"Gheorghe Asachi" Technical University of Iasi, Romania

COMPARISON OF PHOTOCATALYTIC TREATMENT EFFECTIVENESS ON SEWAGE AND INDUSTRIAL WASTEWATERS

Gabriela Pavelescu[1], Ceyda Uyguner-Demirel[2], Miray Bekbolet[2], Luminita Ghervase[1*], Cristian Ioja[3]

[1]National Institute of R&D for Optoelectronics, Magurele, 077125, Romania
[2]Bogazici University, Institute of Environmental Sciences, 34342 Bebek, Istanbul, Turkey
[3]University of Bucharest, CCMESI, Bucharest, 010041, Romania

Abstract

Water samples from two types of sources: *partially treated sewage* generated by a medium-sized city, with a high quantity of total coliforms and *partially treated industrial wastewater,* which contained mostly petroleum products from refineries, were treated using the same concentration of TiO_2 catalyst, for different exposure periods. UV-Vis and fluorescence spectroscopic evaluation of the composition changes of wastewaters under non selective oxidation conditions (achieved by photocatalysis) revealed that the higher removal rate was obtained for the industrial water sample compared to the sewage water sample, with respect to oxidation time. Considering the diverse characteristics and the solution matrix effects of the wastewaters, UV-Vis and fluorescence spectra revealed different patterns by increasing the quantity of TiO_2 catalyst from 0.25 mg mL^{-1} to 1 mg mL^{-1}, denoting that the amount of total coliforms in a sample greatly impacts the degree of photocatalytic oxidation.

1. Introduction

Innovative technologies in water treatment, collectively named "Advanced Oxidation Processes" (AOP), have been increasingly studied, during the past decade, due to the advantages that they present, compared to conventional treatment techniques, like adsorption, coagulation, sedimentation, filtration, chlorination etc. (Podaru et al., 2008; Zhou et al., 2002). Among the AOP methods, the most widely used is the heterogeneous photocatalytic technique with TiO_2 semiconductor catalyst, due to its capacity to degrade a wide range of organic compounds, low cost and non-toxicity. Moreover it is most active in the wavelength domain of 300 - 390 nm and remains stable after repeated catalytic cycles (Malato et al., 2009).

Water systems naturally contain dissolved organic matter (DOM), the ubiquitous fraction in soil and aquatic ecosystem, which represents a heterogeneous mixture of humic substances, fatty acids, amino acids, nucleic acids, carbohydrates, hydrocarbons and other compounds. However, DOM can also derive from anthropogenic activities through the release of human waste, farm waste, industrial waste etc. The dynamics and characteristics of DOM strongly influence a number of key ecosystem processes, including the attenuation of solar radiation, control of nutrient availability, alteration of contaminant toxicity, material and energy cycling.

During the recent years, a novel technique, fluorescence spectroscopy, has been effectively used to determine and characterize DOM and to evaluate its link to water quality. Within the complex mixture of natural DOM, the following components are mostly studied by fluorescence: proteins and humic substances (Carstea et al., 2010; Hudson et al., 2007). The protein fluorescence is given by amino acids and

---

∗ Author to whom all correspondence should be addressed: e-mail: ghervase@inoe.ro, Phone: +40214575757; Fax : +40214575522

is related to the activity of bacterial communities. The humic substances fluorescence indicates the break-down of plant material by biological and chemical processes. Apart from humic substances and proteins, other aromatic compounds can also contaminate the water and can be detected with fluorescence spectroscopy (Ghervase et al., 2010; Patra and Mishra, 2002).

When high quantity of one component is produced or released into the water, the balance of the ecosystem is disrupted with potentially long-term effects. Special attention is given, by the scientific community, to the petroleum products as they can lead to catastrophic deterioration of the ecosystem when accidental releases are produced. Due to their toxic nature, persistence in the environment and presence in any ecosystem, current research must concentrate on identifying the best techniques for early detection and removal of these pollutants.

This study focuses on UV-Vis and fluorescence spectroscopic evaluation of the structural changes of wastewaters originating from different sources under non selective oxidation conditions (achieved by photocatalytic oxidation process).

