U.P.B. Sci. Bull., Series B, Vol. 74, Iss. 2, 2012 ISSN 1454-2331

PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS USING NiO BASED MATERIALS

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Această lucrare prezintă degradarea fotocatalitică a poluanților organici (4-clorfenol, 2,4-diclorfenol şi cristal violet) utilizând nanoparticule de NiO şi nanoparticule de NiO îmbrăcate în silice. Degradarea fotocatalitică a poluanților a fost investigată în diferite condiții de reacție, variind concentrația de catalizator şi, sursa de iluminare, şi folosind catalizatori activați cu radiație gamma sau cu NaOCl. Randamentul de degradare fotocatalitică a crescut, prin utilizarea nanoparticulelor pe bază de NiO activate de la 30% la 55%, pentru un timp de iradiere de 6 ore. Originalitatea acestei lucrari este data de utilizarea nanoparticulelor activate cu radiație gamma în procese fotocatalitice

This paper presents the photocatalytic degradation of organic pollutants (4-chlorophenol, 2,4-dichlorophenol and crystal violet) using NiO and NiO silica coated nanoparticles. Photocatalytic degradation under different experimental conditions: catalyst loadings, irradiation sources and activated catalysts by using gamma rays and respecctively NaOCl. Catalyst activation was made using gamma radiolysis and NaOCl activation. The photocatalytic degradation yield increased from 30% up to 55% when activated NiO based nanoparticles were used for an irradiation time of 6 hours. Uses of gamma activated nanoparticles as photocatalyst represents the main original issues of this paper.

Keywords: organic pollutants, NiO nanoparticles, photocatalysis, gamma radiolysis, NaOCl activation

1. Introduction

In recent years, the use of semiconductor metal oxides as photocatalysts for degradation of pollutants has attracted attention of scientific community. Semiconductor metal oxide nanoparticles have been studied due to their novell optical, electronic, magnetic, thermal and mechanical properties and potential application in catalyst, gas-sensors and photo-electronic devices [1-5]. The most common semiconducting metal oxides are TiO_2 and ZnO due to their catalytic

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activity and stability. Among them, transition metal oxide, NiO appears to be especially efficient as catalyst for wastewater pollution abatement [6-9]. NiO is a p-type semiconductor characterized by a wide band gap between [3.5 eV] valence band [3.1 eV] and conduction band [- 0.5 V] that make it suitable for photocatalytical processes [10-12].

The photocatalytic process starts with the irradiation of a semiconductor material by light with sufficient energy to excite the electrons from the valence band to the conduction band generating extremely reactive electron/hole (e^-/h^+) pairs that migrate to the adsorbed species leading to reactive species such as hydroxyl radicals. The major drawback of the photocatalytic process is the electron/hole pair recombination. To solve this problem metal oxide nanoparticles are embedded into different matrices. The matrix should have an essential influence on the properties of the nanoparticles [13-15]. The most common matrix is silica matrix. The high porosity of amorphous silica materials provides the three dimensional space required for the doping of functional components; moreover they are effective transparent that is unlikely to absorb light in the near-infrared, visible and ultraviolet regions or to interfere with magnetic yields which allows the dopants inside the matrix to keep their optical properties and, finally they are nontoxic as well.

The photocatalytic activity of semiconducting metal oxide can be effectively modified by ionizing radiations. These radiations induce some changes in the structural, textural, electric, magnetic and catalytic properties of the treated solids. For instance gamma-rays have been reported to effect some changes in the chemistry of surfaces of the semiconducting metal oxides [24-28].

On the other hand semiconductor activation with NaOCl induces a higher state of oxidation for the metalic atom. The activity and selectivity of the semiconducting metal oxide depends on the oxidation state of metal ions and their co-ordination in the lattice, the surface action-oxygen bond strength, the content of active oxygen – both total and surface, and the morphology of the material [29-32].

