

# Environmental Analysis of the Zinc Oxide Nanophotocatalyst Synthesis

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**Abstract**—Nanophotocatalysts such as titanium (TiO<sub>2</sub>), zinc (ZnO), and iron (Fe<sub>2</sub>O<sub>3</sub>) oxides can be used in organic pollutants oxidation, and in many other applications. But among the challenges for technological application (scale-up) of the nanotechnology scientific developments two aspects are still little explored: research on environmental risk of the nanomaterials preparation methods, and the study of nanomaterials properties and/or performance variability. The environmental analysis was performed for six different methods of ZnO nanoparticles synthesis, and showed that it is possible to identify the more environmentally compatible process even at laboratory scale research. The obtained ZnO nanoparticles were tested as photocatalysts, and increased the degradation rate of the Rhodamine B dye up to 30 times.

**Keywords**—Environmental impact analysis, inorganic nanoparticles, photocatalysts.

## I. INTRODUCTION

NANOTECHNOLOGY has great potential to contribute to sustainable development through the efficient use of resources; materials production optimization; catalysis; substitution or minimization of hazardous substances; effective detection of byproducts and/or toxic substances; applications in remediation; protection against corrosion, and many other applications [1].

One of the most formidable challenges facing the twenty-first century global society is improving the quality of soil, water and air [2]. Pollutants from various sources, such as oil and other chemicals spills; pesticides and fertilizers, abandoned mining sites or industrial sites runoff; gases and particulate matter emitted by motor vehicles aggravate the situation daily. Contamination of environmental matrices has grown tremendously in recent years, requiring the proposition of new remediation methods for the treatment of contaminated sites [3].

With the increasing environmental requirements and laws, either by governmental or actions by environmental groups, the need for optimization of industrial processes, and the development of green technologies have become a constant

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concern in waste management [4].

The first impacts of nanotechnology research in environmental remediation have been in end-of-pipe technologies. Several laboratory studies showed the potential use of a wide variety of nanoparticles for the removal of pollutants in the environment [5], [6]. Nanoparticles can be used in reactors as solid dispersions or anchored to a solid matrix (such as activated carbon, zeolites or membranes) for the treatment of water, liquid waste or gaseous emissions [7]. For example, nanoparticles of titanium (TiO<sub>2</sub>) [8]–[11], zinc (ZnO) [12], [13], copper (CuO) [14], iron (Fe<sub>2</sub>O<sub>3</sub>) [15], tungsten (WO<sub>3</sub>) [16] and tin (SnO<sub>2</sub>) [17], [18] oxides were used for photocatalytic oxidation of several pollutants.

On the other hand, environmental concerns about the safety of nanotechnology begin to appear [19]. There is no doubt about the fact that the benefits of nanotechnology are greater than its negative impacts. However, there are no excuses for the researchers do not understand and do not try to reduce these potential impacts [20].

Nanoscience is still in the "discovery phase", where new materials are being synthesized by any available route at small scales to test specific physical or chemical properties. Changes in the physical or chemical structure of a particular nanomaterial can modify its interaction with the physical and biological environment, affecting mobility, reactivity, bioavailability, and toxicity [21]. Most of the available studies on nanotechnology environmental health and safety (EHS) are about the transport, persistence, bioavailability and toxicity of end products [22], without considering potential impacts of impurities, by-products, residues, solvents, etc. [23].

Processes and applications that minimize nanotechnology risks and residues are essential for the transition of scientific discoveries to commercial products [24], [25]. Process selection and design decisions in the chemical industry need to reflect the economic and environmental sustainability [26], and these parameters should also be used to evaluate manufacturing processes or applications of nanomaterials [27].

The use of the "Green Chemistry" principles in nanoscience would allow the production and processing of nanomaterials and/or nanostructured devices inherently safer [28]. However, in the literature there are few studies about "green" production or application methods of nanoproductions [29].

In this context, this work presents an analysis of the environmental impacts of selected production methods, and of the use of zinc oxide (ZnO) nanoparticles as heterogeneous photocatalyst.

