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Original Research

Evaluation of UV/TiO$_2$ Photo-Catalytic Process for Removing Humic Compounds from Water

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Abstract

Humic compounds are among the most important natural organic matters (NOM) existing in water resources, and are known as one of the main disinfection by-product (DBP) precursors – particularly trihalomethanes (THMs) and haloacetic acids (HAAs) – which may act as health risk factors. The study objective is to investigate the UV/TiO$_2$ photo-catalytic process in removing humic substances from water. It was conducted in a lab-scale batch photo-catalytic reactor using the experimental method. It may be concluded that the UV/TiO$_2$ process can provide desirable drinking water quality in terms of humic substances, so this process was capable of decreasing 5 mg/L dissolved organic carbon to 0.394 mg/L in optimum conditions. The specific UV$_{254}$ absorbance of 2.79 L/mg.m was attained by photo-catalytic first-order reaction having rate constant of 0.267 min^{-1} after 90 minutes.

Keywords: drinking water, humic substances, photo catalytic oxidation, titanium dioxide

Introduction

Humic substances (HS) are known as a group of heterogeneous organic macromolecules with high molecular weight whose main structures are usually in the form of carbohydrates, proteins, and lignins, and a remarkable percentage of their molecular weight is related to oxygenated agent groups. These agent groups facilitate the reactions between various humic substances, mineral elements, and organic molecules existing in water environments. Humic substances, based on solubility, are divided into three groups: humic acids (HAs), fulvic acids (FAs), and humins. Humic and fulvic acids constitute about 50 percent of dissolved organic carbon (DOC) in surface waters [1-3].

Humic compounds are among the most important natural organic matters (NOM) in water resources, and are known as one of the main disinfection by-product (DBP) precursors – particularly trihalomethanes (THMs) and haloacetic acids (HAAs) – which may act as health risk factors in the form of carcinogens and have unfavorable effects on kidneys, liver, nerves, and sexual organs. Amendments on the safe drinking water act in 1987 in the United States and concerns about potential health effects of DBPs led to the ratification of the first phase of DBP regulations in 1998 by the U.S. Environmental Protection Agency. This regulation, presented in order to create a balance between microbiological and chemical risks, announced the maximum concentration of total THMs 80 ppb and for five HAAs as 60 ppb. In the second phase, the absence of need for initial evaluation in the water distribution system depends on the amount of DBPs in all samples, which should be less than 40 ppb and 30 ppb, respectively. While THM formation potential is more than 100 µg per mg of DOC by organic matters, the British standard for total THMs is 100 µg/L [2, 4, 5].

Since most common water treatment methods cannot provide the minimum remaining DOC in order to meet

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DBP standards, including THMs, in recent years along with the increase of water sources pollution the use of new methods to remove organic matters including advanced oxidation processes as of modern methods for removing DBP precursors have come into consideration [1, 2, 6-9].

Advanced oxidation processes usually entail the generation and utilization of hydroxyl radicals (OH*) as a strong oxidizing agent for decomposition and decay of polluting substances [1, 10].

In advanced oxidation processes using photo-catalytic technology, a semiconductor such as Titanium dioxide (TiO_2) is used for optical excitation of valence band electrons to conduction band (C^+_{CB}) under UV irradiation with more than 3.2 eV (UV with wavelength of less than 387.5 nm). These excited electrons that are moved to the conduction band, plus positive holes created in the catalyst valence band (h^+_{VB}), are used for hydroxyl radical production during various reactions. In this technology, semiconductors act as a catalyzer and their chemical status after each catalytic reaction cycle would be similar to the basic status [1, 10-14]. Thus, there is no need for adding chemical oxidizing substances during treatment in this model of advanced oxidation process. Low costs, high efficiency, and stability are considered among the important advantages of this method [1, 10, 11]. TiO_2 was used for photodegradation of bisphenol A [15], reactive Azo dye [16], natural organic matter [17], persistent pharmaceutical compounds [18], phenol [19], o-cresol [20], and other pollutants.

Murray and Parsons [21] investigated conventional coagulation, Fenton, photo-Fenton, and UV/TiO_2 processes for removal of NOMs from raw water with DOC of 9.64 mg/L and UV_{254} absorption of 38 m^{-1} at the Albert Halifax water treatment plant in England. While the purpose of customized treatment methods is to achieve SUVA≤3, UV/TiO_2 process having the most efficiency (96%) provided the remaining UV_{254} absorption of 1.5 m^{-1}.

