and water at ambient temperature under UV light.

The aim of this work is to synthetize ZnS photocatalyst starting from formerly ZnO prepared with different precursors such as zinc sulphate and zinc nitrate by means of precipitation method. ZnS was then obtained by sulfuration of ZnO particles. The sulfuration step was carried out at 450°C in presence of N_2 gaseous stream containing H_2S at 5 vol%. The prepared photocatalysts were characterized from chemical-physical point of view using different techniques (XRD, BET, UV-vis DRS, Raman).

The photocatalytic tests were carried out in a recirculating batch cylindrical photoreactor irradiated by a UV-LEDs strip (nominal power of 12W/m and wavelength emission peak at about 365 nm) surrounding the external surface of the reactor. The experimental results evidenced that the optimal sample is ZnS obtained from the sulphuration of ZnO synthetized by zinc sulphate. In particular, this sample was able to achieve about 51% PNP degradation after 240 min of UV light irradiation.

1. Introduction

Phenol and its derivatives are found abundantly in wastewater discharged from several industrial units, coal washeries, coke ovens, dyes intermediate manufacturing, pesticides, herbicides, dyes, explosives and pharmaceuticals (Gota and Sundaramurthy, 2014, Narasimha Murthy et al., 2016) . They are irritant and toxic towards plants, microorganisms, animals, and human beings and they are considered priority toxic pollutants by the United States Environmental Protection Agency (Andreozzi et al., 1999, Aslam et al., 2014). For instance, nitrophenols are some of the most refractory substance present in industrial wastewaters because of their high stability and solubility in water, generally detected in agriculture waste and appear in the degradation of pesticides like parathion and nitrofen (Galindo and Kalt, 1999). Phenol and its nitrophenols derivatives are frequently found in the environment due to their widespread use and they are some of the most refractory substance present in industrial wastewaters because of their high stability and solubility in water (Martínková et al., 2016). For this reason, many techniques are available to remove the phenolic compounds from water and/ or wastewater, including coagulation (Solanki et al., 2013), biological degradation (Dai et al., 2009), adsorption (Ahmed and Theydan, 2015) and membrane filtration (Ivančev-Tumbas et al., 2008). High costs, low efficiency, and leaving of dangerous and toxic by-products are among the factors which limit the use of some of these methods of removal (Bazrafshan, 2016). In particular, for phenol and nitrophenols, the efficiency of the above treatments is usually not enough for the complete mineralization of the pollutants. Therefore, effective and low cost alternative water treatment technologies are still required. Over the past two to three decades, there has been a growing interest in advanced oxidation processes involving semiconductor mediated photocatalysis because the process mineralizes many toxic organic pollutants to carbon dioxide and water at ambient temperature under UV/visible light irradiation.

Photocatalytic processes make use of many oxide and sulfide semiconductors such as TiO_2, ZnO, WO_3, $SrTiO_3$, ZrO_2, ZnS and CdS were applied as catalyst and of oxygen as oxidizing agent (Andreozzi et al., 1999, Soria et al., 2017). Among them, ZnS has been considered as a photocatalyst in different chemical reactions due to its relatively wide band gap value (Zhang et al., 2013). In particular, the band gap energy of ZnS semiconductor was 3.6 eV (Hart et al., 2014), meaning that ZnS is able to absorb light with wavelengths below 380 nm. In this work ZnS photocatalyst was synthetized starting from formerly ZnO prepared with different salt precursors (zinc sulphate and zinc nitrate) by means of precipitation method. ZnS was then obtained by sulfuration of ZnO particles. The prepared ZnS samples were tested in the photocatalytic removal of PNP under UV light.