In this paper the photocatalytic activity of NiO based materials, synthesized by microemulsion assisted sol-gel process was investigated for the degradation of crystal violet (CV) and chlorinated phenols (4-chlorophenol: 4-CP, 2,4-dichlorophenol: 2,4-DCP). The effect of key operational parameters on the pollutants photodegradation process such as catalyst loading, light source and type of catalyst was studied.

The effect of gamma-rays and NaOCl on the photocatalytic activity of NiO based nanomaterials has been investigated.

The paper originality is mainly given by the use of activated photocatalysts and by combining gamma-rays activation with photocatlytical process.

2. Experimental

All chemicals were of the highest purity and were used as received without further purification or distillation: methyl violet (crystal violet), 2,4-diclorophenol, NiO commercial nanoparticles (< 50 nm (BET), >50 m^2g^{-1} (SSA), density 6.67 g/mL at 25°C (lit.), bulk density 0.51 g/mL) and sodium hypochlorite (6,5%) from Sigma-Aldrich®, 4-CP purchased from Riedel-de Haën® and TiO_2 Degussa P25. Ultra-pure water (Millipore Corporation) was used.

The photocatalytic degradation experiments of CV were made by contacting a mass of 20 mg of powder catalyst with 100 mL of 10 mg/L crystal violet aqueous solution, under vigorous stirring in a typical photoreactor equipped with cooling jacket. Samples were irradiated with a 1000 W Xenon lamp (6271H, Oriel) by using a UG filter which transmitted light in the range of 250 – 400 nm (max. 330 nm). The temperature of the experiments was maintained at 20ºC. The colour degradation was estimated by spectral changes of 3 mL aliquots at 3 minutes time interval using a JASCO V-670 Spectrophotometer.

Irradiation in UVA, for chlorophenols degradation, was performed with a laboratory constructed „illumination box” equipped with four F15W/T8 black light tubes (Sylvania GTE, USA). The maximum emission of these tubes is around 375 nm, emitting 71.7 $mWcm^{-2}$ at a distance of 25 cm.

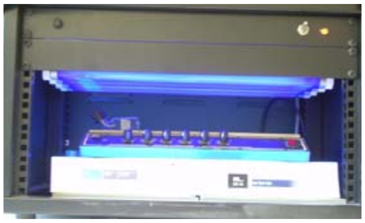

Fig. 1 Illumination box

Pollutant degradation was monitored, after filtration with 0.2 mm filter MILLEX PVDF Durapore-GV Millipore by HPLC, using an HPLC apparatus consisting in a Waters (Milford, MA, USA) Model 600E pump associated with a Waters Model gradient controller, a Rheodyne (Cotati, CA, USA) Model 7725i sample injector equipped with 20 µL sample loop, Lichrospher 100 RP-18 (10 UM) analytical column (25cmx4mm ID) and a Waters Model 486 tunable absorbance detector, set at 280 nm, controlled by the Millenium (Waters) software. The mobile phase was acetonitrile:water (1:1) mixture containing 0.2% acetic acid.

Gamma-radiolysis experiments were performed at room temperature in a ^{60}Co, 6500 Ci Gamma Chamber (4000 A, Isotope Group Bhaba Atomic Research Centre Trombay, India). The irradiation for chlorophenols degradation and gamma radiolysis experiments were performed at the Institute of Physical

Chemistry NCSR “Demokritos”, Catalytic-Photocatalytic Processes (Solar Energy Environment) Laboratory in Athens, Greece.

3. Results and discussion

There are different methods to synthesise NiO based materials reported in the literarature: hydrothermal synthesis [16], microemulsion [17-19], sol-gel methods [20-22], microemulsion assisted sol-gel procedure [13]. Synthesizing NiO based materials by microemulsion assisted sol-gel process presents several advantages: i) the metal oxide nanoparticles are reduced directly in the microemulsion and can be used as a catalyst in suspension without further treatments, ii) the metal oxide nanoparticles size and shape can be controlled to a great extent therefore a narrow particle size distribution can be obtained, iii) the metal oxides nanoparticles are entrapped in the silica network which acts as crystallization nuclei within the microemulsion colloidal aggregates.