## II. EXPERIMENTAL PROCEDURES

## A. ZnO Nanoparticles Preparation

*Method 1 (M1):* ZnO nanoparticles precipitation from 1.0 M zinc sulfate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) and 0.5M sodium hydroxide (NaOH) aqueous solutions, followed by stirring for 12h [30].

*Method 2 (M2):* addition of 0.01mol of zinc acetate dihydrate  $[(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}]$  in 100mL of diethylene glycol (DEEG) under vigorous stirring, followed by heating in a sand bath to 150°C for 8h [31].

*Method 3 (ZnO-M3):* 33.2mL of a 0.552M tetramethylammonium hydroxide  $[(\text{CH}_3)_4\text{NOH} \cdot 5\text{H}_2\text{O}]$  ethanolic solution were slowly added to 100mL of a 0.010M of zinc acetate in dimethylsulfoxide (DMSO) solution [32].

*Method 4 (M4):* 20mL of a 0.2M solution of zinc acetate in dimethylsulfoxide (DMSO) were added drop wise to 10mL 1.2M potassium hydroxide (KOH) ethanolic ( $\text{C}_2\text{H}_6\text{O}$ ) solution at ambient temperature and atmosphere, under moderate agitation. 0.5g of 12-tungstophosphoric acid  $[\text{H}_3(\text{PW}_{12}\text{O}_{40})]$ , a polyoxometalate (POM) with Keggin structure, was used as stabilizer [33].

*Method 5 (M5):* an emulsion was formed with n-decane ( $\text{C}_{10}\text{H}_{22}$ ) as a lipophilic continuous phase, and a 0.10M zinc sulfate ( $\text{ZnSO}_4$ ) / 0.20M potassium hydroxide (KOH) aqueous solution. The fraction of the dispersed aqueous phase was 40% w/w. Polyglycerol polyricinoleate (PGPR 90<sup>®</sup>) and sorbitan oleate (Span 80<sup>®</sup>) were used as emulsifiers at a 3% w/w total concentration, and Tixogel MP100<sup>®</sup> was used to control the emulsion viscosity. The homogenization pressure ranged from 600 up to 1000 Bar. After the ZnO nanoparticles precipitation, water was removed by azeotropic distillation ( $T = 40^\circ\text{C}$ ,  $p = 25\text{mbar}$ ) [34].

*Method 6 (M6):* nanoparticles of zinc carbonate ( $\text{ZnCO}_3$ ) were prepared by adding a flow rate of 10mL/min of a 0.1M of zinc nitrate hexahydrate  $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$  aqueous solution to a 1.0M sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) aqueous solution, under vigorous stirring, and at 60°C temperature. The formed nanoparticles were filtered and washed with deionized water and ethanol, and dried at 80°C for 2 hours. For the zinc oxide synthesis, 2g of the precursor were placed in an open alumina crucible, and heated in an oven under air atmosphere at 700°C for 2h [35].

Deionized water (MilliQ<sup>®</sup>, resistivity  $>18 \text{ M}\Omega/\text{cm}$ , total organic carbon  $\leq 5 \text{ ppb}$ ), and analytical grade Sigma-Aldrich reagents were used for all syntheses. The zinc oxide (ZnO) nanoparticles were prepared under strictly controlled conditions.

## B. Environmental Analysis of the Nanoparticles Synthesis Methods

The environmental analysis of the nanoparticles preparation methods was performed by adapting the methodology proposed by [27]. These authors used the environmentally compatible manufacturing standards recommended by the American Institute of Chemical Engineers (AIChE), and others

listed in the environmental performance table recommended by the United States Environmental Protection Agency (EPA).

The rates of chemical safety and process safety were estimated according the methodology proposed by [36]. The inherent safety index (ITI) of a manufacturing process is the sum of the chemical inherent safety (ICI), and the process inherent safety (IPI) indexes. The inherent safety index (ITI) calculation performed in this work was based in the worst case scenario of each process, and a low ITI value indicated an inherently safer process. The scores assignment was performed by using the parameters proposed by [37] (Table I).

