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Application of titanium dioxide-loaded activated carbon fiber in a pulsed discharge reactor for degradation of methyl orange

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ABSTRACT

The application of titanium dioxide-loaded activated carbon fiber (ACF/TiO_2) in a pulsed discharge reactor for degradation of methyl orange (MO) was investigated. Several factors were considered to explore the applicability and the effect of ACF/TiO_2 in the combined treatment of pulsed discharge and ACF/TiO_2. A synergistic effect appeared in the combined treatment. The increase in COD removal results from the photocatalysis of ACF/TiO_2, as well as the adsorption of ACF/TiO_2. Further, ACF/TiO_2 could be regenerated *in situ* in the combined treatment. The solution conductivity had a major effect on chemical oxygen demand (COD) removal from the MO solution in the combined treatment, while the initial solution pH value had a minor effect on COD removal.

1. Introduction

Titanium dioxide (TiO_2) is extensively used as a photocatalyst due to its high chemical stability, optical and electronic properties. It is a semiconductor that absorbs light at $\lambda < 385$ nm with the corresponding promotion of an electron (e^-) from the valence band to the conduction band. This excitation process leaves behind a positively charged vacancy called a hole (h^+). The hole itself is a very powerful oxidizing agent or it may generate hydroxyl radicals ($HO^\bullet$) in the presence of water and molecular oxygen [1]. However, the quantum yield is lower because of the recombination of electron–hole pairs in the photocatalysis process. In this case, excess ozone (O_3) might prevent the recombination of electron–hole pairs. O_3 can easily accept electrons from the conduction band because of its electrophilic reactivity, leading to formation of the ozonide radical ($O_3^{\bullet -}$), which finally yields $HO^\bullet$ radicals through radical chain reactions and photocatalytic ozonation is produced [2–4]. Moreover, it is difficult to separate fine particles of TiO_2 from solution after reaction. To overcome this problem, many studies have been devoted to immobilizing TiO_2 on activated carbon [5–7]. Activated carbon fiber (ACF), widely used as an effective adsorbent in treatment of polluted water and gas, has been introduced as a photocatalyst support in many studies [8–14].

The technology of wastewater treatment using pulsed discharge has attracted increasing attention [15,16]. In liquid phase pulsed discharge (both anode and cathode immersed in water), the discharge process can generate a number of reactive species when oxygen or air is introduced, such as oxygen and hydroxide radicals and other active molecular species (e.g., H_2O_2, O_3); and simultaneously generate ultraviolet radiation [15]. The technique works primarily by oxidizing and decomposing organic pollutants in water by these reactive species. Previous results obtained by emission spectroscopy showed an intensive radiation from underwater pulsed discharges over a wide range of wavelengths (200–1000 nm) [17–20]. Thus, the combination of pulsed discharge and TiO_2 can enhance the degradation rate of contaminants by utilizing the ultraviolet radiation generated in pulsed discharge. This has recently been proven in several investigations [20–22]. Addition of TiO_2 loaded activated carbon fiber (ACF/TiO_2) to a pulsed discharge reactor may not only be able to avoid the disadvantages of suspensions of fine photocatalyst particles but also to utilize ozone and ultraviolet radiation generated in pulsed discharge. Furthermore, the energy efficiency of the discharge reactor may be improved. However, the application of ACF/TiO_2 in a pulsed discharge reactor has not yet been investigated in wastewater treatment.

The aim of the present research was therefore to evaluate applicable conditions of a combined system of pulsed discharge and ACF/TiO_2, focusing on the effect of ACF/TiO_2 in the combined system. Methyl orange (MO), which has a relatively high toxicity, a

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complex structure, and high resistance to biodegradation, was chosen as a model contaminant in this study.

2. Experimental

2.1. Materials

Commercial viscose-based ACF felt, supplied by the Zichuan Carbon Fiber Limited Company, Qinhuangdao, China, was cut into 3 mm × 3 mm pieces to enable fluidization in the discharge reactor. Distilled water with conductivity less than 5 μS cm^{-1} was used to prepare all solutions and to rinse the ACF. All other chemicals were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. A TiO_2 sol was prepared using the same methods as described in previous references [11,23]. 2.5 g of ACF was added to the TiO_2 sol under vigorous stirring and stirring was continued for 1 h. The sample was taken out and separated one by one to avoid conglutination and dried at 80 °C. The dried sample was finally calcined at 900 °C in a flow of high-purity nitrogen for 2 h, obtaining the ACF/TiO_2 sample [24].