3.1. Degradation of pollutants using NiO based materials

3.1.1. Degradation of CV

CV photodegradation experiments were made by comparing the rate of colour degradation of the solution containing the NiO based materials with those possessed by a well known TiO_2 photocatalyst. The results are illustrated in Figs. 2-4 and show that NiO based materials have also photocatalytic activity, especially NiO/SiO_2 bulk samples. These graphs show that the NiO NP samples have a higher photocatalytic efficiency compared to NiO/SiO_2 NP as they have nanometric size 11 nm, respectively 13 nm and a higher specific surface area 85 m^2g^{-1}, respectively 46,14 m^2g^{-1} [13].

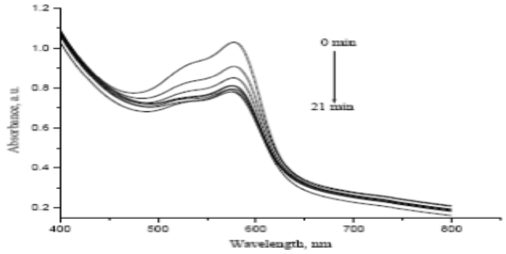

Fig.2. Evolution in time of absorption spectra of crystal violet (10mg/L) aqueous solution with NiO/SiO_2 nanoparticles

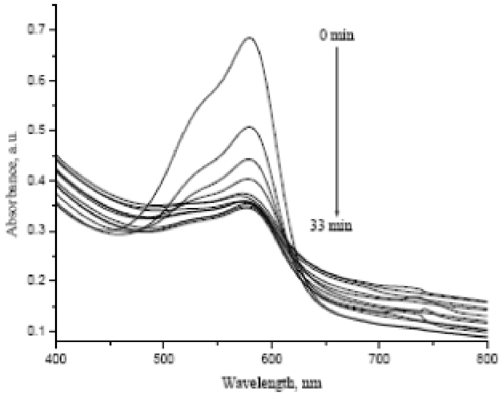

Fig.3. Evolution in time of absorption spectra of crystal violet (10mg/L) aqueous solution with NiO nanoparticles

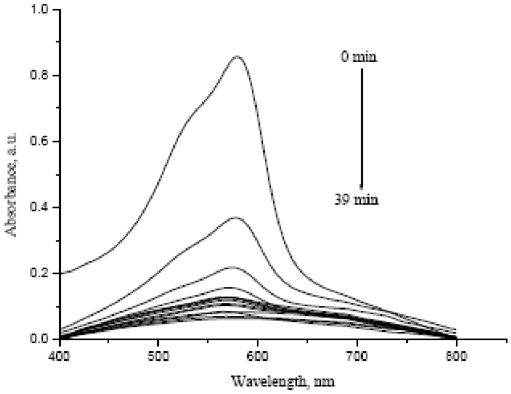

Fig.4. Evolution in time of absorption spectra of crystal violet (10mg/L) aqueous solution with TiO_2 nanoparticles

NiO based materials presents good adsorption properties for crystal violet and these improved the dye photocatalytic degradation.

3.1.2 Degradation of 4-CP

Adsorption test for 4-CP on NiO based materials

In a typical adsorption experiment 10 mL of aqueous 4-CP (15ppm) containing NiO based materials were added to a cylindrical pyrex cell, covered tightly with a serum cap and magnetically stirred, in the dark, at ambient temperature for 240 minutes. Analysis of the poluttant adsorbed was performed after filtration on a 0.2 mm MILLEX PVDF Durapore-GV Millipore filter.