2. Experimental

2.1 Photocatalysts preparation and characterization

ZnO particles were prepared by means of precipitation method (Vaiano et al., 2017). In detail, 8 g of $ZnSO_4$ (Aldrich, 99%) or $Zn(NO_3)_2$ (Aldrich, 99%) was dissolved in 50 mL of distilled water and the precipitate was obtained through the slow addition of an aqueous solution of 25 mL of distilled water containing NaOH (Aldrich, 99%) at room temperature. The preparation has been performed maintaining constant and equal to 2 the molar ratio between NaOH and the precursor salt ($ZnSO_4$ or $Zn(NO_3)_2$). The generated precipitate was centrifuged, washed and calcined at 450 °C for 2 h. Commercial ZnS (Aldrich, 99%) was also used as reference material. The ZnO activation was performed by sulfuration treatment, by converting the metal oxide (ZnO) into Zinc sulfide (ZnS), according to the following reaction:

$$ZnO(s) + H_2S(g) \rightarrow ZnS(s) + H_2O(g)$$
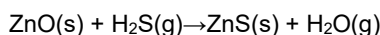
The reaction involves the sulfuration of the metal oxide by H_2S, leading to the formation of the metal sulfide and water.The sulfuration tratment was carried out in a quartz reactor specifically designed and made of a tube with a 300 mm length and internal diameter of 12 mm (Palma et al., 2018) .
ZnO particles were placed in the isothermal zone of the reactor and the measurement of the temperature on the solid particles bed was realized by means of a thermocouple placed in a quartz sheath, concentric to the reactor. The activation step has been realized by feeding a gaseous stream containing 5 vol % of H_2S in a nitrogen flow (400 Ncm^3 min^{-1}) by heating the reactor with a heating rate of 5 °C min^{-1} up to 450 °C and kept in isothermal for 1 h. The samples were named ZnS_c (commercial ZnS, Sigma–Aldrich), ZnS_sF (ZnS from ZnO prepared from $ZnSO_4$), ZnS_nT (ZnS from ZnO prepared from $Zn(NO_3)_2$) and ZnS_sC (ZnS prepared from commercial ZnO). All the prepared photocatalysts were summarized in Table 1.
Physical-chemical characterization of the samples has been performed through X-ray diffraction (XRD) with an X-ray micro-diffractometer Rigaku D-max-RAPID, using Cu-Kα radiation and a cylindrical imaging plate detection. Laser Raman spectra were obtained at room temperature with a Dispersive Micro-Raman (Invia, Renishaw), equipped with 514 nm laser, in the range 200 - 800 cm^{-1} Raman shift.
The specific surface area (BET) of the samples was measured from dynamic N_2 adsorption measurement at -196 °C, performed by a Costech Sorptometer 1042 after pre-treatment at 150 °C for 30 min in He flow. The ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) of the samples were recorded using a Perkin Elmer spectrometer Lambda 35 spectrophotometer using a RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH). The band gap values of photocatalysts were determined through the corresponding Kubelka–Munk function (KM) (which is proportional to the absorption of radiation) and by plotting $(KM \times h\upsilon)^2$ against $h\upsilon$.

2.2 Photocatalytic activity tests

PNP solution was prepared by dissolving 10 mg in 1L of MilliQ-grade water until to obtain an initial concentration equal to 10 mg L^{-1}. The photocatalytic tests were realized using a pyrex cylindrical photoreactor (ID = 2.6 cm, L_{TOT} = 41 cm and V_{TOT} = 200 mL) equipped with an air distributor device (Q_{air}=150cm^3 min^{-1}). UV-LEDs strip (nominal power: 12 W, provided by LEDlightinghut emitting at 365 nm) was positioned around and in contact with the external body of the photoreactor in order to irradiate the volume of the solution uniformly. A peristaltic pump (Watson Marlow) was used to maintain continuously recirculated the suspension inside the reactor. A volume of PNP solution equal to 100mL with a catalyst amount of 1.5 g L^{-1} was employed for the tests. During the irradiation time, slurry samples (about 2 mL) were withdrawn at fixed time and then they were centrifuged to remove the catalyst powders before the concentration measurement by a Perkin Elmer UV-Vis spectrophotometer at 400 nm for determining the residual PNP concentration. The total organic carbon (TOC) contained in a fixed volume of the solution was measured by the high temperature combustion method on a catalyst (Pt-Al_2O_3) in a tubular flow micro-reactor operated at 680 °C. The solution was injected

in the catalytic reactor fed with air to oxidize the organic carbon into CO_2, whose concentration in gas–phase was monitored by a continuous analyzer (Uras 14, ABB) (Sacco et al., 2019).