2.2. Analytical methods

Solution pH values were adjusted with 0.2 M HCl and 0.2 M NaOH and conductivities were adjusted with 0.2 M NaCl. The solution pH and conductivity were measured using a PHSJ-3F pH meter and a DDB-11A conductivity meter (Leici Limited Company, Shanghai, China), respectively. The dissolved ozone concentration was determined by the standard iodometric method [25]. The MO concentration was determined against a prepared standard curve by measuring the absorbance at 465 nm with an ultraviolet spectrophotometer (UV-762, Leici Limited Company, Shanghai, China). The chemical oxygen demand (COD) was measured with a CM-02 COD analyzer (Beijing Shuanghui Corp., China) using acidic oxidation by the dichromate method. The synergetic effect of combined treatment by pulse discharge and ACF/TiO_2 was evaluated using the synergy intensity. The synergy intensity, the regeneration percentages of ACF/TiO_2 and the energy efficiency were calculated as described in previous work [26,27].

2.3. Experimental apparatus

The experimental apparatus consisted of a pulsed power supply which has been previously described [27] and a pulsed discharge reactor [24,28]. The reactor reference conditions were as follows [24]: an input voltage of 46 kV, with 100 pulses s^{-1}; and an oxygen flow rate of 96 L h^{-1}. The reactor was filled with 200 mL MO solution (80 mg L^{-1}, pH 6.1, conductivity 20 μS cm^{-1}), either with or without 0.25 g ACF/TiO_2, and the power was applied. Samples from the reaction solution (5 mL) were taken for analysis at given intervals.

The power supply applied a voltage to the high-voltage electrode and the ground electrode. Electric discharge occurred in the aqueous phase and in the gas phase when oxygen was bubbled into the discharge reactor. $HO^•$ radicals were produced in the liquid phase and O_3 was generated in the gas phase. These active species reacted with organic pollutants and mineralized them to H_2O and CO_2 [28]. ACF/TiO_2 was added to the discharge reactor and suspended under vigorous stirring in a rising air flow. Synergistic combination between the pulsed discharge and ACF/TiO_2 occurred. The operating conditions were estimated by preliminary tests and the absence of diffusion limitations was verified.

3. Results and discussion

3.1. Synergistic effect in the combined treatment

To determine the effect of ACF/TiO_2 in the combined treatment of pulsed discharge and ACF/TiO_2, a set of control experiments was carried out with addition of ACF/TiO_2 to the MO solution in the absence and presence of pulsed discharge. The adsorption of MO on ACF/TiO_2 increased linearly and reached 61.3% in the absence of pulsed discharge. For pulsed discharge alone, MO degradation reached 63.0%, but MO degradation increased to 98.2% in the combined treatment. This shows that there is a synergistic effect in the combined treatment. As shown in Table 1, the synergy intensities were positive within 9 min. This result indicates that the disappearance of MO molecules may result from photocatalysis of ACF/TiO_2, as well as from adsorption of ACF/TiO_2. When the treatment time was extended, the synergy intensities quickly became negative. This may be because most MO molecules have decomposed after a certain time, which means that the probability of reacting with $HO^•$ radicals is reduced. However, $HO^•$ radicals react with byproducts during this period and further mineralize them to H_2O and CO_2.

To determine MO mineralization, COD removal was also examined. COD removal reached 56.7% using pulsed discharge alone, while which reached 92.5% for the combined treatment. For pulsed discharge alone, ozonation leads to the formation of byproducts such as organic acids and aldehydes and the byproducts resist ozone attack [29], which led to the solution pH decreasing from 6.10 to 4.4 and the conductivity increasing from 20 to 54 μS cm^{-1}. The combined treatment significantly increased COD removal. It shows that the byproducts were further mineralized to H_2O and CO_2, which led to an increase in the solution pH and a decrease in the conductivity. The final solution pH and conductivity was 5.56 and 25 μS cm^{-1}, respectively.

In the present study, a discharge reactor energy efficiency of 5.60 g kW^{-1} h^{-1} was achieved for pulsed discharge treatment alone. Further, an energy efficiency of 8.86 g kW^{-1} h^{-1} was obtained for the combined treatment. Compared with pulsed discharge alone, the energy efficiency of the combined treatment system increased by 58.2%. Thus, the combination of pulsed discharge and ACF/TiO_2 can be an effective approach to improving the energy efficiency of the discharge reactor.

3.2. Adsorption of ACF/TiO_2 in the combined treatment

To evaluate adsorption of ACF/TiO_2 in the combined treatment, repeated use of ACF/TiO_2 were performed with the same sample in the presence of pulsed discharge and the adsorption of ACF/TiO_2 on MO was also tested in the absence of pulsed discharge under the same conditions [24]. By comparing COD removal with and without pulsed discharge in previous work, it can be confirmed that adsorption of ACF/TiO_2 on MO in the combined treatment differed from that in the absence of pulsed discharge. The adsorptive capacity of ACF/TiO_2 after the fifth cycle was investigated by measuring the amount of MO adsorbed. The initial adsorptive capacity of ACF/TiO_2 was 112.5 mg g^{-1} and after the fifth cycle this value was 99.5 mg g^{-1}. The result shows that ACF/TiO_2 could be regenerated *in situ* during the combined treatment.