2. Experimental

2.1. Water sampling

Water samples from two types of sources have been collected: *partially treated sewage* (hereafter named sewage) generated by a medium-sized city and *partially treated industrial wastewater* (hereafter named industrial)*,* which contains mostly petroleum products from refineries. Water samples were taken to the laboratory for photocatalytic oxidation and measurements were carried out within 24 h from collection.

2.2. Photocatalytic oxidation process

Both types of samples have been treated using the same concentration of TiO_2 catalyst (Degussa P-25) at several irradiation time intervals, the maximum irradiation time being 3 h. Photocatalytic degradation experiments were performed according to Bekbolet et al. (2002).

The bench-scale system consisted of a cylindrical Pyrex reaction vessel with a working volume of 50 mL as the photoreactor. TiO_2 loading was 0.25 mg mL^{-1} for exposure periods of 30, 60, 90 and 180 min and 30 min for a dose of 1 mg mL^{-1}. A 125 W BLF lamp (maximum intensity: 365 nm) with a photon generation rate of 2.85x 10^{16} quanta s^{-1} was used as the light source.

The degradation experiments were carried out at the natural pH of the solutions. Prior to analysis, TiO_2 was removed from the solution by filtration (0.45 µm membrane filter).

2.3. Sample characterization

Samples have been measured before and after remediation by spectrophotometric methods, fluorescence (excitation–emission matrix and emission spectra) and UV-Vis absorbance and by standard physico-chemical methods.

Raw water samples were analyzed in terms of parameters such as dissolved organic carbon (DOC), chemical oxygen demand (COD), pH, conductivity, total dissolved solids (TDS), total and fecal coliforms according to Standard Methods (APHA, 1998). Specific UV absorbance at 254 nm (SUVA, m^{-1}mg^{-1}L) defined as DOC normalized UV_{254} was evaluated.

Polyaromatic hydrocarbons were detected using standard method of GC-MS Agilent 5975B instrument. UV-Vis spectra and absorbance measurements of the samples at 254 nm (UV_{254}) and 280 nm (UV_{280}) were acquired using Perkin Elmer Lambda 35. Dissolved organic matter content of the samples was determined as dissolved organic carbon (DOC) using the Total Organic Carbon Analyzer (Shimadzu TOC-VWP). Polyaromatic hydrocarbons were detected using standard method of GC-MS Agilent 5975B instrument.

Fluorescence spectra were recorded, in the form of excitation–emission matrices (EEMs), with spectrofluorimeter FLS-920 Edinburgh Instruments using a Xe lamp of 450 W. To acquire the EEMs, the excitation wavelengths were incremented from 230 to 400 nm with 10 nm intervals; for each excitation wavelength the emission was recorded from 250 to 500 nm with 1 nm intervals. The recorded data were treated using ORIGIN 7.5 software.

3. Results and discussion

3.1. Characterization of raw samples

Characterization of wastewaters according to the procedures outlined above evidences high contaminated samples. Higher values of UV_{254}, COD, conductivity and DOC were obtained for industrial sample in comparison with sewage one, as can be seen in Table 1. A high density of fecal coliforms was detected in both samples (sewage and industrial), with higher values for sewage sample, as expected due to domestic discharges in river. The presence of coliforms in the industrial sample, but at a much lower value than of the sewage sample, indicates a probable accidental leakage of human and/or animal wastes in this sample. The physical parameters were as expected for these types of samples, with high values of TDS and conductivity. The organic matter parameters showed generally higher values for the industrial sample than for the sewage. Although UV-Vis spectroscopy does not provide useful information about DOC functionality, it offers structural information about the organic matter content (Weishaar et al., 2003).

Both samples had high values UV_{254}, denoting highly polluted waters. SUVA parameter, calculated using the UV_{254} and DOC measurements, was higher for the industrial sample, revealing a higher content of aromatic components, given by the aromatic hydrocarbons found in the sample.

The high COD value of the industrial sample could be related to the fact that it is highly polluted, indicating a larger amount of oxygen that is needed to chemically oxidize the water contaminants.