TABLE I  
CHEMICAL INHERENT SAFETY INDEX (ICI) AND PROCESS INHERENT SAFETY INDEX (IPI) COMPONENTS AND SCORES

ICI components	Score	IPI components	Score
Reaction heat (main), $I_{rm}$	0 a 4	Inventory, $I_i$	0 a 5
Reaction heat (side), $I_{rs}$	0 a 4	Temperature, $I_t$	0 a 4
Chemical interactions, $I_{int}$	0 a 4	Pressure, $I_p$	0 a 4
Flammability, $I_f$	0 a 4	Equipment, $I_{EQ}$	$I_{ISBL} + I_{OSBL}$
Explosiveness, $I_{ex}$	0 a 4	$I_{ISBL}^{(a)}$	0 a 4
Toxicity, $I_{tox}$	0 a 6	$I_{OSBL}^{(a)}$	0 a 3
Corrosiveness, $I_{cor}$	0 a 2	Safe process structure, $I_{st}$	0 a 5
$ICI_{max}$	28	$IPI_{max}$	25

<sup>(a)</sup> ISBL refers to the equipment located inside battery limit area, while OSBL refers to those located offsite battery limit

Safety analysis was also performed with the GMP-RAM v1.1<sup>®</sup> software developed by EMBRAPA BRAZIL, adapted in accordance with [38]. Toxicity, corrosiveness, flammability, and explosiveness data of the chemical reagents were obtained from their respective Material Safety Data Sheet (MSDS). These data were used as parameters for assigning the values of (1) low, (2) moderate or (4) high for damage and/or exposure; of (1) local, (2) regional or (4) national (4) for the extent of the damage, and of (1) naturally reversible, (2) reversible with simple management, (4) reversible with complex remediation or (8) irreversible for the reversibility of the damage, without taking into account previous events. These values were assigned considering the occurrence of a massive groundwater contamination by the reagents used in each of the selected methods for the ZnO nanoparticles synthesis.

## C. ZnO Nanoparticles Purification and Characterization

Colloidal dispersions of the nanoparticles were dialyzed against deionized water. After the dispersion drying, the obtained solid was analyzed by Fourier transform infrared spectroscopy (FTIR) performed on a Thermo Scientific Nicolet 6700 FTIR equipment between 400 and 4000 $\text{cm}^{-1}$ .

## D. Rhodamine B Photolysis, and Photocatalytic Decomposition in the Presence of ZnO Nanoparticles

The photocatalytic activity of the ZnO nanoparticles was evaluated by the decomposition of Rhodamine B (RHB) dye in aqueous medium. 120mg ZnO catalyst were dispersed in 120mL of an aqueous solution of  $1 \times 10^{-5}\text{M}$  RHB. The dispersion was stirred in the dark for 60 minutes to establish

the adsorption/desorption equilibrium between the RHB and the catalyst. All tests were performed with UV irradiation from a 26W electronic black light lamp. Samples of the reaction medium were collected every 10 minutes to measure the UV/vis spectrum of the aqueous phase. A UV/vis spectrophotometer (HP 8351) was used to record the absorbance at the RHB absorption maxima (550nm). The pseudo-first order reaction rate constants ( $k_{wexp}$ ) were obtained from the logarithm of absorbance versus time plots [39].

*E. Electric Energy Consumption for the Photocatalysis*

The electric energy consumption, a major component of operating costs of any decontamination process involving photocatalysis, was calculated according to the procedure proposed by [40]. The electrical energy per order ( $E_{EO}$ ) was defined as the number of kWh used to reduce the pollutant concentration in a unit volume of contaminated water by an order of magnitude. For a batch type reactor, the  $E_{EO}$  (kWh/m<sup>3</sup>.order) was calculated by using (1)

$$E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C_0}{C}\right)} \quad (1)$$

where  $P$  is input power to the photocatalysis lighting system (kW),  $t$  is the irradiation time (min),  $V$  is the water volume in the reactor (L) and  $C_0$  and  $C$  are the initial and final concentrations the pollutant, respectively.

III. RESULTS AND DISCUSSION

*A. Environmental Analysis of the ZnO Nanoparticles Preparation Methods*

Methods  $M1$ ,  $M2$ , and  $M3$  showed to be the more suitable for a possible development to the industrial scale in terms of process complexity, since  $M4$ ,  $M5$ , and  $M6$  methods require industrial installations with a greater number of equipments, and high temperature and/or pressure conditions (compare Figs. 1 and 2).

