Photocatalytic Elimination of Diatrizoate and I⁻ Formation: Influence of Dissolved Oxygen, Metal Ions and Natural Organic Matter (NOM)

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Abstract A simplified model of environmental conditions was developed to evaluate the effect of natural organic matter (NOM) and metal ions on the Pt/TiO₂ photocatalytic degradation of diatrizoate and I⁻ formation in the presence of different dissolved oxygen (DO) level. The results showed that the photocatalytic degradation of diatrizoate was strongly influenced by the amount of DO present and by the presence of metal ions. The DO concentration and the presence of NOM severely affected the formation of I⁻. The high R² values of the model signify that the models obtained are able to give a reasonably good estimate of response for the system in the range studied.

Keywords Photocatalytic, Diatrizoate, Dissolved Oxygen, Metal Ions, NOM

ionic ICM, was chosen as a model compound in this paper. It was rarely removed when passing through the municipal sewage treatment plant, was found in ground water frequently and persisted for a long time without any removal [7].

Figure 1. Structure of diatrizoate (C₁₁H₉I₃N₂O₄)

1. Introduction

Iodinated x-ray contrast media (ICM) is a substance used to enhance the contrast of structures or fluids within the body in medical imaging. Because of its resistance to human metabolism, it has been widely used in various diagnostic imaging approaches. Worldwide use of ICM has been reported to be on the order of 3.5×10^6 kg yr⁻¹ [1]. Due to the low reactivity, water solubility and high polarity, ICM and its metabolic compounds reflected in adsorbable organohalogen (AOX) are resistant in wastewater treatment plants and by their easily reach natural aquatic systems. Elevated concentrations of ICM and AOX have been detected in hospital and domestic wastewater, treated wastewater effluents, surface water, groundwater, and even finished drinking water [2-4]. In addition, the released I⁻ have been determined in fresh and ocean water samples can undergo reactions with humic substances (HS) [5]. This HS/iodine species could form a high risk trihalomethane during wastewater disinfection [6]. Diatrizoate (Fig. 1), an

Due to the low degradation efficiency of ICM in biological wastewater treatment plants [8, 9], advanced oxidation processes (AOPs) have been introduced. Powerful non-selective hydroxyl radicals generated from ozonation showed some success in removing or transforming ICM [10]. Although, the successes of ozonation and ozone-based AOPs on ICM degradation have been impressive, searching for other attractive approach is still awaited to be improved. Photocatalysis as an outstanding AOP has also been used for organic pollutants in recent years, those achievements on organic pollutants transformation were significant. Doll and Frimmel [11] reported the significant photocatalytic degradation of ICM (iomeprol and iopromide). However, little work exists on the photocatalytic degradation of ICM and released I⁻ concentration under environmentally relevant conditions.

In wastewater treatment plant further complications caused by various substances such as NOM [12, 13], metal

ions [14, 15] and oxygen content can affect the elimination of organic pollutants. NOM is ubiquitous in natural water and plays a fundamental role in the function of the aquatic environment. This is derived from the diverse structure of NOM, which is aliphatic and highly aromatic, as well as highly charged to uncharged. NOM is quite important in the binding and transport of inorganic and organic micropollutants, and it may promote the formation of harmful by-products during advanced oxidation and disinfection processes in water treatment [16]. It can also function as a substrate for undesired heterotrophic bacterial growth in water distribution systems. There are several publications dealing with the role of NOM on the photocatalysis [17, 18]. However, most of them use humic material from peat or coal extracts redissolved in water instead of aquatic natural organic matter. In our research, a raw sample from a brown water lake of the Black Forest in the south west of Germany was taken as NOM resource which can simulate the real aquatic system extremely.

The generation of reactive oxygen species and free metal ions in the water system influence the pathways and the yield of the degradation processes as well [19, 20]. Additionally, the coordination, adsorption or weak interaction between metal ions and oxygen can further influence the oxygen activation [21, 22]. The species of photogenerated radicals were also influenced by the energy or electron transfer between metal ions and oxygen [23, 24].

Therefore the aims of the work were to (1) reveal systematically the effects of components in natural water system (DO, metal ions and NOM) on the diatrizoate degradation by using Pt/TiO₂; (2) investigate the effect of DO, metal ions and NOM at different levels; and (3) characterize the relationship between DO and NOM, DO and metal ions, and NOM and metal ions.