Table 1. Characteristics of water samples

Parameters	Units	Sewage water sample	Industrial water sample
Organic matter parameters			
UV_{254}		0.1782	0.6923
UV_{280}		0.1399	0.4546
Dissolved organic carbon, DOC	mg Org C L^{-1}	11.11	20.57
Specific UV absorbance, SUVA	m^{-1} mg^{-1} Org C L	1.60	3.36
Chemical oxygen demand, COD	Mg O_2 L^{-1}	37	140
Physical parameters			
pH	-	7.30	6.93
Total dissolved solids, TDS	mg L^{-1}	479	559
Conductivity	µS/cm at 25 °C	1187	1366
Microbiological parameters			
Total coliforms	CFU/100 mL	$1x10^7$	$2x10^5$
Fecal coliforms	CFU/100 mL	$3.6x10^6$	$1x10^2$

Fluorescence EEM records have revealed the spectral fingerprints of sewage and industrial wastewater with specific peak maxima (Fig. 1). Sewage water sample presents the fluorescence signal of the microbial component, peaks at λ_{ex} / λ_{em} - 235 nm / 330-360 nm and λ_{ex} / λ_{em} - 275 nm / 315-323 nm. The industrial sample fluorescence matrix shows a lower intensity peak from the microbial
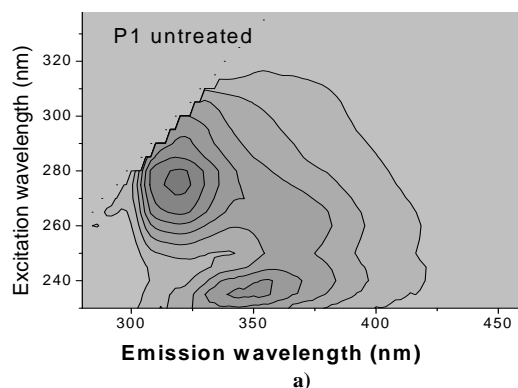
component at λ_{ex} / λ_{em} - 275 nm / 317 - 333 nm and two very intense fluorescence peaks at λ_{ex} / λ_{em} - 235 nm / 320 - 360 nm and 260 nm / 355-365 nm, which correspond to products that contain aromatic hydrocarbons. The emission wavelength is proportional to the number of aromatic rings of the hydrocarbon. According to Pharr et al. (1992) and Abbas et al. (2008) 2 aromatic ring components, such as naphthalene, show a fluorescence peak between 310 and 330 nm, and 3 aromatic ring components, like phenanthrene, between 345 nm and 355 nm. This leads to the conclusion that the fluorescence of the two peaks, λ_{ex} / λ_{em} - 235 nm / 320 - 360 nm and 260 nm / 355-365 nm, is given by 2 and 3 aromatic rings hydrocarbons, naphthalene and phenanthrene, respectively. The emission wavelength can vary slightly, among different studies, because it depends on the concentration of petroleum products, as demonstrated by Divya and Mishra (2008).

Several mono- and polyaromatic hydrocarbons were detected in the industrial sample through the GC-MS analysis: xylene 0.008 mgL-1, benzene C3 0.053 mg L-1, benzene C4 0.143 mg L-1, dimethyl naphthalene 0.03 mg L-1, phenanthrene trimethyl 0.05 mg L-1, biphenyl methyl 0.03 mgL-1. However, monoaromatic components, such as xylene and benzene, which have an emission wavelength closer to 300 nm, easily evaporate and have a lower quantum efficiency compared to polyaromatic hydrocarbons, which makes them very difficult to detect by fluorescence spectroscopy.

