5th INTERNATIONAL CONFERENCE ON SMALL AND DECENTRALIZED WATER AND WASTEWATER TREATMENT PLANTS

SWAT

THESSALONIKI, AUGUST 26-29, 2018

Under the aegis of the Ministry of Environment and Energy

CONFERENCE PROGRAM

POSTER PRESENTATIONS

MONDAY, AUGUST 27, 2018

Morning session (11:00 – 14:00)

A01	DRY ANAEROBIC DIGESTION OF SEWAGE SLUDGE IN SMALL AND MEDIUM WASTEWATER TREATMENT PLANTS *L. Pastor, J.E. Sánchez-Ramírez, S. Doñate, E. Aymerich, M. Esteban-Gutiérrez, J. Garcia-Aguirre, R. Romaguera, C. Lardin and E. Mino*	A12	PHOTOCATALYTIC REMOVAL OF PESTICIDES IN WATER BY TIO_2/GRAPHENE OXIDE COMPOSITES *C. Berberidou, G. Z. Kyzas, and I. Poulios*
A02	SMALL AND DECENTRALIZED WASTEWATER TREATMENT PLANTS IN SMALL MUNICIPALITIES OF EAST CRETE *M. P. Kavvalakis and E. G. Dialynas*	A13	"AQUASENSE": ADAPTIVE WATER CONSUMPTION MANAGEMENT SERVICE *D. Chondrogianni, S.Karatzas and P.G.Saranti*
A03	STUDY ON THE TREATMENT OF ALCOHOL DISTILLERY WASTEWATER WITH ENERGY MICROALGAE *Zongxin Ran, Jiang Yu , Ye Du, Wei Wei, Weidong Peng, Yulong Hea and Yunxiao Peng*	A14	REMEDIATION STUDY OF HERBICIDE terbuthylazine IN CONSTRUCTED WETLAND MICROCOSM PLANTED BY Typha latifolia L. *N. Papadopoulos and G. Zalidis*
A04	INTELLIGENT SUSTAINABLE URBAN DRAINAGE SYSTEMS (I-SUDS): A FRAMEWORK FOR FLOOD MITIGATION AND RAINWATER REUSE *S. Karatzas, D. Chondrogiani and P. Saranti*	A15	EFFECTIVENESS OF PLANT GROWTH-PROMOTING RHIZOBACTERIA INOCULATION OF CUPRESSUS SEMPERVIRENS IRRIGATED BY TREATED WASTE WATER *M. Girgis and M. El-Sayed*
A05	OPTIMIZATION OF SILICA EXTRACTION FROM DIATOMACEOUS EARTH (DE) USING RESPONSE SURFACE METHODOLOGY (RSM) *O Izevbekhai, W Gitari and N Tavengwa*	A16	QUALITATIVE ASSESSMENT OF WATER PARAMETERS IN THE AREA OF THESSALONIKI *I. Giannakis, C. Emmanouil and A. Kungolos*
A06	NOBLE METAL MODIFIED TIO2 NANOPARTICLES FOR EFFICIENT PHOTOCATALYTIC PURIFICATION OF DRINKING WATER *C. Berberidou and I. Poulios*	A17	ANALYSIS OF SOME METALS IN THE SOLID-LIQUID PHASES FROM SOUTHEASTERN MEDITERRANEAN BASIN, EGYPT *Maha Ahmed Mohamed Abdallah*
A07	ELIMINATION OF EMERGING POLLUTANTS WITH MEMBRANE PROCESSES: A REVIEW *J. Jaime Sadhwani Alonso, B. Del Río-Gamero and C. Méndez-Montes*	A18	IMPROVING PERFORMANCES OF NANO-CARBON MEMBRANES WITH ELECTROCHEMICAL ASSISTANCE FOR WATER TREATMENT *Xie Quan, Haiguang Zhang, Xinfei Fan*
A08	ENVIRONMENTAL SOLUTIONS AND DEODORIZATION APPLICATIONS WITH DIATOMACEOUS EARTH *A.S. Dounavis, M. Nakou, A. Peleka, A. Maragkoulidis and X. Papanikos*	A19	DIRECT RENEWABLE ELECTRICITY GENERATION FROM MUNICIPAL WASTEWATER SLUDGE SIMULTANEOUS WITH ITS DIGESTION BY A NOVEL TWO-CHAMBERED AEROBIC DIGESTER FOR SMALL COMMUNITIES *H. Rasouli Sadabad, G. Badalians Gholikandi, M. Amouamouha*
A09	A COMPARATIVE STUDY OF THE CHARACTERISTICS OF RAW LEACHATES FROM TWO LANDFILL SITES (AN OPEN AND A CLOSED) IN THE THESSALONIKI PREFECTURE *A. I. Koumalas, A.S. Dounavis, E.M. P. Barampouti and S. Th. Mai*	A20	SYNTHESIS AND CHARACTERIZATION OF MEMBRANE BASED ON CHITOSAN AND THEIR APPLICATION IN THE ENVIRONMENT: DISCOLORATION OF POLLUTED INDUSTRIAL WATERS *H. Laribi-Habchi , L. Adour , W. Arbia, A. Hamdoune and W. Ghomaid*
A10	INDUSTRIAL SYMBIOSIS: FUR INDUSTRY WASTE UTILIZATION AS SECONDARY FUEL FOR SEWAGE SLUDGE DRYING (KOZANI WASTEWATER TREATMENT PLANT) *A. T. Zamanis, P. Barouchas and A. Zoumboulis*	A21	ECO-SUSTAINABLE TEXTILE TREATMENTS TO MITIGATE THE RELEASE OF MICROPLASTICS IN THE WASTEWATER OF LAUNDRY PROCESSES *F. De Falco, V. Guarino, G. Gentile, R. Avolio, M. E. Errico, V. Ambrogi, E. Di Pace, M. Avella and M. Cocca*
A11	CLOUD POINT EXTRACTION FOR ORGANICS ACIDS RECOVERY FROM TABLE OLIVE WASTEWATERS *J. Raiti, A. El-Abbassi, H. Kiai, A. Hafidi*	A22	SEWAGE CHALLENGE IN THE AREA OF ZGHARTA – NORTH OF LEBANON *S. AbiDib Antoun*