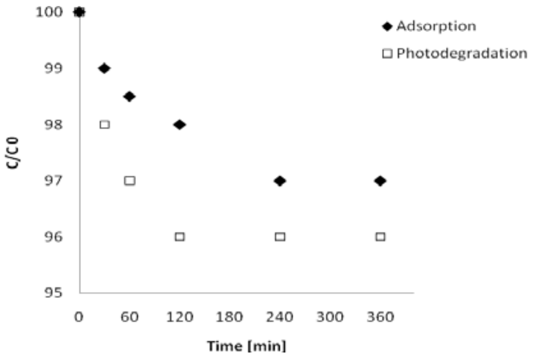

Fig.5. Variation of 4-CP concentration during adsorption and photodegradation experiment using NiO nanoparticles

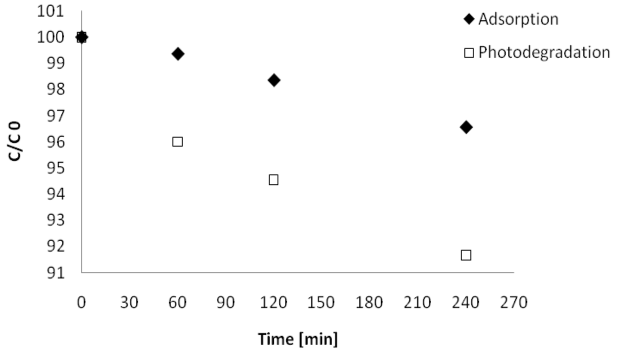

Fig.6. Variation of 4-CP concentration during adsorption and photodegradation experiment using NiO/SiO$_2$ nanoparticles

In a typical photocatalytic experiment 10 mL of aqueous 4-CP (15ppm) containing the NiO based materials were added to a cylindrical pyrex cell, oxygenated and covered air tightly with a serum cap. Photolysis was performed at ambient temperature in the photolysis apparatus. The solutions were magnetically stirred throughout the experiment. Analysis of the photolysed solutions was performed after filtration with a 0.2 mm MILLEX PVDF Durapore-GV Millipore filter.

Adsorption and photodegrdataion tests for NiO based materials (fig. 5 and 6) show that the photocatalytic yield is similar with adsorbtion yield.

Photocatalytic tests for photodegradation on 4-CP were made using different experimental conditions: catalysts (NiO and NiO/SiO$_2$), irradiation sources (UVA, UVC) and catalyst loading (200, 600 ppm). The results presented in Figs. 7-9 confirm that yield changes in the photocatalytic degradation of 4-chlorophenol is mainly due to adsorption process.

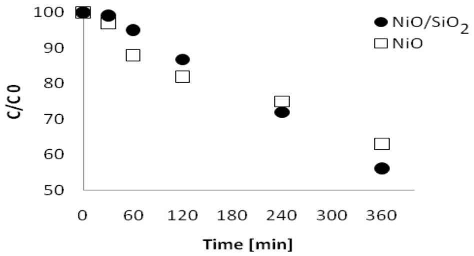

Fig. 7. Variation of 2,4-DCP concentration during photodegradation experiment using NiO based materials

NiO/SiO_2 presents slightly better photocatalytic efficiency than NiO for 4-chlororphenol photodegradation (fig.7).

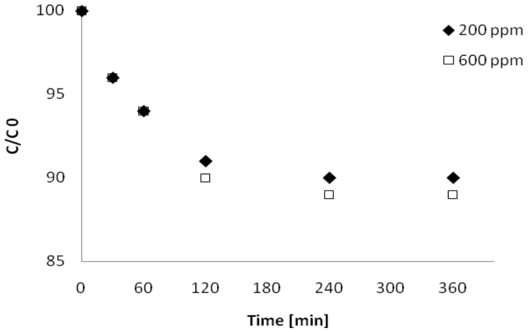

Fig. 8. Variation of 4-CP concentration during photodegradation experiment using different NiO/SiO_2 loading

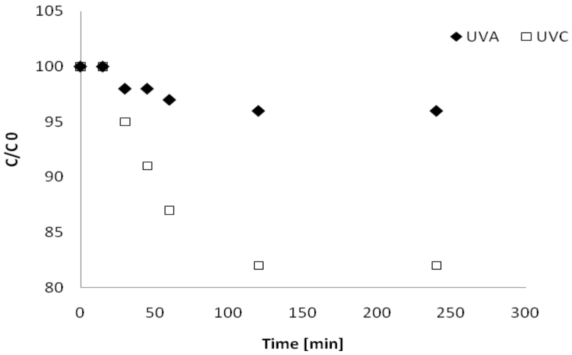

Fig. 9. Variation of 4-CP concentration during photodegradation experiment using NiO nanoparticles and different irradiation sources