Murray and Parsons [5] used TiO_2 fixed film instead of TiO_2 suspension to remove NOM from raw water in the investigated treatment plant. In this research, efficiency for removal of UV_{254} absorption and DOC was specified as 89% and 1.336 g/m^2 slide.

Le-Clech et al. [12] used UV/TiO_2 and membrane process in the form of a hybrid to remove 2.3 ppm NOMs. Removal efficiency was found to be 87–90%.

Sanly et al. [22] removed 90% DOC and 95% UV_{254} absorption using the UV/TiO_2 process.

The objective of this study is to investigate humic substance removal from water using the UV/TiO_2 photo-catalytic process as well as to specify the optimal conditions of the process and the reaction Kinetic.

Experimental Procedures

The study was conducted using the experimental method for complying with aims. On this basis, impressibility of the remaining humic acid was analyzed as the dependent variable against operating parameters such as initial concentration of humic acid, TiO_2 dosage, pH, and reaction time as independent variables.

Table 1. Physical characteristics of a photo reactor.

Parameter	Unit	Amount
Steel reactor length	cm	92
Steel reactor diameter	cm	7.6
Ultimate bearable pressure	bar	5
Quartz coating length	cm	92
Quartz coating diameter	cm	3
Steel reactor effective volume	L	2.8
Power supply (transformer)	Volt	220-240
Lamp lifetime	hour	5,000
Irradiation dose	µw.s/cm^2	50,000

The study was performed in a batch laboratory-scale photo-catalytic reactor that was made in a cylindrical shape from stainless steel in order to provide maximum irradiation reflex. UVC beam with 253.7 nm wavelength was provided by a low-pressure UV mercury vapor 55-watt lamp that was axially centered inside an extremely smooth quartz cover with 3 cm diameter. Reactions on water were conducted between quartz and steel covers, having a total volume of 2.8 L. The photo reactor was connected to a 5 L tank for loading, sampling, and air injection. An aquarium pump (Philco, Italy) was located in the path of the 5 L tank to the main chamber of photo reactor for complete mixture and continuous circulation of the reactor contents. Aeration of water under reaction was also provided by an air pump (Rena, France). The scheme and physical specifications of the photo-reactor are presented in Table 1 and Fig. 1.

Raw water for the study of humic substances removal by UV/TiO_2 photo-catalytic oxidation was prepared by dissolving certain volumes of 1,000 ppm of humic acid (Merck) stock solution in 4.5 L deionized distilled water in order to obtain the specified DOC concentration. 150 mL of prepared sample was separated for control of initial DOC and UV absorption in 254 nanometer wavelength (UV_{254} Abs.), and the rest (4.35 L) was

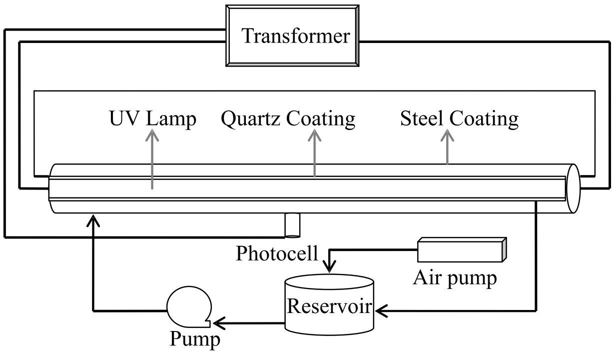

Fig. 1. The scheme and equipment used in the photo reactor.

transferred to a 5 L tank after adding the specified titanium dioxide powder (Degussa P25).

After pure UV irradiation to reactor contents per half hour, two separated samples were taken after filtration by 0.45 µm Millipore filter (Merck Millipore, Germany) for specifying DOC and UV$_{254}$ absorbance.

DOC, UV absorption at 254 nm, and specific UV$_{254}$ absorbance (SUVA) parameters were measured for each raw sample containing humic acid and samples taken from photo-catalytic and other evaluated processes. DOC was determined by high-temperature combustion using a Shimadzu TOC-VCSH analyzer (Shimadzu Co., Japan) after filtration of the samples by 0.45 µm Millipore filter (Merck Millipore, Germany). UV$_{254}$ absorbance was specified by a DR 5000 spectrophotometer (HACH Co., Germany), and then the amount of SUVA was obtained by dividing UV$_{254}$ absorbance into DOC concentration [1, 23].