Table 1
Synergy intensities in the combined treatment (initial solution pH 6.1 and conductivity 20 μS cm^{-1}).

Time (min)	3	6	9	12	15
Synergy intensity	37.6	23.9	4.7	−11.3	−21.0

Table 2
Dissolved ozone concentrations at various pH values after reaction in the combined treatment (initial solution conductivity 200 μS/cm).

	Solution pH values	4	6.1	10
Dissolved ozone concentration (mM)	Discharge alone	0.0156	0.0157	0.0144
	Combined treatment	0.0044	0.0050	0.0034

3.3. ACF/TiO_2 photocatalysis in the combined treatment

In the pulsed discharge/ACF/TiO_2 system, the ultraviolet light (included in the streamer) in the plasma channels would induce photocatalytic reactions of TiO_2. The primary reactions are given as follows [1–3,30]:

$$TiO_2 + h\nu\,(\text{streamers}) \rightarrow e_{cb}^{-} + h^{+} \quad (1)$$

$$e_{cb}^{-} + O_{3(ads)} \rightarrow O_3^{\bullet -} \quad (2)$$

In the photocatalysis process, dissolved ozone accepts electrons from the conduction band to produce $O_3^{\bullet -}$, and dissolved O_2 can also accept TiO_2 conduction band electrons and generate $O_2^{\bullet -}$. Subsequently, $HO^{\bullet}$ radicals are generated by radical chain reactions. The recombination of electrons and positive holes can be inhibited by the reaction among ozone and oxygen and electrons on the surface of titanium dioxide, thereby accelerating the photocatalytic reaction.

To investigate the effect of ozone on the photocatalytic process in the combined treatment, the dissolved ozone concentration was measured at various pH after the reaction, as shown in Table 2. Compared with pulsed discharge alone, the dissolved ozone was depleted during the combined treatment. This shows that ozone is concerned with the photocatalytic reaction. The ACF can create a high ozone concentration in a contiguous zone of its surface by adsorption, which increases the probability of photo-electrons being captured by O_3 and enhanced $HO^{\bullet}$ radical generation on the surface of ACF/TiO_2. As a result, the limitation of interphase mass transfer caused by the immobilization of TiO_2 is offset.

According to the above analysis, it could be suggested that ACF acts as an adsorption center, assembling the reactants in its surface contiguous zone by adsorption, while TiO_2 loaded on the ACF surface acts as a decomposition site, accelerating the transformation of O_3 into $HO^{\bullet}$ radicals and decomposing MO and its byproducts to CO_2 and H_2O [24]. The MO and its byproducts concentration in the bulk solution decrease continuously because of the oxidation of reactive species produced during pulsed discharge and the adsorption of ACF/TiO_2. Thus, the MO and its byproducts adsorbed within the ACF micropores diffuse to the bulk solution and they are further degraded on the decomposition site and in the bulk solution during the diffusion. As a result, the adsorption sites within the ACF are vacated and the regeneration of ACF is achieved *in situ*.

3.4. Influence of solution conductivity on the combined treatment

The influence of solution conductivity on the combined treatment was investigated at initial solution pH 6.1 and the result is shown in Fig. 1. It shows that COD removal decreased with increased solution conductivity. Similar results were reported in previous literatures [17,18]. The generation of H_α (radical line at 656.3 nm), O (777.1 and 844.6 nm), and $HO^{\bullet}$ radicals (309, 620 and 927 nm) by pulsed discharge in water have been proven by emission spectroscopy in the visible and ultraviolet ranges [17,18,22]. The emission intensity depended on solution conductivity. As the conductivity increased, the streamer channel length, as well as the $HO^{\bullet}$ intensity, increased. The intensity reached a maximum at a conductivity of 10–80 μS/cm. The emission intensity became weak again when the conductivity was further increased because it was difficult to build up a strong electric field in the high conductivity liquid. At the higher conductivity, the $HO^{\bullet}$ band could be masked by the blue wing of the H_γ (H_β) line [18], which could lower the responsiveness of the photocatalyst. In addition, other active species generated by pulsed discharge could also be reduced at the higher conductivity [19]. Changes in dissolved ozone concentrations at various conductivities in the combined treatments are shown in Table 3. The experimental result is in good agreement with the literature [19]. On the other hand, the increased ionic strength would reduce ozone solubility in the bulk solution because of the salting out effect, which would also likely affect the extent of oxidation.