3.2. Effect of treatment process on wastewater samples

Both wastewater samples: 'sewage' and 'industrial' were oxidized by photocatalytic oxidation using 0.25 mg mL^{-1} TiO_2 Degussa P-25. Oxidation of wastewater samples is completely different than that of humic acid which is also regarded as a recalcitrant organic macromolecule, characterized by approximately 50% adsorption onto TiO_2 surface (Uyguner et al., 2007). Resistance to photocatalytic oxidation was evidenced by low removal percentages for the two wastewater samples as can be seen in Figs. 2a and 2b, this is especially true for the sewage water sample.
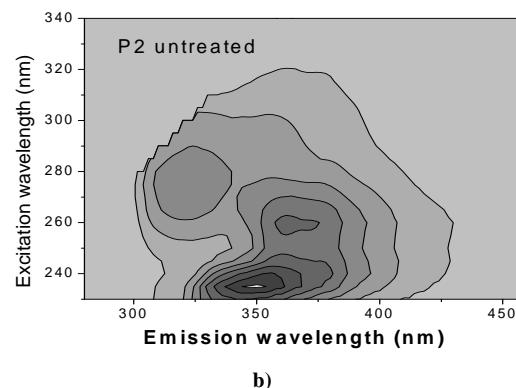
Fig. 1. Fluorescence spectra of a) sewage and b) industrial wastewater samples
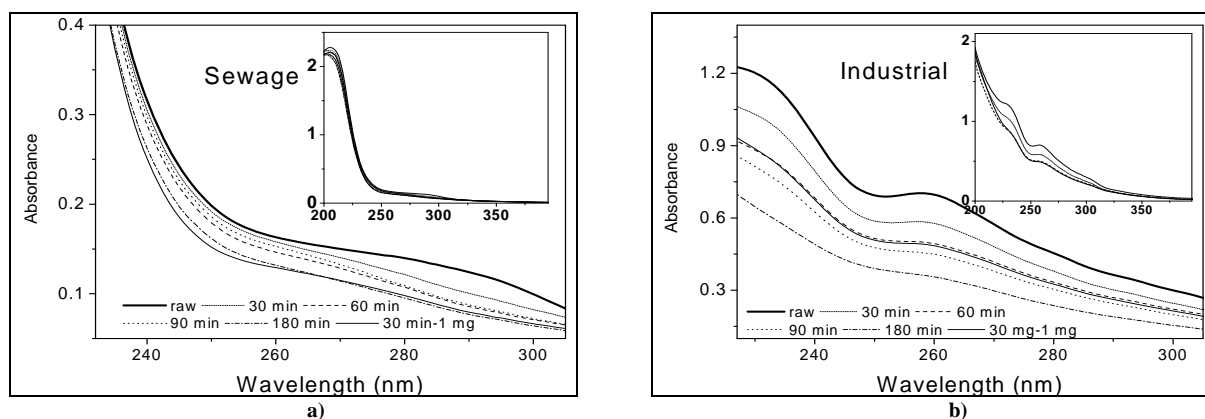
Fig. 2. UV-Vis spectra of oxidized sewage (a) and industrial wastewater (b)

As presented in Figs. 2, UV-Vis spectroscopic results have indicated that higher photocatalysis treatment efficiency was achieved for the industrial water sample compared to the sewage one. Sewage water sample displays smooth UV-Vis spectra with no significant spectroscopic changes with respect to photocatalytic oxidation time. On the other hand, for the industrial wastewater, UV-Vis spectra displaying two minor peaks around 220 nm and 250 nm decrease in absorbance with remarkable differences with respect to irradiation time.

Considering the diverse characteristics and the solution matrix effects of the wastewaters, absorption spectra reveal different patterns after photocatalytic oxidation. The reduced treatment efficiency on the sewage sample could be caused by the high concentration of microbial fraction which can have an inhibitory effect on the photocatalytic breakdown process. According to Bekbolet (1997) and Rizzo (2009), the density of initial total coliforms might also influence the effectiveness of photocatalytic treatment. The researchers found that treatment effectiveness decreased with the increasing number of total coliforms and proposed the solution to increase the quantity of TiO_2 to strengthen the treatment process.

UV absorbing moieties, UV_{254} and UV_{280}, presented in Fig.3, were selected in order to reveal the removal percentage of absorbing compounds, such as aminoacids and polycyclic aromatic hydrocarbons. Higher removal percentages (~ 16-48 %) can be seen for the industrial sample, in comparison with the sewage one, due to its TPH content. For the sewage sample, the 0.25 mg L^{-1} TiO_2 concentration induced lower removal percentages: between 3 and 18 % for UV_{254} and between 13 and 31 % for UV_{280}. Due to high initial bacterial load of sewage wastewater (Table 1), photocatalytic breakdown of bacteria has an inhibitory effect. Competitive accumulation of microbial breakdown for sewage wastewater and the presence of organics in industrial wastewater lead to high percent removals after 180 min of photocatalytic oxidation.