3. Results and Discussion

3.1 Characterization of the samples

The Raman spectra of the samples are shown in Figure 1. For all the prepared samples the main modes are observed at 271 and 352 cm^{-1} and can be referred to TO and LO mode of cubic blende zinc sulfide (Nilsen, 1969). In addition, it is important to underline that all the samples obtained after the sulfuration treatment (ZnS_sC, ZnS_nT and ZnS_sF) evidenced the same Raman signals of the commercial ZnS. These results confirm that the preparation method is able to completely convert zinc oxide into zinc sulfide by means of sulfuration process. The crystalline phases of samples were also determined by XRD analysis (Figure 2). All the samples have shown the diffraction patterns at 2θ values of 28.5°, 33.1°, 47.4°, 56.3°, 69.4° and 76.7°, associated to the crystalline planes of the face centered cubic structure of ZnS (Soltani et al., 2012). All the patterns found in the case of prepared ZnS samples are similar without any additional peaks due to ZnO crystalline phase (Zak et al., 2011).] Moreover, no patterns corresponding to impurities were detected, indicating the high purity of the prepared samples. The specific surface areas were also measured for all the ZnS samples and reported in Table 1. In particular, the value of specific surface area of all the prepared ZnS particles was lower (3 m^2 g^{-1} for ZnS_nT; 6 m^2 g^{-1} for ZnS_sC and 10 m^2 g^{-1} for ZnS_sF) with respect to the commercial ZnS (17 m$^2 \cdot$g^{-1}). The band gap values, estimated from the UV-Vis DRS spectra using the Kubelka–Munk function, are reported in Table 1. From the comparison between the band gap (E_{bg}) values, it can be seen that the use of different ZnO in sulfuration treatment not only determined a different value of specific surface area but also a different band edge. In fact, E_{bg} of commercial sample (ZnS_c) is equal to 3.5 eV, whereas for all prepared samples is lower and equal to 3.2 eV for ZnS_sC and 2.5 eV for ZnS_nT and ZnS_sF catalysts.

3.2 Photocatalytic activity tests

Figure 3 shows the photocatalytic results of PNP degradation and mineralization using all the photocatalysts under UV irradiation. In particular, the best results in terms of degradation and mineralization were obtained using ZnS_sF sample leading to a degradation (Figure 3a) of 51% and mineralization (Figure 3b) of 20% after 240 min of UV irradiation. A lower activity was achieved using commercial ZnS sample ZnS_c that allowed to achieve only 7% PNP degradation (Figure 3a) and 6% mineralization (Figure 3b) after 240 min of UV irradiation. This result could be due to the lower band gap value of ZnS_sF (2.5 eV) compared to ZnS_c (3.5 eV). Generally, the main aspects that one should consider to compare the experimental photocatalytic performance of different semiconductor are three. The first is the electronic structure, which determines the optical properties and band structure (band gap) of the photocatalysts (D'Amato et al., 2018). In fact, in agreement with the experimental results (Figure 3), the lower band gap of the ZnS_sC, ZnS_nT and ZnS_sF compared to ZnS_c led to a higher photocatalytic degradation of PNP pollutant. The second aspect is the crystallinity of the samples, which, as it is possible to observe from the XRD pattern (Figure 2), confirmed that all the samples showed high crystallinity, which is beneficial to lowering the e- -h+ recombination rate (Patrocinio et al., 2015). The final key aspect that it is necessary to take into account is the surface characteristic of the photocatalysts and in particular the specific surface area that usually plays an important role on the photocatalytic oxidation reaction (Kumar, 2017). Therefore, considering the experimental results, it is possible to argue that the difference observed in the photocatalytic degradation of PNP using the ZnS_cF and ZnS_nT samples (PNP removal equal to 51% and 33% of after 240 min of UV irradiation time) could be attributed to the different specific surface area that in the case of ZnS_sF is equal to 10 m^2 g^{-1} while for ZnS_nT is equal to 3 m^2 g^{-1}.