Results

The Effect of TiO$_2$ Concentration on UV/TiO$_2$ Process

TiO$_2$ concentrations of 0, 0.05, and 0.1 g/L were evaluated according to Figs. 2 and 3 in order to specify optimized TiO$_2$ concentration for humic acid removal through a UV/TiO$_2$ photo-catalytic process in pH 6.5, initial DOC 5 mg/L, and dissolved oxygen (DO) 5.6 mg/L. As seen, Titanium dioxide in a 0.1 g/L concentration after two hours had the most efficiency with 95.6% DOC removal and 98.62% UV254 absorbance removal.

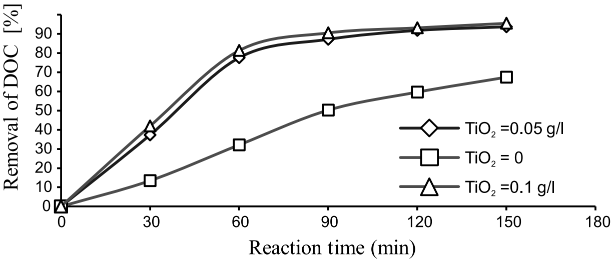

Fig. 2. Effects of TiO$_2$ concentration on DOC removal by UV/TiO$_2$ photo-catalytic oxidation (pH=6.5, initial DOC=5ppm, DO=5.6 ppm).

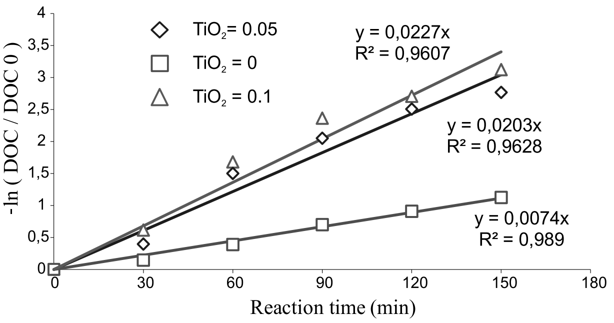

Fig. 3. TiO$_2$ concentration effects on DOC removal rate by UV/TiO$_2$ photo-catalytic oxidation (pH=6.5, initial DOC=5ppm, DO=5.6 ppm).

Findings showed that rate coefficients of 0.0074 min^{-1}, 0.02 min^{-1}, and 0.022 min^{-1} were achieved in TiO$_2$ concentrations of 0, 0.05, and 0.1g/L, respectively.

The Effect of pH on UV/TiO$_2$ Process

For this purpose, variations of DOC and UV254 absorbance over reaction time were investigated in pH values of 5, 6.5, and 8. According to Fig. 4, the UV/TiO$_2$ process in pH 5 had the most efficiency, having 98.1% of DOC removal and 99.44% of UV254 absorbance removal. Based on Fig. 5, rate coefficients of 0.0267 min^{-1}, 0.227 min^{-1}, and 0.0212 min^{-1} were found in pH 5, 6.5, and 8, respectively.

The Effect of Humic Acid Concentration on UV/TiO$_2$ Process

The UV/TiO$_2$ process was loaded with DOC, corresponding to humic acid, of 2, 5, and 10 mg/L in

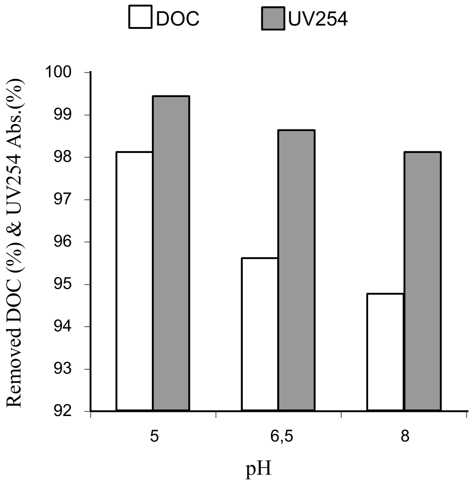

Fig. 4. Effects of pH on DOC removal by UV/TiO$_2$ photo-catalytic oxidation (TiO$_2$=0.1 g/L, initial DOC=5ppm, DO=5.6 ppm, reaction time=2.5 hr.)