In this study, the parameter UV_{280} has shown that, under the same experimental conditions of exposure time, at a quantity of TiO_2 of 1 mg mL^{-1},

the sewage wastewater sample is treated more effectively compared to the treatment with 0.25 mg mL^{-1} of TiO_2. Under an exposure time of 30 min, increasing TiO_2 loading from 0.25 mg/mL to 1.0 mg mL^{-1}, resulted in an increase of UV_{280} removal from 13% to 31%. For the industrial wastewater sample, increasing the TiO_2 loading by four fold led to a removal percent of UV_{280} from 17% to 28%, as can be seen in Fig 4. Same trend was observed for the UV_{254} parameter.

Fluorescence analysis shows a decrease after 180 min of more than 90% for all fluorescence components of industrial sample and about 30% for sewage sample (example at 260 nm excitation wavelength in Figs. 5a and 5b). For the industrial wastewater sample, fluorescence spectroscopy indicated that, at 0.25 mg mL^{-1}, the treatment was more efficient, as was observed at the UV_{280} parameter. This could be explained by the fact that the industrial sample contained lower total coliforms density compared to the sewage sample, allowing more active sites on the photocatalyst for other contaminants. The apparent low decrease of the fluorescence intensity of the sewage sample could prove that the amount of total coliforms in a sample greatly impacts the degree of photocatalytic oxidation. Rizzo (2009) stated that photocatalysis provokes irreversible injuries to bacteria, thus it could be hypothesized that peptide or amino acid residues might have formed in the water samples after treatment. These residues could be fluorescent if they contained the amino acids, tryptophan and tyrosine, hiding the actual degree of pollutant removal. It could also be assumed that TiO_2 might have greater affinity in binding hydrocarbons than microbial matter.

The ratio between fluorescence values after and before treatment, showed very high removal efficiency for the peaks belonging to hydrocarbons (Table 2). This is in agreement with the findings of Saien and Nejati (2007) who obtained high removal rates for monoaromatic hydrocarbons, such as benzene, toluene and ethyl-benzene. In the present study, it was observed that polyaromatic hydrocarbons are effectively removed after photocatalytic treatment. Furthermore, the 3 aromatic

ring hydrocarbons (emission wavelength 358 nm) presented slightly lower after/before ratios as compared to 2 aromatic ring hydrocarbons (emission wavelength 320 nm). It could be presumed that the treatment increases its efficiency with the increasing number of aromatic rings.

The effect of oxidation process on sewage and industrial wastewaters is better evidenced in percentage decrease of fluorescence emission corresponding to microbial and hydrocarbon components. The percentage of oxidation efficiency, indicating the decrease of fluorescence intensity corresponding to emission at 358 nm is presented in

Figs. 6a and 6b for the sewage and industrial samples. As can be seen in Fig. 6a the fluorescence emission of the microbial fraction from domestic discharges presents a reduction of up to 40% after 180 min irradiation time.