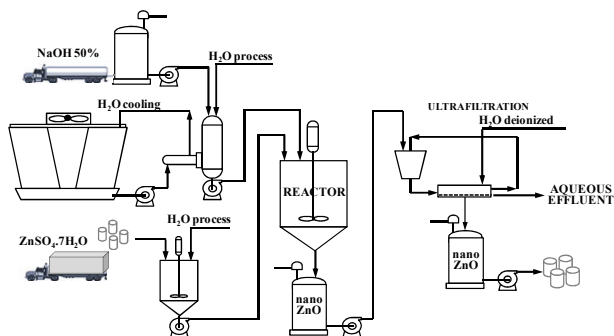


Fig. 1 Simplified flowchart for an industrial process based on the  $M1$  method for ZnO nanoparticles synthesis

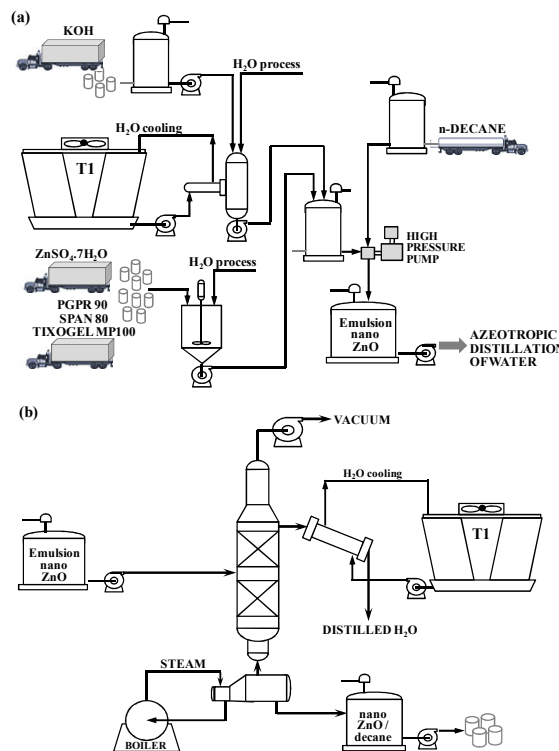


Fig. 2 Simplified flowchart for an industrial process based on the  $M5$  method for ZnO nanoparticles synthesis: (a) plant for nanoparticles production, and (b) installation for ZnO nanoparticles separation from the emulsion

The six selected methods for ZnO nanoparticles synthesis were compared by using some of the Green Chemistry related parameters, taking into account the described laboratory procedures of each method (Table II).

TABLE II  
GREEN CHEMISTRY PARAMETERS ANALYSIS FOR THE SELECTED METHODS FOR ZNO NANOPARTICLES SYNTHESIS

Parameter	M1	M2	M3	M4	M5	M6
Zinc source (g)	11.49	0.219	2.195	43.900	0.323	1.261
Base source (g)	3.200	3.312	0	67.332	0.224	4.239
ZnO (g) <sup>(a)</sup>	3.256	0.081	0.814	16.282	0.163	0.326
Solvent (mL)	0	100	200	280	60	100
Water (mL)	40	0	0	0	20	40
Additives (g)	0	0	0	0.5	3	0
kg reagents/kg ZnO	4.51	43.38	2.70	68.6	21.79	16.89
L solvents/ kg ZnO	0.0	1228.0	122.8	16.0	368.5	307.1
L water/ kg ZnO	27687	1105923	110552	16	308746	890.6
Temperature (°C)	25	25	160	60	40	80
20.000 RPM (h)	-	-	-	0.25	-	-
Vacuum (Barr)	-	-	-	-	0.025	-
Pressure (Barr)	1	1	1	1	800	1
kWh/kg ZnO	598.8	199.6	6387.4	414.6	9028.4	650.0
Atomic economy (%EA)	22.16	2.31	37.09	14.57	4.59	5.63

<sup>(a)</sup>Synthesis yield = 100 %.