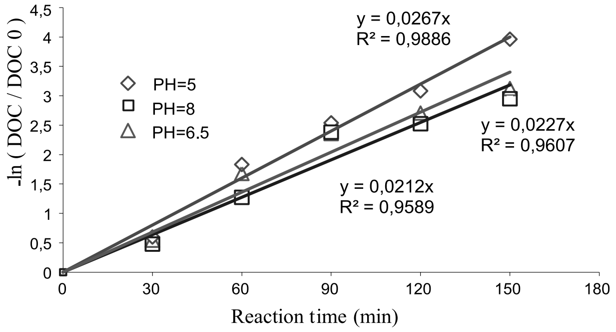

Fig. 5. Effects of pH on DOC removal rate by UV/TiO$_2$ photo-catalytic oxidation (TiO$_2$=0.1 g/L, initial DOC=5ppm, DO=5.6 ppm, reaction time=2.5 hr.).

order to verify the effects of humic acid concentrations on process efficiency in optimized conditions (pH 5, TiO_2 0.1g/L, and DO 5.6 mg/L). The obtained results are presented in Figs. 6 and 7.

Humic Acid Removal by Absorption on TiO_2, Oxidation Using UV, and Aeration

According to Fig. 8, absorption on 0.1 g/L of TiO_2 in darkness, oxidation using UV, and aeration removed 25.8% , 69.6%, and 6.6%, respectively, of 5 mg/L initial DOC at pH 5 after 2.5 hours.

Comparing UV/TiO_2/H_2O_2 and UV/H_2O_2 with UV/TiO_2 in Humic Acid Oxidation

Although the efficiency of humic acid removal by the UV/H_2O_2 process was more than the UV/TiO_2 process prior to an hour, this situation was reversed after one hour, so 84% of DOC and 94.68% of UV254 absorbance were removed by the UV/TiO_2 process over an hour. Whereupon the UV/TiO_2 process provided 0.8 mg/L residual DOC, 1.9 m^{-1} UV254 absorbance and 2.375 L/mg.m SUVA after one hour, which is an acceptable result regarding provision of the DOC standard.

In order to investigate the effect of increasing H_2O_2 upon the UV/TiO_2 process, 1mM of H_2O_2 was added to the system in optimized conditions (5 mg/L initial DOC, 0.1 g/L TiO_2, pH 5, 5.6 ppm DO). Based on Fig. 9, the UV/TiO_2/H_2O_2 process provided 0.48 mg/L residual DOC, 0.1 m^{-1} UV absorption and 0.2 L/mg.m SUVA in one hour.

Discussion

HAs are considered highly reactive compounds in the environment and their removal from water is necessary during water treatment [2, 17]. For this reason, the aim of our current study is to investigate the removal of humic substances from water through the UV/TiO_2 photo-catalytic process.

The increase of catalyst concentration leads to an increase of active surface available for adsorption and degradation processes. Furthermore, the turbidity of the solution increases, thus photon penetration is confined. Hence the initial rate of photoreaction and its effectiveness are directly proportional to catalyst dose. However, when the critical concentration is exceeded, the reaction rate is independent from it and remains constant or even decreases with the catalyst dose increase [13]. In this study, since the kinetics of the UV/TiO_2 process in 0.05 g/L and 0.1 g/L TiO_2 did not have considerable difference, and more increase of TiO_2 would have a negative effect on UV penetration as a photon source,

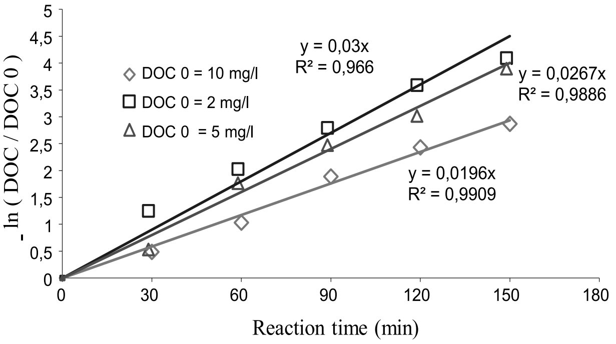

Fig. 6. Effects of initial DOC on DOC removal rate by UV/TiO_2 photo-catalytic oxidation (pH=5, TiO_2=0.1 g/L, initial DOC=5ppm, DO=5.6 ppm).