An important decrease of fluorescence emission for all types of contaminants is shown in Fig. 6b for the industrial wastewater sample. In accordance with the UV-Vis spectra shown in Fig. 2, the oxidation efficiency of industrial wastewater in terms of fluorescence intensity ratios decreases abruptly with irradiation time compared to sewage wastewater.
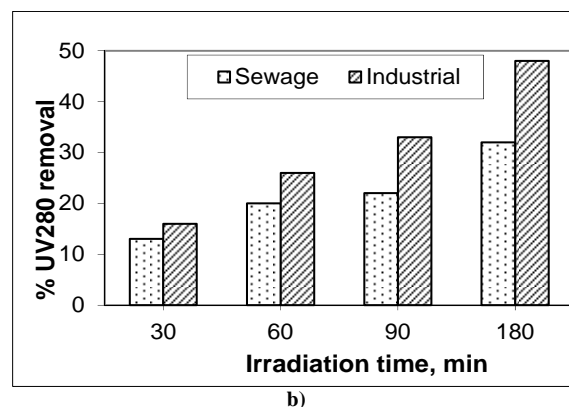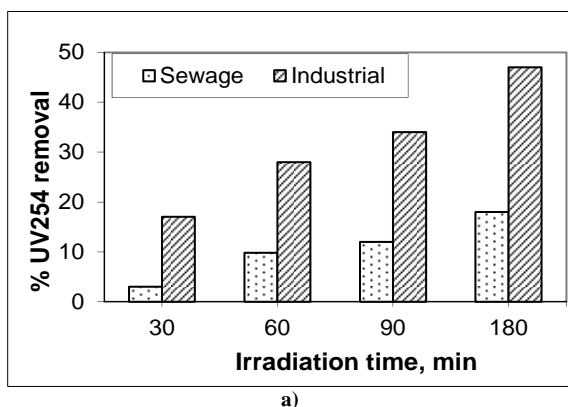

Fig. 3. Percent removal of UV_{254} and UV_{280} for sewage and industrial wastewater samples 0.25 mg mL^{-1} TiO$_2$ and different irradiation time
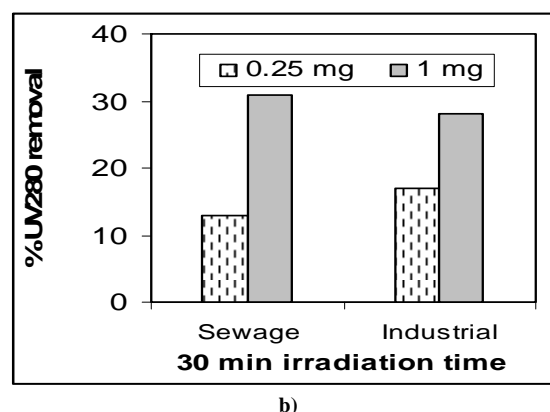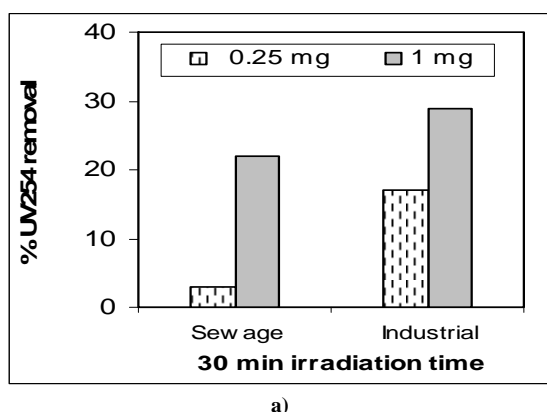

Fig. 4. Percent removal of UV_{254} and UV_{280} for sewage and industrial wastewater samples for 30 min irradiation time, TiO$_2$:0.25 mg mL^{-1} and 1 mg mL^{-1}
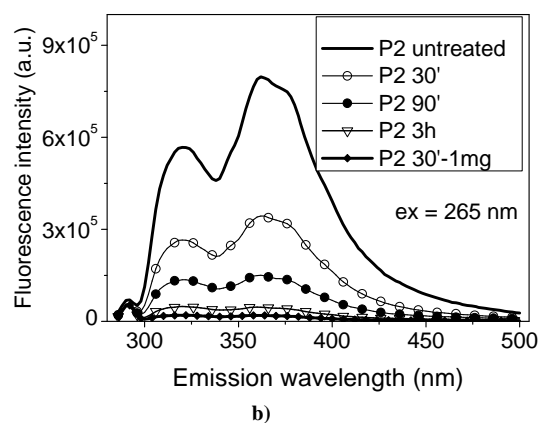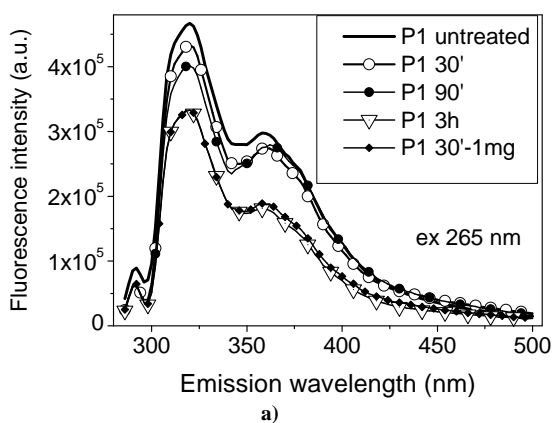