The present work represents a simplified model of environmental conditions to identify the effects of special factors in the photocatalytic elimination of diatrizoate and I⁻ formation in the presence of different concentration of DO, metal ions (Fe(III), Zn²⁺ and Ca²⁺) and NOM.

2 Materials and Methods

2.1. Reagents and Materials

All chemicals used were analytical grade, and they were used without further purification. Diatrizoate (99%) was purchased from Sigma-Aldrich. Pt precursor was H₂PtCl₆ · 6H₂O (Alfa Aesar, 99%). CaCl₂ (>94%) from Carl Roth (Germany) was used to prepare an aqueous solution (c(Ca²⁺)=10 µmol L⁻¹). Fe(III) and Zn²⁺ solution were prepared from FeCl₃ (Sigma-Aldrich, 98%) and ZnCl₂ (Sigma-Aldrich, 97%), respectively in aqueous concentration c(Meⁿ⁺)=10 µmol L⁻¹. NOM was taken from Lake Hohloh (HO24, p(DOC)=16.5 mg L⁻¹), a brown water lake of the Black Forest in the south west of Germany (for the data see [25]).

TiO₂ P25 (approx. 75% anatase and 25% rutile) from Degussa was used as photocatalyst precursor. It had a surface area (BET) of 50 m² g⁻¹. The size of the primary particles ranged from 20 to 30 nm (manufacturer's data). In aqueous suspension P25 agglomerates with a diameter of >300 nm. All the solutions and suspensions were made up by ultrapure water (Milli-Q water, 18.2 MΩ cm⁻¹).

2.2. Catalyst Preparation

Pt modified TiO₂ (Pt/TiO₂) was prepared by using photodeposition. A calculated volume (1.1 mL) of an aqueous solution of hexachloroplatinic (IV) acid hexahydrate (c(H₂PtCl₆ · 6H₂O)=40 mmol L⁻¹) was added to an aqueous suspension of TiO₂ (5 weight% (wt.%)), followed by addition of methanol (at a 500:1 methanol to metal molar ratio). The suspension was irradiated with a 1000 W Xe short-arc lamp for 6 h under continuous stirring. Afterwards, the solutions were filtered and the solid samples were washed twice with deionized water, centrifuged, calcined at a temperature of 450 °C for 2 h and grinded carefully.

2.3. Analyses

The concentration of diatrizoate was measured by high performance liquid chromatography (HPLC) using an HP 1100 HPLC system (column RP 18e, 5µm; mobile phase acetonitrile : water 60:40; v=1 mL min⁻¹) with detection at 254 nm by a UV detector. The samples were filtered through 0.45 µm polycarbonate membrane filters (Millipore, Ireland) prior to analysis.

Inorganic anions (I⁻) was quantified by ion chromatography (790 Personal IC, Metrohm, Switzerland) using a Metrosep A Supp 5 (100×4.0mm, 5µm packing material) analytical column and an electronic conductivity detector.

DOC analysis was performed using a Shimadzu TOC-V CSE analyzer with inorganic carbon remover and automatic sampler. The AOX measurements were done by an ECS 1200 (Euroglas Analytical Instrument). For the determination of AOX 50 mg activated carbon were added to each sample according to DIN 38409-14 (1985). After shaking for 1 h the samples were filtered. The covered filters containing the loaded activated carbon were inserted into the AOX-furnace. The AOX concentration was measured by using a pyrolytic micro coulometer according to DIN 38409-14(1985). The relative standard deviation of the concentration values was <8%.

2.4. Sample Preparation

All the samples were prepared by dissolving diatrizoate in ultrapure water. The samples were stirred for several hours and placed in an ultrasonic bath for 15 min to ensure complete dissolution. For the irradiation experiments the catalyst suspension was freshly prepared by suspending

Pt/TiO₂ in ultrapure water and ultrasonification for 5 min. In order to investigate the effect of DO on the diatrizoate degradation, high (32 mg L⁻¹), medium (8 mg L⁻¹) and low (< 0.4 mg L⁻¹) DO level solutions were prepared by purging pure O₂, air and N₂ for 20 min prior to the photocatalytic reactions. The oxygen concentrations of each solution were maintained during the whole reaction process by continuously purging of the respective gases. The DO concentrations were checked by a DO meter during the reactions to confirm a constant oxygen concentration.