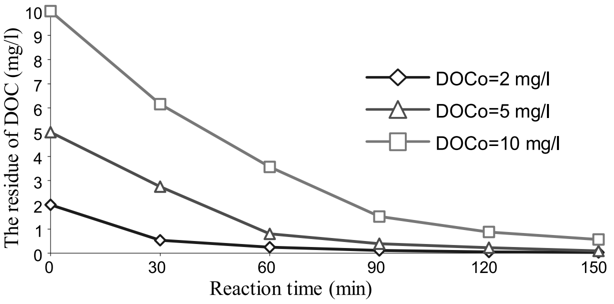

Fig. 7. Remaining DOC by UV/TiO_2 photo-catalytic oxidation against initial DOC (pH=5, TiO_2=0.1 g/L, initial DOC=5ppm, DO=5.6 ppm).

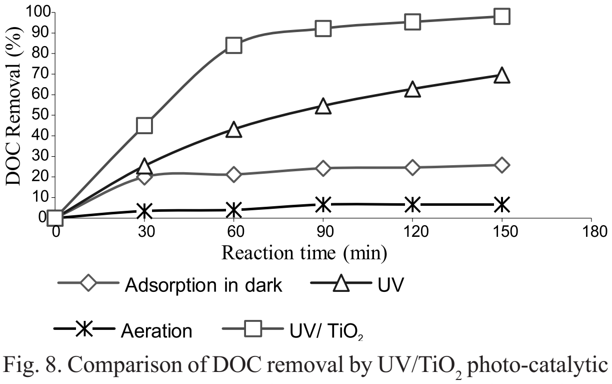

Fig. 8. Comparison of DOC removal by UV/TiO_2 photo-catalytic oxidation DOC, aeration, absorption on TiO_2, and UV photo-oxidation (pH=5, TiO_2=0.1 g/L, initial DOC=5ppm, DO=5.6 ppm).

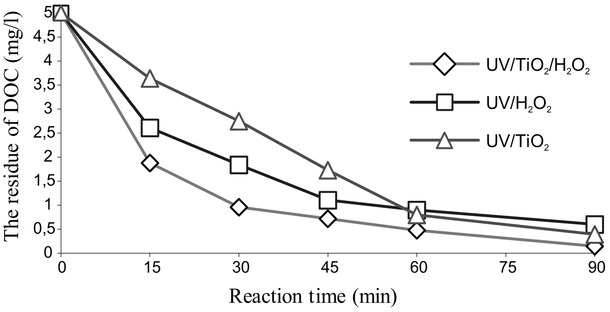

Fig. 9. Remaining DOC by UV/TiO_2, UV/H_2O_2, and UV/TiO_2/H_2O_2 processes (pH=5, TiO_2=0.1 g/L, initial DOC=5ppm, DO=5.6 ppm, H_2O_2=1 mM).

0.1 g/L TiO_2 was selected as the optimized concentration for humic acid removal by the UV/TiO_2 process.

Dziedzic et al. [24] showed that the increase of TiO_2 concentration in suspension caused not only the enhancement of degradation rate due to the increase of the available catalyst surface area, but also the increase of the HA amount adsorbed at the TiO_2 surface as well as the decrease in degradation rate due to the increase in light dispersion.

Based on the results of the present study, since the oxidation rate of DOC resulting from humic acid through the UV/TiO_2 process is directly proportional to the concentration of the reactant (DOC), the photo-catalytic reaction of DOC corresponding to HA follows first-order kinetic. The more the initial DOC concentration, the less the rate coefficient. So the rate constants of 0.03 min^{-1}, 0.0267 min^{-1}, and 0.0196 min^{-1} were obtained in the initial DOC concentration of 2, 5, and 10 mg/L, respectively. As a result, the UV/TiO_2 photo-catalytic process requires reaction times of 30, 90, and 150 min. to favorably reduce DOC per mentioned initial DOC concentrations, respectively. These results are consistent with the findings of Sanly et al. [22].