Methods  $M1$ ,  $M3$ , and  $M4$  presented significantly higher

atomic economy percentages compared to the other three methods. It is worthwhile to mention that the intensive water use of methods *M1*, *M2*, and *M3* resulted from the used laboratory scale purification process (dialysis), which should be replaced by a more efficient method (ultrafiltration, for instance) at the process scale-up.

Fig. 3 shows the illustration of the environmental contamination risk assessment performed with the adapted software GMP-RAM v.1.1® for the ZnO nanoparticles production.

Fig. 3 Environmental contamination risk assessment performed with the adapted software GMP-RAM v.1.1 for the production of ZnO nanoparticles

The GMP-RAM v.1.1® Risk Assessment Matrix showed that for *M1* method the risk and significance indexes (4 – 8) are low, meaning that its large scale use should not require restrictions. The methods *M2* and *M5* presented intermediate risk and significance indexes (16 – 16), requiring remediation management after an eventual environmental contamination. On the other hand, methods *M3*, *M4*, and *M6* showed higher risk and significance indexes (16 – 32), indicating restrictions for use/installation.

The evaluation of the complementary Green Chemistry parameters (Table III), and the analysis of the inherent safety

index (Table IV), and were performed only for *M1*, *M2*, and *M3* methods as representatives of low, medium, and high risk indexes, respectively.

According to the toxicity parameters (Table III), method *M1* uses a corrosive reagent, while *M2* method uses an organic solvent and a corrosive reagent, resulting effluent with organic contamination. *M3* method also uses a corrosive reagent, and might generate a potentially toxic effluent with at least traces of two organic solvents. Therefore, *M1* method appears to be the most environmentally acceptable.

TABLE III  
TOXICITY PARAMETERS FOR THE TESTED METHODS

Parameter	M1	M2	M3
hazardous raw materials	NaOH: corrosive	DIEG: flammable explosive	Ethanol, DMSO: flammable explosive
Hazardous subproducts	Basic wastewater	DIEG contaminated wastewater <sup>(a)</sup>	Ethanol/DMSO contaminated, basic wastewater <sup>(a)</sup>
Raw materials: DL <sub>50</sub> rat (mg/kg)	Zn(SO <sub>4</sub> ): 245 NaOH 0.5 M: >90	(CH <sub>3</sub> COO) <sub>2</sub> Zn: 794 DIEG: 12,565	(CH <sub>3</sub> COO) <sub>2</sub> Zn: 794 (CH <sub>3</sub> ) <sub>4</sub> NOH: 350 Ethanol: 7,060 DMSO: 14,500 (CH <sub>3</sub> COO) <sub>2</sub> Zn: 20 mg (eyes)
Raw materials: HTPE (mg/kg)	Zn(SO <sub>4</sub> ): 420 µg (eyes/rabbit) NaOH 0.5 M: 1% (eyes/rabbit)	(CH <sub>3</sub> COO) <sub>2</sub> Zn: 20 mg (eyes) DIEG: 11,890 (skin/rabbit)	(CH <sub>3</sub> ) <sub>4</sub> NOH: 2 (eyes/humans) Ethanol: 500 (eyes/rabbit) DMSO: 40,000 (skin/rat)
Dialysis water (L/kg ZnO)	27,687	1,105,923	110,551

<sup>(a)</sup> Requires solvent recovery before wastewater treatment.

TABLE IV  
COMPONENTS OF THE INTRINSIC CHEMICAL SAFETY (ICI) INDEX, OF THE INTRINSIC PROCESS SAFETY (IPI) INDEX, AND OF THE TOTAL INTRINSIC PROCESS SECURITY (ITI) INDEX FOR THE TESTED METHODS

ICI components	M1	M2	M3
Reaction heat (main reaction)	0	0	0
Chemical interactions	3	3	2
Flammability	0	3	1
Explosiveness	0	1	1
Toxicity	2	2	2
Corrosiveness	0	0	0
<i>I<sub>csi</sub></i>	5	9	6
IPI Components	M1	M2	M3
Inventory	0	0	0
Temperature	0	0	0
Pressure	0	0	0
Equipment	2	2	2
Process structure	5	5	4
<i>I<sub>psi</sub></i>	7	7	6
<i>ITI</i>	12	16	12

From Table IV data, it is possible to observe that the *M1* and *M2* methods present the lowest values of the inherent safety index (*ITI*).