Figure 2. Schematics of the irradiation reactor: A, reactor; B, UV lamp; C, cooling system; D, air/ O₂/N₂ supply.

2.5. Irradiation Experiments

Samples for photocatalytic degradation were irradiated by using a lab-batch scale glass cylinder (Fig. 2). The radiation source was a low-pressure mercury lamp (14 W, Katadyn GmbH, Germany), equipped with the doped quartz to cut off

the VUV irradiation, had monochromatic spectrum at $\lambda = 254$ nm and 4 $\mu\text{E s}^{-1}$ irradiance. It was turned on at least 30 min prior to start of the irradiation reaction in order to insure a constant photon flux. The irradiated sample volume was 130 mL, and the catalyst concentration was 0.1 g L⁻¹. During the photoreaction, samples were collected at different time intervals for analysis. Before irradiation, adsorption was allowed to take place for at least 30 min in the dark. The pH value of the samples was between 5.5 and 6.7.

2.6. Full Factorial Design

In the case of processes influenced by multiple variables, statistical experimental design has been shown to be a powerful tool for determining the effects of operational factors and their interactions. This technique has been used widely in the chemical industry. In order to systematically explore the experimental region, we turned to a full factorial design for 3 variables in 2 levels (2³ experimental runs), which comprises all possible combinations of the +1 and -1 levels shown in Table 1. The experimental matrices and results are shown in table 2.

Table 1. Experimental factors

Factors	Levels	
	-1	+1
O ₂ (x _A) mgL ⁻¹	0	8
Men+(x _B) μmolL^{-1}	0	10
NOM (DOC)(x _C)mgL ⁻¹	0	1.6

Table 2. Factorial design matrix with experimental responses

(a) Factorial design matrix with experimental photocatalytic degradation rate constants of diatrizoate

Run	Coded values of independent variables			Rate constant (min ⁻¹)		
	x _A	x _B	x _C	*	**	***
1	-1	-1	-1	0.508	0.508	0.508
2	+1	-1	-1	0.529	0.529	0.529
3	-1	+1	-1	0.408	0.385	0.305
4	+1	+1	-1	0.498	0.427	0.503
5	-1	-1	+1	0.444	0.444	0.444
6	+1	-1	+1	0.579	0.579	0.579
7	-1	+1	+1	0.372	0.331	0.286
8	+1	+1	+1	0.641	0.575	0.549

(b) Factorial design matrix with experimental formed I⁻ concentrations

Run	Coded values of independent variables			I ⁻ (mgL ⁻¹)		
	X _A	X _B	X _C	*	**	***
1	-1	-1	-1	3.05	3.05	3.05
2	+1	-1	-1	3.05	3.05	3.05
3	-1	+1	-1	2.72	2.40	2.39
4	+1	+1	-1	2.57	2.72	3.26
5	-1	-1	+1	2.74	2.74	2.74
6	+1	-1	+1	3.79	3.79	3.79
7	-1	+1	+1	2.45	2.25	1.87
8	+1	+1	+1	3.81	4.29	4.02

*: present metal :Fe(III); **: present metal: Zn²⁺; ***: present metal: Ca²⁺

The factorial design can cover the main and interaction effects of the parameters within the whole range of selected parameters. According to the sparsity of effects principle in factorial design, it is most likely that main (single factor) effects and two-factor interactions are the most significant effects, and the higher order interactions (three-factor interactions) are negligible. Considering the general function expressing the interaction between the independent and dependent variables a second order model was employed (eq. 1):

$$Y = b_0 + \sum_{i=A}^C b_i X_i + \sum_{i=A}^C \sum_{j=B^1}^C b_{ij} X_i X_j + e \quad (1)$$

Where Y is the predicted response, x_i are levels of the factors, β_0 is a constant, β_i are the main effect coefficients for each variable and β_{ij} are the interaction effect coefficients.

3. Results and Discussion

3.1. Photocatalytic Reaction Kinetics of Diatrizoate

The experimental results (Fig. 3) demonstrate that the photocatalytic activity of Pt/TiO₂ was somewhat higher than that with pure TiO₂, owing to the lower recombination of photogenerated electrons (e⁻) and holes (h⁺) in the Pt/TiO₂.

Figure 3. Concentrations profiles for diatrizoate, DOC, AOI and I⁻ as a function of irradiation time in the presence of two different catalyst (a: p_0 (TiO₂) = 0.1 mg L⁻¹; b: p_0 (Pt/TiO₂) = 0.1 mg L⁻¹).