Table 1: Summary of physicochemical properties of prepared photocatalysts.

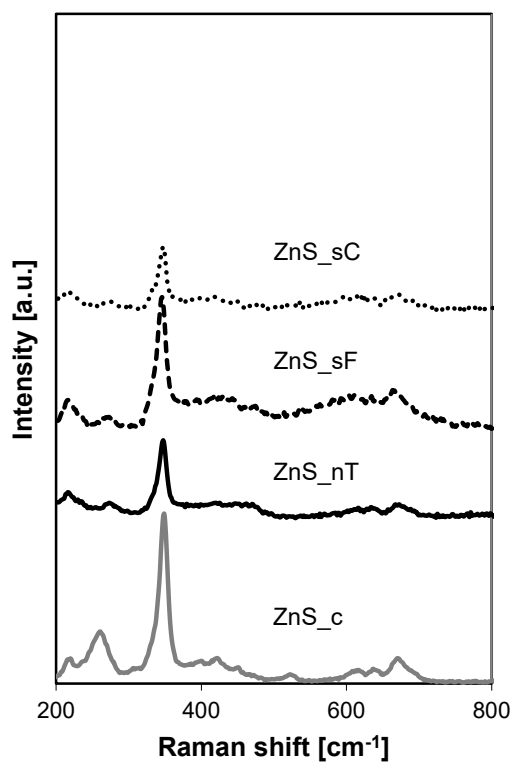| Sample	Specific surface area [m^2 g^{-1}]	E_{bg} [eV]
ZnS_c	17	3.50
ZnS_sC	6	3.20
ZnS_nT	3	2.50
ZnS_sF	10	2.50

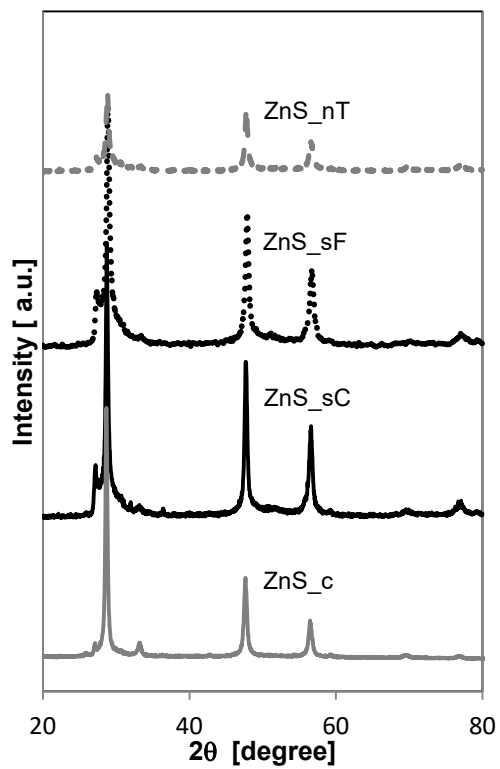*Figure 1: Raman spectra of ZnS_c, ZnS_sC, ZnS_nT and ZnS_sF.*