PHOTOCATALYTIC REMOVAL OF PESTICIDES IN WATER BY TiO_2/GRAPHENEOXIDE COMPOSITES

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ABSTRACT

There is a huge body of evidence supporting the hypothesis of pesticides being one of the main environmental stressors and their direct correlation with diverse impacts on human health. Several studies have established the epidemiological association between pesticide exposure and elevated rate of chronic diseases such as different types of cancers, diabetes, neurodegenerative disorders like Parkinson and, Alzheimer, birth defects, and reproductive diseases. United Nations estimates that approximately 99% of pesticides used in agriculture contaminates soil, air and especially water, with unpredictable consequences. Indeed, alternative, environmentally friendly, yet, efficient methods of water purification, have become an urgent need. In this context, Advanced Oxidation Processes (AOPs) have been particularly effective in the decomposition of a wide range of pollutants present in various environmental media. Among them, heterogeneous photocatalytic oxidation in the presence of semiconducting oxides, mainly TiO_2, has served as one of the most promising alternatives for drinking water processing. Due to its associated advantages, various modifications of the TiO_2 photocatalytic process have been suggested, including coupling of TiO_2 with graphene-based materials.

In the present study, preparation of graphene oxide and its' conjugation with TiO_2 has been conducted, aiming to the enhancement of the photocatalytic efficiency of TiO_2 and/or the exploitation of visible light spectrum. Various parameters have been investigated, including the amount of graphene oxide and the type of TiO_2 employed in the synthesis of the TiO_2/GO composites. Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid), a systemic herbicide from the chemical class of pyridine compounds, often detected in drinking water, served as a model pollutant for the evaluation of the photocatalytic efficiency of the prepared mixed oxides.

Keywords: *clopyralid, graphene oxide, photocatalytic, TiO_2.*

Acknowledgements

This research is implemented through the State Scholarships Foundation (IKY) program and co-financed by the European Union (European Social Fund-ESF) and Greek national funds through the action “Reinforcement of Postdoctoral Researchers”, in the framework of the Operational Program ”Human Resources Development Program, Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF) 2014-2020.

PHOTOCATALYTIC REMOVAL OF PESTICIDES IN WATER BY TiO_2/GRAPHENE OXIDE COMPOSITES

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Introduction and Objectives

There is a huge body of evidence demonstrating that pesticides are, indeed, on top of the list of the main environmental stressors with diverse impacts on human health. According to United Nations, approximately 99% of pesticides used in agriculture contaminates soil, air and especially water, with unpredictable consequences.

In this context, Advanced Oxidation Processes (AOPs) and TiO_2 mediated photocatalytic oxidation, in particular, have been remarkably effective in the decomposition of a wide range of pollutants present in various environmental media. Due to its associated advantages, various modifications of the TiO_2 photocatalytic process have been suggested, including coupling of TiO_2 with graphene-based materials.