In the presence of Pt/TiO₂, total photocatalytic degradation of diatrizoate was reached within 20 min, while no significant loss of DOC occurred. The lower mineralization indicated that diatrizoate is recalcitrant. During the irradiation of the diatrizoate the concentration of I⁻ increased and the concentration of AOI decreased accordingly. After photocatalytic irradiation of 30 min, the elimination of the diatrizoate concentration was 17.97 $\mu\text{mol L}^{-1}$, and the formed I⁻ concentration was about 42 $\mu\text{mol L}^{-1}$. Based on the assumption that each degraded diatrizoate molecule lost 3 I⁻ ions, this equals 14 $\mu\text{mol L}^{-1}$. The eliminated diatrizoate was theoretically de-iodinated for 77.6% which is consistent with the elimination rate of adsorbable organic iodine (AOI) (74.4%). The increasing I⁻ concentration and the decreasing AOI concentration over the irradiation time indicates the stepwise de-iodination of the tri-iodinated contrast media diatrizoate and also the formation of partially iodinated intermediates during the photocatalytic degradation.

3.2. Full Factorial Design and Data Analysis

Tab. 2a and b show the design matrix used in the 2³ full factorial design, along with the reaction rate constants and the formed I⁻ concentrations in each run. The effects of the studied factors and interaction effect between factors on diatrizoate photocatalytic degradation rate constants and formed I⁻ concentration are presented comparatively in Fig. 4. Analysis of the effect of principal factors showed that in the considered range of parameters, DO and metal ions are the main intense single factors and the interaction between those is the most significant variable in achieving maximum rate constant of the photocatalytic degradation of diatrizoate. According of the positive effect of DO, increasing in oxygen concentration enhanced the rate constant and the formed I⁻ concentration. In comparison, the presence of metal ions decreased the rate constant. DO and metal ions have the opposite tendency for I⁻ formation, while Ca²⁺ plays more negative role than Fe(III) and Zn²⁺. The interaction between DO and NOM is the most intense for I⁻ formation. In this analysis, interaction effect between metal ions and NOM was very low for diatrizoate degradation rate constant and I⁻ formation, and can be neglected.

Figure 4. Estimated effects of factors on photocatalytic degradation rate constant of diatrizoate and I⁻ formation using fractional factorial design (a: present metal: Fe(III); b: present metal: Zn²⁺; c: present metal: Ca²⁺).

3.3. Analyses for Rate Constant

The effect of DO on photocatalytic degradation of diatrizoate was investigated by addition of various amounts of metal ions and NOM and the results are shown in Fig. 5. As can be seen, when the oxygen concentration increased, the rate constant increased accordingly caused by the oxidation of $^1\text{O}_2$ and $\bullet\text{HO}_2^-$, and $\bullet\text{O}_2$ formed by DO in the photocatalysis process [22].

Figure 5. Interaction effect between parameters in photocatalytic degradation rate constant of diatrizoate (a: present metal: Fe(III); b: present metal: Zn²⁺; c: present metal: Ca²⁺).

Figure 6. Influence of the second-order interactions on the photocatalytic degradation rate constant of diatrizoate: (a) DO and Fe(III), (b) DO and Zn²⁺ and (c) DO and Ca²⁺.

It was also found that all the selected metal ions (Fe(III) , Zn^{2+} and Ca^{2+}) decreased the rate constant. In the low DO concentration, metal ions significantly influenced the removal of diatrizoate, especially Ca^{2+} . With the increase of the DO concentration, the influence of metal ions decreased gradually. It is attributed that the presence of metal ions inhibits the formation of superoxide anion-radicals, radical intermediates and peroxo titanium species by the competitive reaction of photogenerated electrons with metal ions [26]. The best way to visualize the effect of the independent variables on the dependent ones is to draw 2D contour curves response lots of the model, which were done by varying two variables within the experimental range and holding the other constant. Fig. 6 shows the 2D contour curve of the interactions between DO and metal ions on the rate constants. It was observed the increasing of DO concentration and the decreasing of the concentration of metal ions leads to better results of photocatalytic degradation of diatrizoate.