Fig. 5. Fluorescence spectra of oxidized sewage (a) and industrial wastewater (b)

Table 2. Fluorescence intensity changes of sewage and industrial samples before and after photocatalytic oxidation

Excitation (nm)	Emission (nm)	Fluorescence intensity of sewage sample			Fluorescence intensity of industrial sample		
		Before treatment (a.u.)	After treatment (a.u.)	Ratio after /before	Before treatment (a.u.)	After treatment (a.u.)	Ratio after /before
235	350	404800	284900	0.70	1349000	104600	0.08
260	320	466800	332100	0.71	567300	48800	0.09
	358	297700	181200	0.61	764300	45780	0.06
275	320	550100	393200	0.71	643100	54050	0.08
	358	268000	164200	0.61	529300	35750	0.07
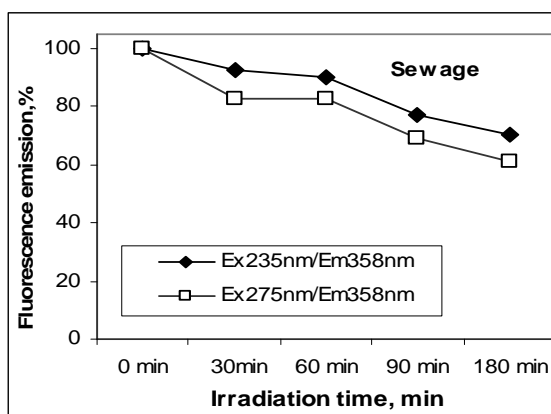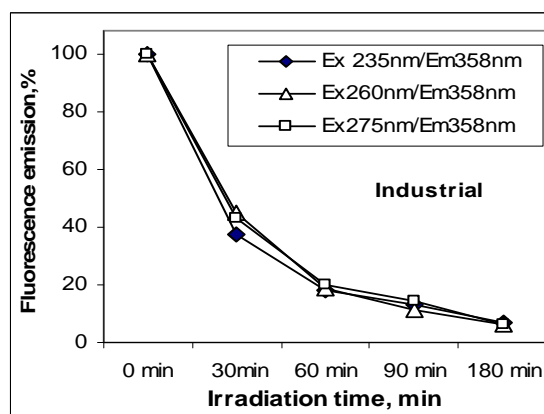
Fig. 6. Influence of the photocatalytic oxidation process upon fluorescence emission intensity
a) Sewage wastewater b) Industrial wastewater

The different slopes and percentage values of oxidation efficiency reveal the diverse result in treatment of the two types of samples. This can be attributed to the complex composition of the polluted waters, including initial total coliforms density or the type of hydrocarbons.

4. Conclusion

Photocatalytic degradation experiments were performed on two types of water samples: *sewage* sample, highly contaminated with microbial components and *industrial* sample, which contains mostly petroleum products. UV-Vis and fluorescence spectroscopy indicated that higher photocatalytic oxidation treatment efficiency was obtained for the industrial water sample compared to the sewage one with respect to oxidation time.

Under the same experimental conditions of exposure time, by increasing the quantity of TiO_2 catalyst from 0.25 mg mL^{-1} to 1 mg mL^{-1}, an increase of UV_{280} removal for the sewage wastewater, slightly higher compared to the industrial sample, was observed. On the contrary, fluorescence spectra indicated higher percent removal for the industrial sample, of about 90%, compared with the sewage one, of only 30%.

The different removal efficiency, for the sewage sample compared to the industrial sample, resulting from UV-Vis and fluorescence spectroscopy, could prove that the amount of total

coliforms in a sample greatly impacts the degree of photocatalytic oxidation. In the case of highly microbial contaminated samples, due to the fact that residues formed after treatment could be fluorescent, complementary analyses of total coliforms are needed to quantify the degree of pollutant removal.