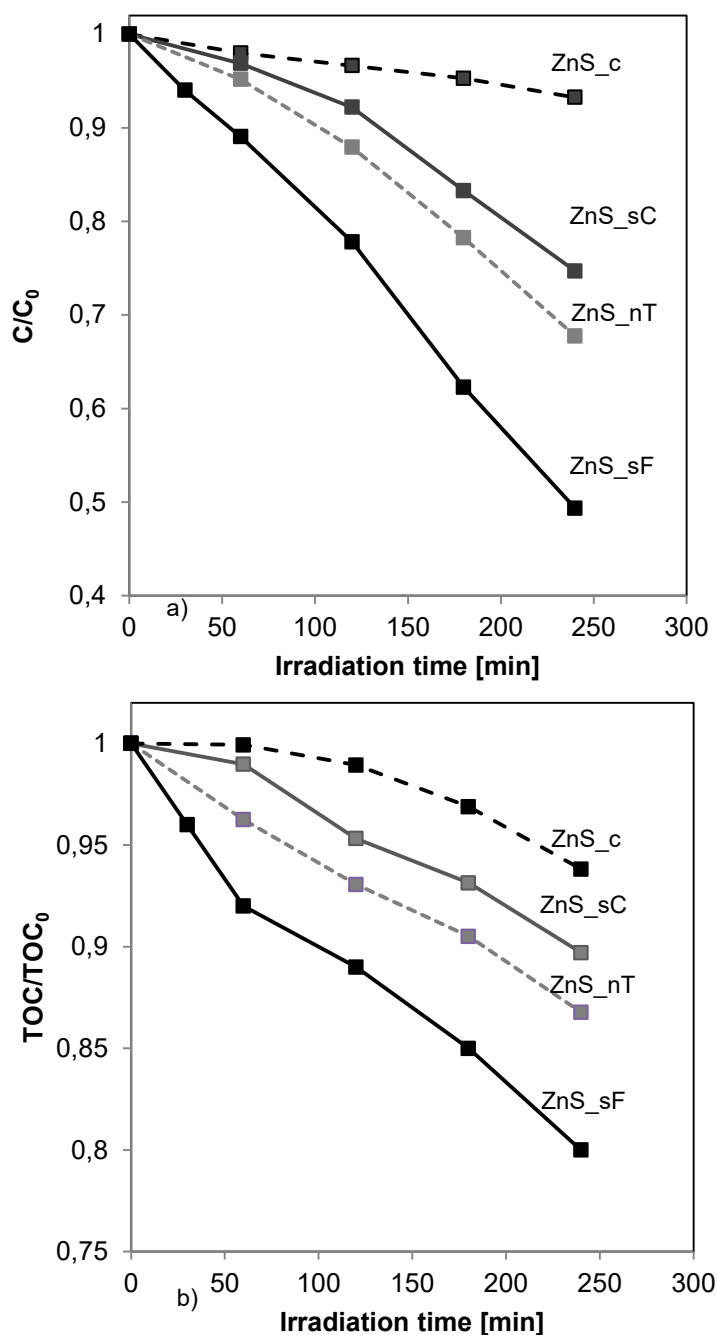*Figure 2: XRD patterns of ZnS_c, ZnS_sC, ZnS_nT and ZnS_sF.*

Figure 3: Photocatalytic a) degradation and b) mineralization of PNP using ZnS_c, ZnS_sC, ZnS_nT and ZnS_sF phtocatalysts.

4. Conclusions

In this work, ZnS photocatalyst was prepared starting from commercial ZnO, or ZnO synthetized using precipitation method. The corresponding ZnS samples were then obtained by sulfuration of ZnO particles carried out at 450°C in presence of N_2 gaseous stream containing H_2S at 5 vol%. The XRD results showed that all samples have high crystallinity and no impurities are detectable. The best photocatalytic results in terms of degradation and mineralization of PNP were obtained on ZnS_sF sample, with a degradation of 51% and mineralization of 20% after 240 min of UV irradiation. The ZnS_sF photocatalyst has the lowest band gap energy value (2.5 eV) together with the higher specific surface area (10 m^2 g^{-1}) compared with the other prepared ZnS samples. These features permit a more efficient electron/hole separation, enhancing the

photocatalytic reactivity towards the PNP removal from aqueous solutions. Due to the value of band gap energy, further experimental studies should be directed to test the ZnS_sF photocatalytic activity also under visible light.

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