In the present study, preparation of graphene oxide (GO) and its' conjugation with TiO_2 has been conducted, aiming to the enhancement of the photocatalytic efficiency of TiO_2. Clopyralid, a systemic herbicide from the chemical class of pyridine compounds, often detected in drinking water, served as a model pollutant for the evaluation of the photocatalytic efficiency of the prepared mixed oxides.

Materials and Methods

GO was synthesized with the modified Hummers method (Hummers and Offeman, 1958). Commercial graphite powder was stirred in the presence of concentrated H_2SO_4 at 0°C. $KMnO_4$ was slowly added to the suspension, at temperature below 20°C. The reaction mixture was cooled to 2°C and was then stirred at room temperature for 30 min. Distilled water was slowly added to the reaction vessel, keeping the solution temperature below 98°C. The suspension was stirred for additional 15 min, was further diluted with distilled water and 30% w/w H_2O_2 was added. The mixture was left overnight. Precipitated GO was separated by decantation. The remaining suspension was transferred to dialysis tubes. Dialysis was carried out until no precipitate of $BaSO_4$ was detected by addition of aqueous solution of $BaCl_2$. Then, GO was separated by centrifugation. The gel-like material was freeze dried and a fine dark brown powder of GO was obtained.

GO/TiO_2 mixed oxides were prepared as shown in Fig. 1. The desired amount of GO was added to isopropanol and was sonicated for 2h. TiO_2 P25 (Evonik) was added to the exfoliated GO and was stirred for 2h at 50-70 °C. The suspension was then sonicated for 1h and was then , dried at 75 °C o/n. The mixed oxide was then left to cool at RT, grinned and washed 5 times with doubly distilled water. The final product, a grey powder, was obtained after drying at 75 °C o/n.

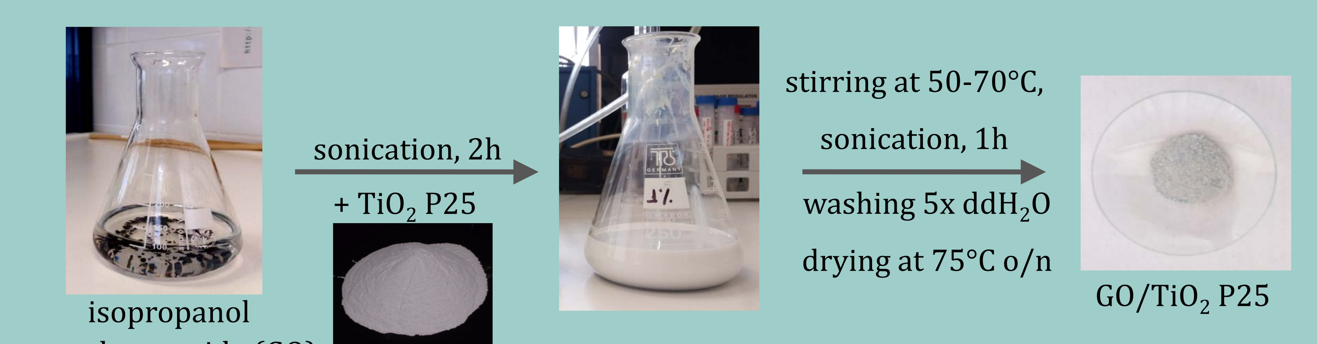

Figure 1: *Route of preparation of graphene oxide/TiO_2 P25 composites.*

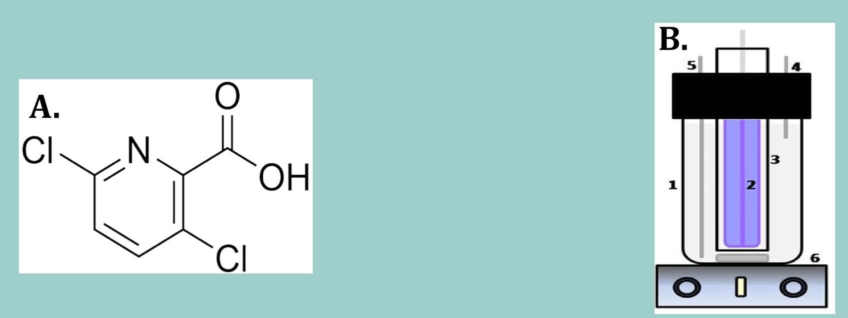

Figure 2 A*: Clopyralid (3,6-dichloro-2-pyridine-carboxylic acid, CAS No. 1702-17-6, Mr: 192 g mol^{-1}).* ***B****: Sketch of the photocatalytic reactor employed in the photocatalytic oxidation of clopyralid: 1. reaction vessel, 2. irradiation source, 3. borosilicate glass, 4. air inlet, 5. air outlet, 6. stirrer.*

Photocatalytic oxidation of clopyralid was performed in a closed Pyrex cell of 300 mL capacity, fitted with a central Osram Dulux 9W/78 lamp, under magnetic stirring (Fig. 2B). The cell had inlet and outlet ports for bubbling CO_2 free air. Photocatalysis was conducted at a working volume of 250 mL, at 3.8±0.1 initial pH and constant temperature (25±0.1°C).