References

Abbas O., Rebufa C., Dupuya, N., Permanyer A., Kister J., (2008), Assessing petroleum oils biodegradation by chemometric analysis of spectroscopic data, *Talanta,* **75**, 857–871.

Bekbolet M., (1997), Photocatalytic bactericidal activity of TiO_2 in aqueous suspensions of E. coli, *Water Science and Technology*, **35**, 95-100.

Bekbolet M., Boyacioglu Z., Ozkaraova B., (1998), The influence of solution matrix on the photocatalytic removal of color from natural waters, *Water Science and Technology*, **38**, 155-162.

Carstea E.M., Baker A., Bieroza M., Reynolds D., (2010), Continuous fluorescence excitation emission matrix of river organic matter, *Water Research*, **44**, 5356-5366.

Divya, O., Mishra, A.K., (2008), Understanding the concept of concentration-dependent red-shift in synchronous fluorescence spectra: Prediction of λ_{SFS}^{max} and optimization of $\Delta\lambda$ for synchronous

fluorescence scan, *Analytica Chimica Acta,* **630**, 47–56.

Ghervase L., Carstea E.M., Pavelescu G., Savastru D., (2010), Laser induced fluorescence efficiency in water quality assessment, *Romanian Reports in Physics*, **62**, 652–659.

Ghervase L., Ioja C., Carstea E.M., Savastru D., (2012), Human daily activities reflected by the ecological state of natural water resources, *Environmental Engineering and Management Journal*, **11**, 567-571.

Hudson N., Baker A., Reynolds D., (2007), Fluorescence analysis of dissolved organic matter in waste and polluted waters-A review, *River Research and Application,* **23**, 631–649.

Malato S., Fernandez-Ibanez P., Maldonado M.I., Blanco J., Gernjak W., (2009), Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, *Catalysis Today,* **147**, 1-59.

Podaru C., Manea F., Vlaicu I., Patroescu V., Danielescu C., Burtica G., (2008), Studies regarding surface water treatment using a microfiltration-ultrafiltration pilot plant, *Environmental Engineering and Management Journal,* **7**, 711-715

Patra D., Mishra, A.K., (2002), Total synchronous fluorescence scan spectra of petroleum products, *Analytical and Bioanalytical Chemistry,* **373**, 304–309.

Pharr D.Y., McKenzie J.K., Hickman A.B., (1992), Fingerprinting Petroleum Contamination Using Synchronous Scanning Fluorescence Spectroscopy, *Ground Water,* **30**, 484–489.

Rizzo L., (2009), Inactivation and injury of total coliform bacteria after primary disinfection of drinking water by TiO2 photocatalysis, *Journal of Hazardous Materials*, **165**, 48–51.

Saien J., Nejati H., (2007), Enhanced photocatalytic degradation of pollutants in petroleum refinery wastewater under mild conditions, *Journal of Hazardous Materials,* **148**, 491–495.

APHA, (1998), APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 20th Edition, American Water Works Association, USA.

Uyguner C.S., Suphandag S.A., Kerc A., Bekbolet M., (2007), Evaluation of adsorption and coagulation characteristics of humic acids preceded by alternative advanced oxidation techniques, *Desalination*, **210**, 183-193.

Uyguner C.S., Bekbolet M., (2009), Application of photocatalysis for the removal of natural organic matter in simulated surface and ground waters, *Journal of Advanced Oxidation Technologies,* **12**, 87-92.

Wei L., Shifu C., Wei Z., Sujuan Z., (2009), Titanium dioxide mediated photocatalytic degradation of methamidophos in aqueous phase, *Journal of Hazardous Materials,* **164**, 154–160.

Weishaar J.L., Aiken G.R., Bergamaschi B.A., Fram M.S., Fujii R., Mopper K., (2003), Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, *Environmental Science and Technology*, **37**, 4702-4708.

Zhou H., Smith D.W., (2002), Advanced technologies in water and wastewater treatment, *Journal of Environmental Engineering and Science*, **1**, 247–264.