DOI: http://doi.org/10.21698/simi.2023.ab04

METAL – TITANIUM DIOXIDE DOPED CATALYSTS FOR WASTEWATER TREATMENT UNDER SIMULATED SOLAR LIGHT

Lucian Alexandru Constantin, Ioana Alexandra Ionescu, Mirela Alina Constantin, Mihai Stefanescu, Nicoleta Mirela Marin

National Research and Development Institute for Industrial Ecology – ECOIND Bucharest, 57-73 Drumul Podu Dambovitei, 060652, Bucharest, lucian.constantin@incdecoind.ro, Romania

Keywords*: degradation, metal doped TiO2, photo catalysis, solar radiation*

Introduction

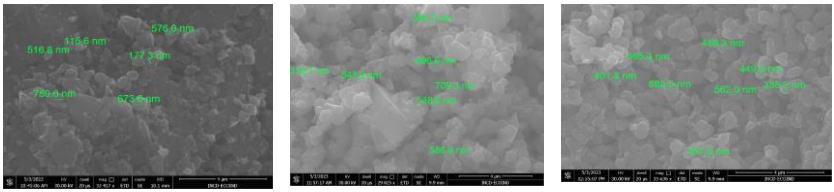
TiO2 assisted photo catalysis was widely studied in the last years for the advanced degradation or organic compounds from aqueous systems, mainly for those not removed by conventional treatment processes. The main drawback of TiO2 is that is activated only by UV radiation and uses only about 5% of available solar radiation. TiO2 doping with metals proved to be a good method to improve its photocatalytic properties and to enhance its response to solar radiation.

Materials and methods

Three types of metal-doped TiO2 catalysts (Fe-TiO2, Ni-TiO2, Co-TiO2) were prepared using sol-gel method. The TiO2 precursor was titanium (IV) isopropoxide (Sigma Aldrich) and Fe(NO3)3 · 9 H2O (Sigma Aldrich), Ni(NO3)2 · 6 H2O (Sigma Aldrich), Co(NO3)2 · 6 H2O (Sigma Aldrich) were used as metal sources. Catalysts with 1wt%, 2wt%, 5wt% were prepared. A lamp with the following characteristics: 35W, 380-800 nm, 1000 lumens, photosynthetic photon flux density 300 µmol quanta/m2·s was used to simulate solar radiation. Dimensional analyse was performed using a Mastersizer 2000 – Malvern equipment and a FEI Quanta FEG 250 scanning electronic microscope was used for morphological characterisation and EDX (energy dispersive X – ray spectroscopy) characterisation. Two sets of experiments were performed using a synthetic solution of methylene blue - MB (Merck) and real wastewater from a municipal wastewater treatment plant.

Results and conclusions

Prepared catalysts were first characterized from the point of view of particle dimensions. The obtained results showed the following dimensional parameters: Fe-TiO_2 [d (0.1) = 0.388 µm; d(0.5) = 0.505 µm; d(0.9) = 0.979 µm]; Ni- TiO_2 [d (0.1) = 0.176 µm; d(0.5) = 0.331 µm; d(0.9) = 0.634 µm]; Co- TiO_2 [d (0.1) = 0.176 µm; d(0.5) = 0.330 µm; d(0.9) = 0.630 µm]. Morphological characterisation confirmed the results of dimensional analyses showing that Ni-TiO_2 and Co-TiO_2 exhibits smaller dimensions compared with Fe-TiO_2. Moreover, SEM images (Figure 1) showed that particles present non-regular shapes with the dimensions in the domain of hundreds of nanometres. EDX analyses confirmed the dopants presence within catalysts structure (Table 1).



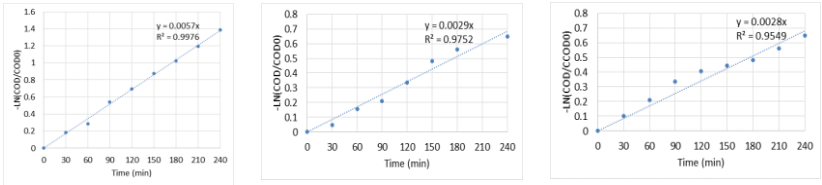
1wt% Fe-TiO_2 1wt% Ni-TiO_2 1wt% Co-TiO_2

Figure 1. *SEM images of metal doped titanium dioxide catalysts*

Table 1. *EDX results*

1wt% Fe-TiO_2		1wt% Ni-TiO_2		1wt% Co-TiO_2	
Element	Atomic %	Element	Atomic %	Element	Atomic %
O	66.43	O	66.97	O	70.53
Fe	0.22	Ni	0.21	Co	0.90
Ti	33.35	Ti	32.82	Ti	28.57

Photocatalytic activity of all catalysts were tested using a MB (as model organic compound) solution. MB initial concentration and after 3 hours of exposure to solar simulated radiation and a catalyst dose of 100 mg/L were measured based on the absorbance at 662 nm (corresponding to maximum MB absorbance). Best results were obtained for 2wt% Metal – TiO_2 catalysts with a MB degradation efficiency of 6.00% for 2%wt Co-TiO_2, 6.91% for 2wt% Ni-TiO_2 and 13.82% for 2%wt Fe-TiO_2. The 2wt% Metal-TiO_2 catalysts were further used for treatment of real wastewater samples varying the initial catalyst concentration. The best degradation efficiencies for organic compounds (expressed as chemical oxygen demand - COD) after 120 minutes of irradiation were obtained for the following catalysts doses: 200 mg/L for 2wt% Ni-TiO_2 (28.57%), 100 mg/L for 2wt% Co-TiO_2 (33.33%) and 100 mg/L for 2wt% Fe-TiO_2 (50.00%). Further increase of irradiation time to 240 minutes for optimum catalysts doses led to a degradation of organic compounds (expressed as COD) of 47.69% for both 2wt% Ni-TiO_2 and 2wt% Co-TiO_2 and 75.00% for 2wt% Fe-TiO_2. This behaviour is sustained also by the linearized pseudo-first order kinetic profiles for the optimum catalysts type and doses (Figure 2).



100 mg/L; 2wt% Fe-TiO_2 200 mg/L, 2wt% Ni-TiO_2 100 mg/L, 2wt% Co-TiO_2

Figure 2. Pseudo-first order kinetic for optimum catalysts, irradiation time 240 min

Acknowledgement. This work was carried out through the "Nucleu" Program within the National Research Development and Innovation Plan 2022-2027 with the support of Romanian Ministry of Research, Innovation and Digitalization, contract no. 3N/2022, Project code PN 23 22 03 01.