Results

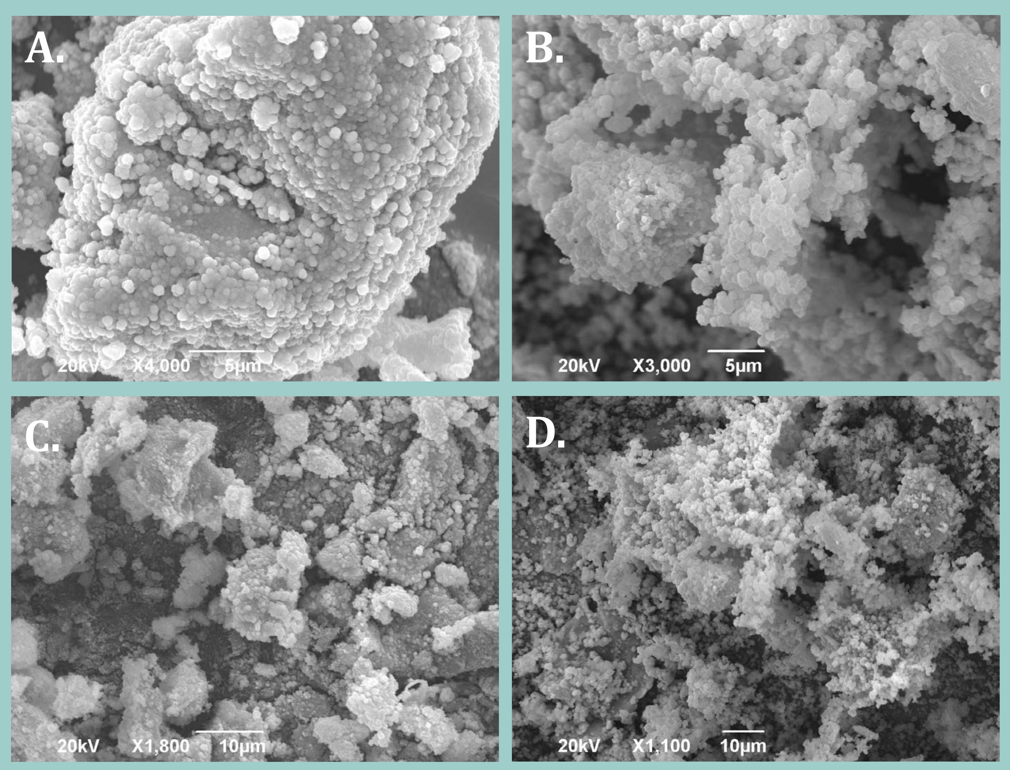

Figure 2. *SEM of 1 and 5% GO/TiO_2 P25 composites. A-B: 5 μm, C-D: 10 μm magnification.*

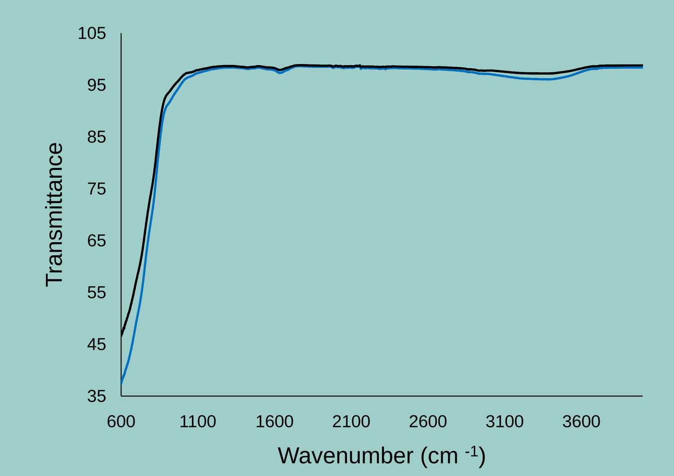

Figure 3. *FTIR specrta of graphene oxide and TiO_2 P25 composites. Blue line: 1% GO/TiO_2 P25, black line: 5% GO/TiO_2 P25.*