3.2. Degradation of pollutants using activated NiO based materials

3.2.1 Activation of NiO based nanomaterials with NaOCl

NiO based nanomaterials activated with NaOCl [21-23] was obtained by mixing an aqueos solution of NiO nanomaterials with NaOCl 13%, under vigorous stirring for 30 minutes, washed with water, centrifuged at 15000 rpm for 10 minutes and dried in air atmosphere.

NaOCl activation of NiO nanoparticles generated an increase in their photocatalytic efficiency from 25% up to 55% as shown in Fig. 10. When using NiO/SiO_2 activated nanoparticles no signifficant changes were noticed on the photodegradation yield (Fig. 11).

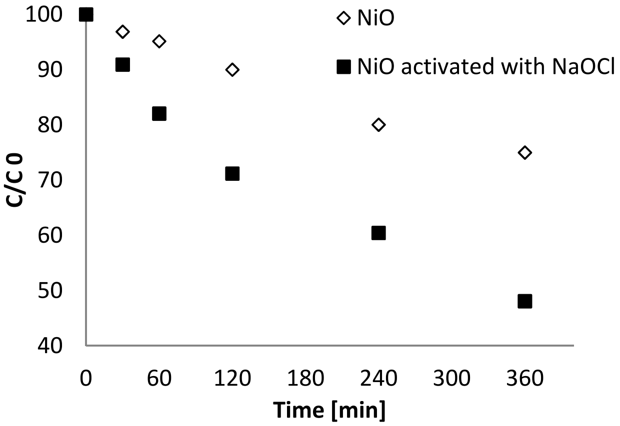

Fig.10. Variation of 2,4-DCP concentration during photodegradation experiment using NiO and NiO activated with NaOCl nanoparticles

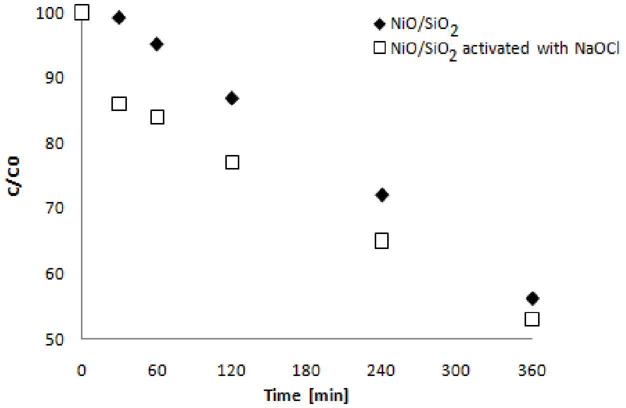

Fig.11. Variation of 2,4-DCP concentration during photodegradation experiment using NiO/SiO_2 and NiO/SiO_2 activated with NaOCl nanoparticles

3.2.2. NiO based materials activated with γ-rays

The dose rate for the irradiation of NiO based nanomaterials were determined with Fricke's dosimeter and were found equal to 7.98 kGy (correspondig to a 24 h irradiation), respectively 15.96 kGy (48h).

The photocatalytic efficiency of NiO nanoparticles irradiated with 7.98 kGy increase with 30% in comparison with the non-irradiated nanoparticles. The photocatalytic activity of gamma-irradiated NiO nanoparticles was found to vary as a function of the irradiated dose applied. The photocatalytic efficciency for NiO 15.96 kGy is lower than for NiO 7.98 kGy (Fig.12).

In the case of NiO/SiO_2 irradiated samples the photocatalytic efficiency improves slightly when using 15.96kGy and remains unchanged for 7.98 kGy (Fig. 13).