We should know that TiO_2 is neutral in pH 6.5 and this pH is known as the point of zero charge (PZC) for TiO_2. However, in pH less than PZC, TiO_2, having a positive charge, absorbs humic acid well due to negative charges by electrostatic forces. Moreover, TiO_2 in positive charge status has more potential to produce the hydroxyl radical and exhibits more efficiency in humic acid decomposition [9, 13, 22, 25]. For this reason, the UV/TiO_2 process had more efficiency in pH 5 and thus this pH was selected as the optimum one in this study. Nevertheless, pH 6.5 had sufficient efficiency to provide the residual DOC standard.

The process, in pH of 5 after 1.5 h, reduced DOC, UV254 absorbance, and SUVA to 0.394 mg/L, 1.1 m^{-1}, and 2.79 L/mg.m, respectively, which has sufficient acceptability for humic acid removal as a DBP precursor.

The results illustrated that humic acid oxidation using UV/TiO_2 photo-catalysis follows the first-order kinetic in acidic, neutral, and alkaline pH.

None of partial processes (absorption on TiO_2, aeration, and oxidation by UV) could provide standard residual DOC. These results are consistent with the findings of Dziedzic et al. [24]. Indeed, aeration in the UV/TiO_2 process is conducted in order to increase the oxygen as an excited electrons acceptor and ultimately generation of hydroxyl radical (OH*) for humic acid oxidation [10]. The concentration of the dissolved oxygen in the UV/TiO_2 process is very important as it provides for efficient electron scavenging in the conductive band and prevents their recombination. The presence of the dissolved oxygen also influences the formation of oxygen-containing radicals other than hydroxyl ones, and guarantees the stability of semi-radicals [13].

The electrostatic absorption of humic acid on TiO_2 as a quick reaction in acidic conditions, increases oxidation by hydroxyl radicals generated in the photo-catalytic process according to [22, 24]. According to the obtained findings, H_2O_2's role, as an irreversible electron acceptor (IEA), was verified in increasing the efficiency of the UV/TiO_2 process; so the UV/TiO_2/H_2O_2 process had more efficiency in humic acid oxidation because of generating more hydroxyl radical.

Of course, because the UV/TiO_2 process can provide standard residual DOC, it is recommended for removal of humic substances from water. These results are consistent with the findings of Sanly et al. [22].

The absence of need for requiring oxidant materials is the most important advantage of the UV/TiO_2 process against the UV/H_2O_2 process [19, 26, 27].

Conclusions

The UV/TiO_2 process can effectively reduce from 2 to 10 mg/L of DOC corresponding humic acid during 30 to 150 min, so it provides favorable drinking water quality in terms of humic acid based on DOC, UV_{254} absorbance, and SUVA. Consequently, this process can be one of the most effective methods for removal of humic substances from water sources in the case of integration with a membranous system or using TiO_2 fixed phase.

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References

1. LIU X., FITZPATRICK C.S.B. Removal of humic substances using solar irradiation followed by granular activated carbon adsorption. Water Science and Technology: Water Supply, **10** (1), 15, **2010**.
2. MATILAINEN A., SILLANPÄÄ M. Removal of natural organic matter from drinking water by advanced oxidation processes. Chemosphere. **80**, 351, **2010**.
3. VANLOON G.W., DUFFY S.J. Environmental Chemistry. 3rd Ed., Oxford University Press: UK, pp 271, **2010**.
4. GRÜNWALD A., ŠŤASTNÝ B., SLAVÍČKOVÁ K., SLAVÍČEK M. Formation of haloforms during chlorination of natural waters. Acta Polytechnica, **42**, 56, **2002**.
5. MURRAY C.A., PARSONS S.A. Preliminary laboratory investigation of disinfection by-product precursor removal using an advanced oxidation process. Water and Environment Journal. **20** (3), 123, **2006**.
6. DE JULIO M., DI BERNARDO L., DE JULIO T.S., DE CAMPOS S.X., VIEIRA E.M. Removal of humic substances with different apparent molecular sizes using Fenton's reagent. Desalination Water Treatment, **46**, 139, **2012**.
7. KIM H.C., YU M.J. Characterization of natural organic matter in conventional water treatment processes for selection of treatment processes focused on DBPs control. Water Res. **39** (19), 4779, **2005**.