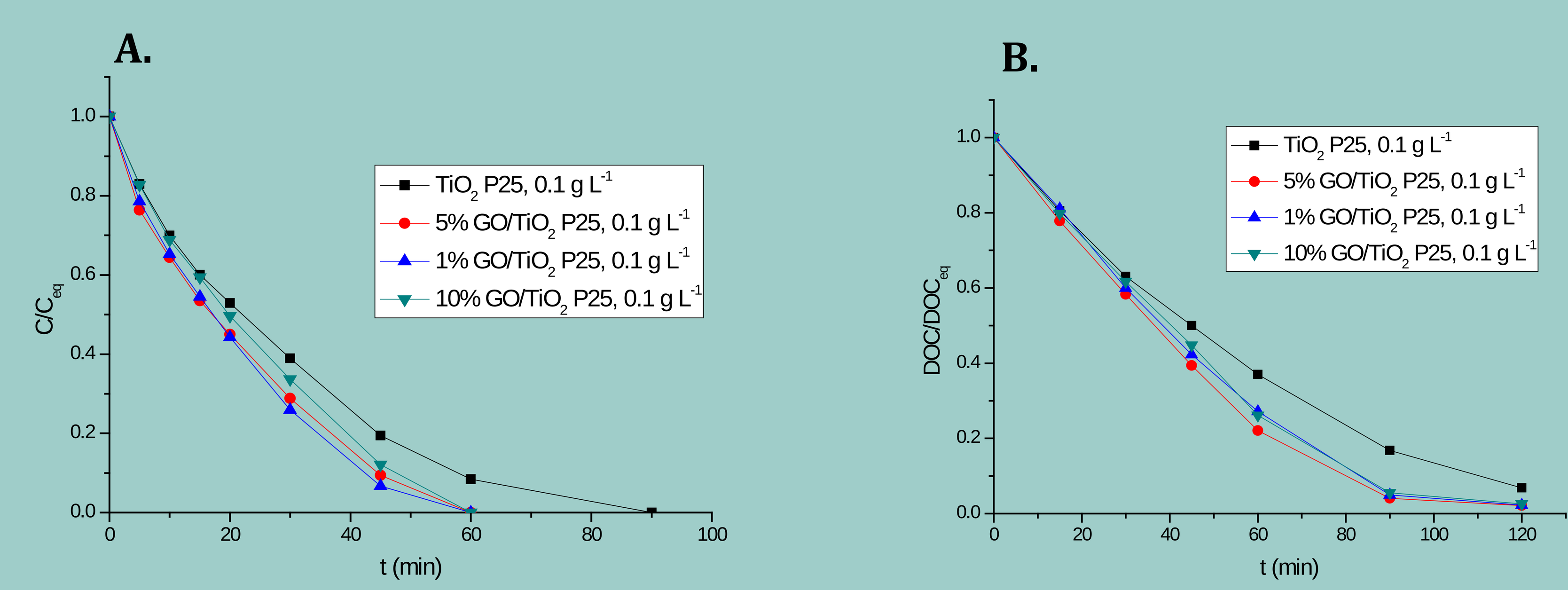

Figure 4. *Photocatalytic oxidation (A) and mineralization (B) of 20 mg L^{-1} clopyralid in the presence of UV-A irradiation and 0.1 g L^{-1} GO/TiO_2 P25 composites.*

Discussion and Conclusions

- GO was successfully prepared from graphite according to the modified Hummers method. It was then, combined with commercial TiO_2 P25 resulting to three different composites with 1, 5 or 10% GO content (nominal).
- SEM images revealed the successful preparation and complexation of GO with TiO_2, demonstrating small sphere-like pTiO_2 particles smoothly deposited onto the GO sheets (Fig. 2).
- FTIR spectra reveal interesting findings about the prepared GO/TiO_2 P25 composites. First, a shift from 1600 cm^{-1} to ~1640 cm^{-1}, characteristic of the conjugation of the carbonyl groups of GO with functional groups on the surface of TiO_2. Second, the slight difference in the transmittance between 1% and 5% sample at 3300 cm^{-1} can be attributed to the different concentration of GO in the prepared mixed catalysts, which corresponds to different ratios of functional groups (-OH) in each sample (Fig. 3).
- In all cases, the initial degradation rates during photocatalytic degradation of the herbicide clopyralid, in the presence of UV-A irradiation, were enhanced in comparison to the bare TiO_2 P25 (Fig. 4A). Similarly, mineralization of the herbicide was faster under UV-A irradiation, when either of the three GO/TiO_2 P25 composites was employed (Fig. 4B).

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