The rate constants were also enhanced by the NOM. It is attractive to assume the formation of triplet excite states formed by NOM under UV irradiation[27]. No obvious interaction between DO and NOM was observed. In comparison, NOM decreased the rate constants in the presence of metal ions (Fig. 7). The contour curves are nearly perpendicular to the metal ions axis, which shows that the metal ions have a more pronounced influence than the NOM.

The resulting model can be presented by eq. 2. (2) to (4)

$$Y_{\text{Rate constant}} = 0.51 + 0.052x_A - 0.03x_{B(\text{Fe(III)})} + 0.024x_C + 0.038x_Ax_{B(\text{Fe(III)})} + 0.024x_Ax_B \quad (2)$$

$$Y_{\text{Rate constant}} = 0.485 + 0.043x_A - 0.055x_{B(\text{Zn}^{2+})} + 0.023x_C + 0.029x_Ax_{B(\text{Zn}^{2+})} + 0.027x_Ax_C \quad (3)$$

$$Y_{\text{Rate constant}} = 0.475 + 0.065x_A - 0.065x_{B(\text{Ca}^{2+})} + 0.014x_C + 0.051x_Ax_{B(\text{Ca}^{2+})} \quad (4)$$

Figure 7. Influence of the second-order interactions on the photocatalytic degradation rate constant of diatrizoate: (a) NOM and Fe(III), (b) NOM and Zn²⁺ and (c) NOM and Ca²⁺.

The predicted data from the model were also compared with the experimental data measured (Fig. 8). The high R^2 (0.93, 0.92 and 0.98 for Fe(III), Zn²⁺ and Ca²⁺, respectively) values signify that the model is able to give a reasonably good estimate of response for the system in the range studied.

Figure 8. Comparison of experimental and predicted photocatalytic degradation rate constant of diatrizoate (a: present metal: Fe(III); b: present metal: Zn²⁺; c: present metal: Ca²⁺).

3.4. Analyses for I⁻ Formation

The effects of DO, metal ions and NOM on I⁻ formation are shown in Fig. 9. In contrast to the rate constant, no effect of DO on the final I⁻ concentration in the system was observed. While, the de-iodination rate of diatrizoate increased with the increase of oxygen concentration obviously (Fig. 10). The indistinctive final I⁻ concentration might result from the consumption I⁻ in the presence of high DO concentration (eq. 5).

Figure 9. Interaction effect between parameters in I^- formation (a: present metal: Fe(III); b: present metal: Zn^{2+} ; c: present metal: Ca^{2+}).

Figure 10. (a) I^- concentration as a function of irradiation time in the presence of different DO levels; (b) the ratio of I^- concentration and eliminated diatrizoate in the presence of different DO levels.

Similar with the rate constant, it was also found that all the selected metal ions (Fe(III), Zn^{2+} and Ca^{2+}) decreased the I^- formation in the low DO concentration. With the increase of the DO concentration, the effects of metal ions were various. Notably, in the presence of Fe(III), I^- concentration in the solution decreased with the increase of oxygen concentration, which might be caused by the oxidation consumption of I^- (eq. 6). The inhibiting effects of Zn^{2+} and Ca^{2+} weakened with the increasing of oxygen, especially Ca^{2+} . The I^- concentration increased by adding Ca^{2+} in the presence of high DO concentration, which implied that inhibition effect of Ca^{2+} was completely covered by the enhanced influence of

DO.

NOM decreased the final I^- concentration significantly in the low DO concentration, while in the high DO level, I^- concentration increased obviously by adding NOM. As discussed, the interaction between DO and NOM is the most intense for I^- formation, and the 2D contour curves (Fig. 11) of the interaction between NOM and DO revealed that the simultaneous increase of both factors lead to the largest I^- formation. And there is a synergistic effect between NOM and DO which means the influence of NOM increased with

the increase of DO concentration.

The resulting model can be presented by eq. (7) to (9)

$$Y_{I^-} = 3.02 + 0.28x_A - 0.13x_{B(Fe(III))} + 0.18x_C + 0.32x_Ax_C \quad (7)$$

$$Y_{I^-} = 3.04 + 0.43x_A - 0.12x_{B(Zn^{2+})} + 0.23x_C + 0.16x_Ax_{B(Zn^{2+})} + 0.35x_Ax_C \quad (8)$$

$$Y_{I^-} = 3.02 + 0.51x_A - 0.14x_{B(Ca^{2+})} + 0.09x_C + 0.25x_Ax_{B(Ca^{2+})} + 0.29x_Ax_C \quad (9)$$

The predicted data from the model were also compared with the experimental data measured (Fig. 12). Using all coefficients in Eq. (7) to (9) results in an almost perfect fit of the data (R^2 of 0.97, 0.95 and 0.98 for Fe(III), Zn^{2+} and Ca^{2+} , respectively).