### B. Analysis of the ZnO Nanoparticles as Photocatalysts

After drying at 105°C, the infrared spectra of the solids obtained by methods M1, M2, and M3 showed the characteristics bands of the zinc oxide at 611 ( $\nu_{\text{Zn-O}}$  Zn-O), 3200-3600 ( $\nu_{\text{-OH}}$ ), and 1680 ( $\nu_{1\text{-OH}}$ )  $\text{cm}^{-1}$  [41].

The variation of the natural logarithm of the absorbance with time indicates that the Rhodamine B degradation reaction under UV irradiation by photolysis or by heterogeneous photocatalysis in the presence of ZnO nanoparticles occurs by a pseudo-first order mechanism with respect to the dye (Fig. 4).

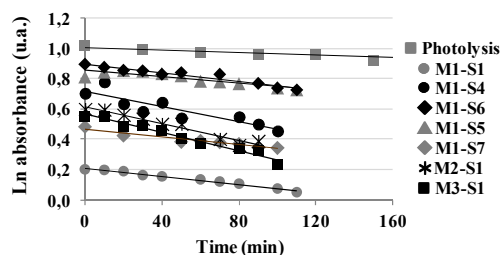


Fig. 4 Variation of  $\ln(\text{absorbance})$  versus time for solutions of RHB under UV irradiation (26 W) at 25°C, with and without ZnO nanoparticles from different synthesis performed by using methods M1, M2, and M3

The modulus of the slope of each line depicting the experimental results at Fig. 4 corresponds to the respective value of the experimental rate constant ( $k_{\Psi_{\text{exp}}}$ ) for the degradation reaction [42]. The degradation rate of the Rhodamine B dye can be increased up to 30 times in the presence of the ZnO nanoparticles obtained by the tested methods, with the consequent reduction of electric energy consumption (Table V).

TABLE V  
PSEUDO-FIRST ORDER RATE CONSTANTS AND ELECTRIC ENERGY CONSUMPTION FOR THE DEGRADATION OF RHODAMINE B BY PHOTOLYSIS, AND BY HETEROGENEOUS PHOTOCATALYSIS IN THE PRESENCE OF ZNO NANOPARTICLES

Test	$k_{\Psi_{\text{exp}}}$ ( $\text{s}^{-1}$ )	Catalytic factor <sup>(a)</sup>	$E_{\text{EO}}$ ( $\text{kWh/m}^3 \cdot \text{order}$ )	$E_{\text{EO}}$ ( $\text{kWh/m}^3 \cdot \text{order}$ )
Photolysis1	0.0003	--	24438.3	
Photolysis2	0.0003	--	30068.2	23030 ± 8446
Photolysis3	0.0005	--	14584.0	
M1-S1	0.0113	30.5	764.7	
M1-S2	0.0089	24.1	952.7	1138 ± 558
M1-S3	0.0058	15.7	1695.6	
M2-S1	0.0062	16.8	1447.1	
M2-S2	0.0049	13.2	1675.7	1311 ± 499
M2-S3	0.0097	26.2	812.6	
M3-S1	0.0039	10.5	886.3	
M3-S2	0.0021	5.7	1149.6	1162 ± 288
M3-S3	0.0069	18.6	1449.5	
M1-S4	0.0025	6.8	3345.2	
M1-S5	0.0011	3.0	8976.0	6457 ± 3112
M1-S6	0.0010	2.7	5564.1	
M1-S7	0.0014	3.8	7943.5	

<sup>(a)</sup> Catalytic factor =  $k_{\Psi_{\text{exp}}}$  photocatalysis/  $k_{\Psi_{\text{exp}}}$  photolysis

### IV. CONCLUSION

The realized environmental assessment for six different methods of ZnO nanoparticles synthesis showed that it is possible to identify the more environmentally compatible process even at laboratory scale research.

Heterogeneous photocatalysis with ZnO nanoparticles showed to be an alternative for the treatment of wastewater contaminated with organic dyes. However, the tested methods produce ZnO nanoparticles particles with a significant performance variation as photocatalysts. The reasons for this variation have yet to be investigated, and must be controlled to allow its commercial application.

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