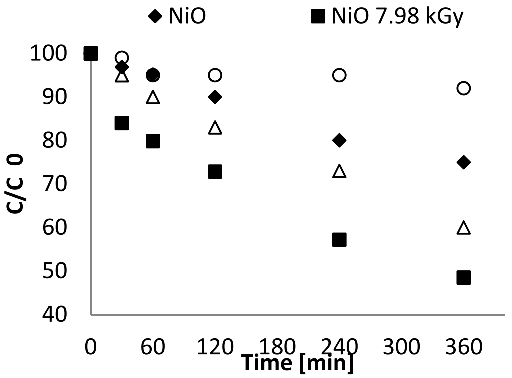

Fig.12. Variation of 2,4-DCP concentration during photodegradation experiment using NiO and NiO gamma activated nanoparticles

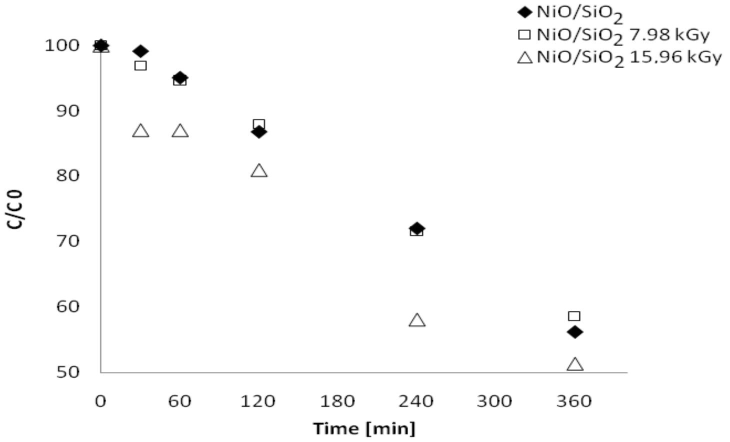

Fig.13. Variation of 2,4-DCP concentration during photodegradation experiment using NiO/SiO_2 and NiO/SiO_2 gamma activated nanoparticles

For comparison NiO commercial nanoparticles purchased from Sigma-Aldrich were tested (Fig. 14). The synthesized NiO nanoparticles presented a higher photocatalytic efficiency for 2,4-chlorophenols photodegration (25%) then the commercial nanoparticles (21 %).

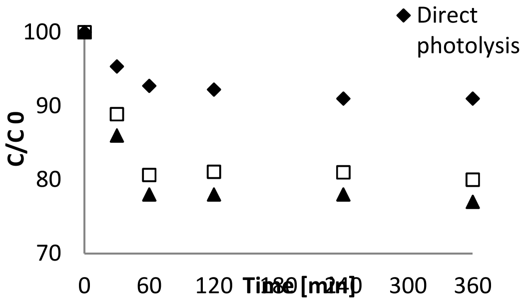

Fig.14. Variation of 2,4-DCP concentration during photodegradation experiment using NiO (Sigma-Aldrich) nanoparticles

4. Conclusion

NiO based nanomaterials were used as photocatalysts for degradation of dyes and organics.

For crystal violet photodegradation NiO proved to be more efficient than NiO/SiO_2, photocatalitic efficiency obtained was 50% in 33 minutes in comparison with 20% in 21 minutes for NiO/SiO_2 nanoparticles.

The efficiency obtained for chlorophenols photocatalytic degradation was 25% when using NiO, respectively 45% for NiO/SiO_2.

Photocatalytic efficiency of synthesized nanomaterials improved when gamma activated and NaOCl activated nanomaterials were used as photocatalysts.

NiO based materials proved to be more effiecient for photocatalytic degradation of dyes than organics and the results recommends further studies in order to improve their properties by combining them with other photocatalyst like TiO_2 and ZnO.

Aknowledgements

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/6/1.5/S/19.

PhD student Alina-Florentina Comănescu is grateful to Dr. Anastasia Hiskia, Dr. Kyriakos Papadopoulos and Dr. Theodoros Triantis for technical support and encouragement in extending this work.

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