The results of the photocatalytic experiments showed an effective removal of diatrizoate and the formation of I^- . The experimental design results revealed that the degradation of diatrizoate was strongly affected by the amount of DO present and by the presence of metal ions, increasing the DO concentration and decreasing the metal ions concentration led to the highest reaction rate constant of the photocatalytic degradation of diatrizoate. The DO concentration as well as NOM had the most intense influence on I^- formation, and the simultaneous increase of both led to the highest I^- formation. In addition, there was a synergistic effect between NOM and DO on I^- formation. The empirical models were developed for diatrizoate elimination and I^- formation, and the high R^2 values signify that the models obtained are well suited to describe the response of the system in the range studied. Investigating major water constituents in competitive application under well defined reaction conditions opens the door for the identification of the drivers of the reactions useful for the basic understanding of aquatic systems and for water treatment as well.

4. Conclusions

Figure 11. Influence of the second-order interactions of DO and NOM on I^- formation.

Figure 12. Comparison of experimental and predicted I⁻ concentration (a: present metal: Fe(III); b: present metal: Zn²⁺; c: present metal: Ca²⁺).

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REFERENCES

- [1] A. Putschew, S. Wischnack, M. Jekel, Occurrence of triiodinated X-ray contrast agents in the aquatic environment, *The Science of the Total Environment* (2000) 129-134.
- [2] F. Sacher, F.T. Lange, H.-J. Brauch, I. Blankenhorn, Pharmaceuticals in groundwaters Analytical methods and results of a monitoring program in "Baden-Württemberg, Germany, *Journal of Chromatography A*, (2001) 199-210.
- [3] W. Seitz, W.H. Weber, J.Q. Jiang, B.J. Lloyd, M. Maier, D. Maier, W. Schulz, Monitoring of iodinated X-ray contrast media in surface water, *Chemosphere*, 64 (2006) 1318-1324.
- [4] K. Kuemmere, T. Erbe, S. Gartiser, L. Brinker, AOX-Emissions From Howitals into Municipal Waste Wter, *Chemosphere*, 36 (1998) 2437-2445.
- [5] G. Radlinger, K.G. Heumann, Transformation of iodide in natural and wastewater systems by fixation on humic substances, *Environmental Science & Technology*, 34 (2000) 3932-3936.
- [6] A.K. Venkatesan, R.U. Halden, Wastewater Treatment Plants as Chemical Observatories to Forecast Ecological and Human Health Risks of Manmade Chemicals, *Scientific Report-Uk*, 4 (2014).
- [7] T.A. Ternes, M. Bonerz, N. Herrmann, B. Teiser, H.R. Andersen, Irrigation of treated wastewater in Braunschweig, Germany: an option to remove pharmaceuticals and musk fragrances, *Chemosphere*, 66 (2007) 894-904.
- [8] A.L. Batt, S. Kim, D.S. Aga, Enhanced biodegradation of iopromide and trimethoprim in nitrifying activated sludge, *Environmental Science & Technology*, 40 (2006) 7367-7373.
- [9] J.L. Kormos, M. Schulz, H.P.E. Kohler, T.A. Ternes, Biotransformation of Selected Iodinated X-ray Contrast Media and Characterization of Microbial Transformation Pathways, *Environmental Science & Technology*, 44 (2010) 4998-5007.
- [10] J. Jeong, J. Jung, W.J. Cooper, W. Song, Degradation mechanisms and kinetic studies for the treatment of X-ray contrast media compounds by advanced oxidation/reduction processes, *Water Research*, 44 (2010) 4391-4398.