8. SUTZKOVER-GUTMAN I., HASSON D. SEMIAT R. Humic acid removal by deep-bed filtration and by UF membranes. Desalination and Water Treatment, **31**, 42, **2011**.
9. ZHOU H., SMITH D.W. Advanced technologies in water and wastewater treatment. Journal of Environmental Engineering and Science. **1**, (4), 247, **2002**.
10. U.S. ENVIRONMENTAL PROTECTION AGENCY. Handbook advanced photochemical oxidation processes. BiblioGov: Columbus, Ohio, pp 10-35, **2012**.
11. GE B.Z., ZHANG J., LEI P., NIE M.Q., JIN P.K.Study on degradation behavior of N,N-dimethylacetamide by photocatalytic oxidation in aqueous TiO_2 suspensions. Desalination Water Treat. **42**, 274, **2012**.
12. LE-CLECH P., LEE E.K., CHEN V. Hybrid photocatalysis/membrane treatment for surface waters containing low concentration of natural organic matters. Water Res. **40** (2), 323, **2006**.
13. BODZEK M., RAJCA M. Photocatalysis in the treatment and disinfection of water. Part I. Theoretical backgrounds, Ecological Chemistry and Engineering (S). **19**, 489, **2012**.
14. SOBCZYŃSKI A., DOBOSZ A. Water Purification by Photocatalysis on Semiconductors. Pol. J. Environ. Stud. **10** (4), 195, **2001**.
15. CHA-YIN K., YA-HUI Y. Exploring the photodegradation of Bisphenol A in a sunlight/Immobolized N-TiO_2 System. Pol. J. Environ. Stud. **23** (2), 379, **2014**.
16. GENÇ N., CAN-DOĞAN E. Photooxidation: A decolorization procedure and a pre-treatment step for biodegradation of reactive azo dye. Pol. J. Environ. Stud. **15** (1), 73, **2006.**
17. VALENCIA S., MARÍN J.M., RESTREPO G., FRIMMEL F.H. Evaluations of the TiO_2/simulated solar UV degradations of XAD fractions of natural organic matter from a bog lake using size-exclusion chromatography. Water Res. **47** (14), 5130, **2013**.
18. LAOUFI N.A., HOUT S., TASSALIT D., OUNNAR A., DJOUADI A., CHEKIR N., BENTAHAR F. Removal of a Persistent Pharmaceutical Micropollutant by UV/TiO_2 Process Using an Immobilized Titanium Dioxide Catalyst: Parametric Study. Chemical Engineering Transactions. **32**, 1951, **2013**.
19. CZECH B. Effect of H_2O_2 addition on phenol removal from wastewater using TiO_2/Al_2O_3 as photocatalyst. Pol. J. Environ. Stud. **18**, (6), 989, **2009**.
20. ZMUDZINSKI W., Removal of o-cresol from water by adsorption photocatalysis. Pol. J. Environ. Stud. **19** (6), 1353, **2010**.
21. MURRAY C.A., PARSONS S.A. Advanced oxidation processes: Flow sheet options for bulk natural organic matter removal. Water Supply. **4**, (4), 113, **2004**.
22. SANLY M.L., CHIANG K., AMAL R., FABRIS R., CHOW C., DRIKAS M. A study on the removal of humic acid using advanced oxidation processes. Separ. Sci. Technol. **42** (7), 1391, **2007**.
23. APHA, AWWA, WEF. Standard Methods for the Examination of Water and Wastewater. 21st Ed., American Public Health Association: New York, **2005**.
24. DZIEDZIC J., WODKA D., NOWAK P., WARSZYŃSKI P., SIMON C., KUMAKIRI I. Photocatalytic degradation of the humic species as a method of their removal from water – comparison of uv and artificial sunlight irradiation. Physicochem. Probl. Miner. Process. **45**, 15, **2010**.
25. DOLL T.E., FRIMMEL F.H. Photocatalytic degradation of Carbamazepine, colofibric acid and imeprol with P25 and hombikat in the precence of NOM and other organic water constituents. Water Res. **39** (2-3), 403, **2005**.
26. ANDAYANI W., BAGYO A.N.M. TiO_2 beads for photocatalytic degradation of humic acid from peat waters. Indonesian J. Chemi. **11**, 253, **2011**.
27. HAN I., SHIN J.W., KIM H.C. Photocatalytic oxidation of aquatic humic substances using TiO_2/UV in a rotating photoreactor. Water Science & Technology: Water Supply, **6** (2), 93, **2006**.