- [11] T.E. Doll, F.H. Frimmel, Photocatalytic degradation of carbamazepine, clofibrac acid and iomeprol with P25 and Hombikat UV100 in the presence of natural organic matter (NOM) and other organic water constituents, *Water Research*, 39 (2005) 403-411.
- [12] Y. Matsui, D.R. Knappe, R. Takagi, Pesticide adsorption by granular activated carbon adsorbers. 1. Effect of natural organic matter preloading on removal rates and model simplification, *Environmental science & technology*, 36 (2002) 3426-3431.
- [13] A.M. Comerton, R.C. Andrews, D.M. Bagley, The influence of natural organic matter and cations on the rejection of endocrine disrupting and pharmaceutically active compounds by nanofiltration, *Water Research*, 43 (2009) 613-622.
- [14] D. Vogna, Kinetic and chemical assessment of the UV/H₂O₂ treatment of antiepileptic drug carbamazepine, *Chemosphere*, 54 (2004) 497-505.
- [15] A.L. Faria, T.C.O. Mac Leod, M.D. Assis, Carbamazepine oxidation catalyzed by iron and manganese porphyrins supported on aminofunctionalized matrices, *Catalysis Today*, 133-135 (2008) 863-869.
- [16] S. Halladja, A. Ter Halle, J.P. Aguer, A. Boulkamh, C. Richard, Inhibition of humic substances mediated photooxygenation of furfuryl alcohol by 2,4,6-trimethylphenol. Evidence for reactivity of the phenol with humic triplet excited states, *Environmental Science & Technology*, 41 (2007) 6066-6073.
- [17] L. Haroune, M. Salaun, A. Menard, C.Y. Legault, J.P. Bellenger, Photocatalytic degradation of carbamazepine and three derivatives using TiO₂ and ZnO: Effect of pH, ionic strength, and natural organic matter, *Science of the Total Environment*, 475 (2014) 16-22.
- [18] M.N. Sugihara, D. Moeller, T. Paul, T.J. Strathmann, TiO₂-photocatalyzed transformation of the recalcitrant X-ray contrast agent diatrizoate, *Applied Catalysis B: Environmental*, 129 (2013) 114-122.
- [19] B.S. Karnik, S.H. Davies, M.J. Baumann, S.J. Masten, The effects of combined ozonation and filtration on disinfection by-product formation, *Water Research*, 39 (2005) 2839-2850.
- [20] Y. Guo, C. Cheng, J. Wang, Z. Wang, X. Jin, K. Li, P. Kang, J. Gao, Detection of reactive oxygen species (ROS) generated by TiO₂(R), TiO₂(R/A) and TiO₂(A) under ultrasonic and solar light irradiation and application in degradation of organic dyes, *Journal of Hazardous Materials*, 192 (2011) 786-793.
- [21] H. Fu, Z.J. Du, W. Zou, H.Q. Li, C. Zhang, Simple fabrication of strongly coupled cobalt ferrite/carbon nanotube composite based on deoxygenation for improving lithium storage, *Carbon*, 65 (2013) 112-123.
- [22] A.R. Canario, L. Guillemot, J. Diaz-Valdes, J.E. Valdes, P. Vargas, V.A. Esaulov, Electron transfer and energy loss processes in fluorine scattering on oxygen covered Ag(110) - Crystal azimuthal dependence, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 315 (2013) 36-41.
- [23] W. Zhang, Y. Li, J.F. Niu, Y.S. Chen, Photogeneration of Reactive Oxygen Species on Uncoated Silver, Gold, Nickel, and Silicon Nanoparticles and Their Antibacterial Effects, *Langmuir*, 29 (2013) 4647-4651.
- [24] Y. Yang, C.Q. Zhang, Z.Q. Hu, Impact of metallic and metal oxide nanoparticles on wastewater treatment and anaerobic digestion, *Environmental Science-Processes & Impacts*, 15 (2013) 39-48.
- [25] F.H. Frimmel, G. Abbt-Braun, K.G. Heumann, B. Hock, H. Lüdemann, M. Spiteller, *Refractory organic substances in the Environment*, first ed., Wiley-VCH, Darmstadt, 2002.
- [26] V. Brezova, A. Blazkova, E. Borosova, M. Ceppan, R. Fiala, The Influence of Dissolved Metal-Ions on the Photocatalytic Degradation of Phenol in Aqueous TiO₂ Suspensions, *Journal of Molecular Catalysis A: Chemistry*, 98 (1995) 109-116.
- [27] F.H. Frimmel, H. Bauer, J. Putzien, P. Murasecco, A.M. Braun, Laser Flash-Photolysis of Dissolved Aquatic Humic Material and the Sensitized Production of Singlet Oxygen, *Environmental Science & Technology*, 21 (1987) 541-545.