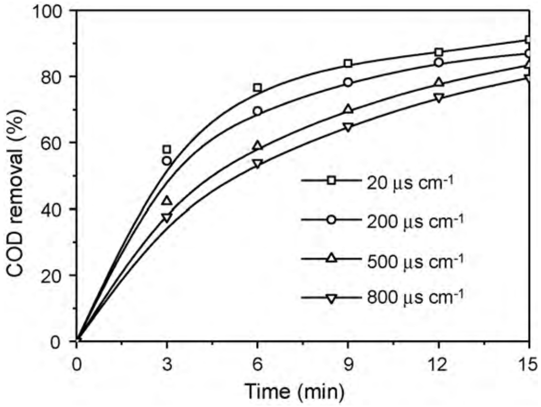

Fig. 1. Influence of solution conductivities on COD removal (initial solution pH 6.1).

3.5. Influence of initial solution pH on the combined treatment

The influence of initial solution pH value on the combined treatment was investigated in the pH interval 4–10 and the result is shown in Fig. 2b. For comparison, the adsorption of MO on ACF/TiO_2 was also measured in the absence of pulsed discharge and the result is shown in Fig. 2a. There were minor effects on the adsorption at various pH values. The MO molecular size (calculated using the ChemOffice software) is 1.54 nm × 0.48 nm × 0.28 nm. Given the existence of micropores and mesopores within ACF/TiO_2, MO molecules can be adsorbed with flat configurations, oblique configurations and terminal group interactions. As a result, ACF/TiO_2 showed rather fast adsorption in the MO solution in both acidic and alkaline environments.

Fig. 2b shows that COD removal was more effective at pH 4 than that at other two pH values for pulsed discharge alone. Similar results were reported in previous literatures [29,31–33]. The

Table 3
Changes in dissolved ozone concentrations at various conductivities (initial solution pH = 6.1).

Conductivity (μS/cm)		20	200	500	800
Dissolved ozone concentration (mM)	Distilled water experiment	0.0162	0.0157	0.0145	0.0122
	Combined treatment	0.0054	0.0050	0.0044	0.0031

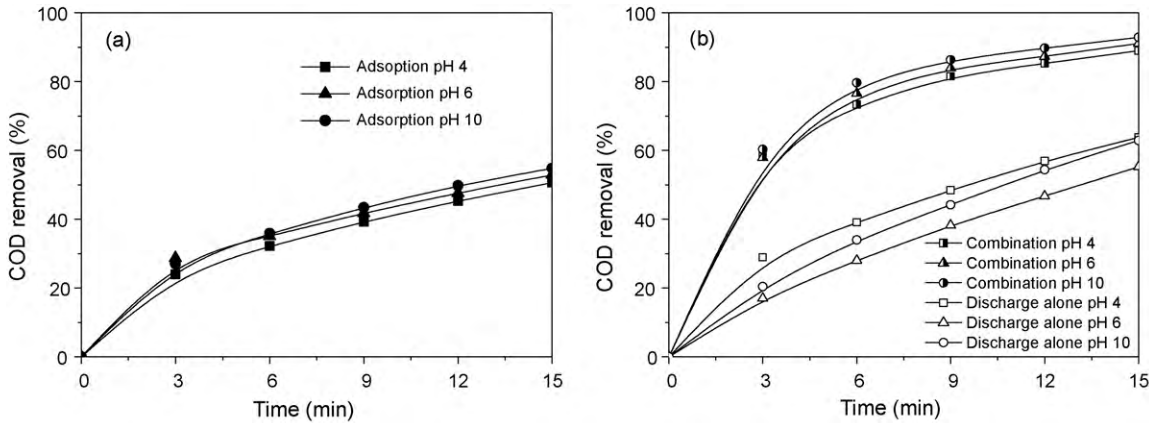

Fig. 2. (a) COD removal by adsorption of ACF/TiO_2 in the absence of pulsed discharge and (b) COD removal in the combined treatment (initial solution conductivity 200 μS/cm at all pH values).

COD removal was lower at pH 10 than that at pH 4 within 12 min but at the end of the reaction the COD removal was almost equivalent to that achieved at pH 4. A similar result was reported in previous literature [34]. For the decomposition of organic compounds by ozone oxidation, different reaction routes would take place under different solution pH values. The direct ozonation pathway would dominate under acidic or neutral solution conditions. But under alkaline conditions, the radical-type chain reaction of ozone would be promoted, which accelerates the transformation of ozone into $HO^\bullet$ radicals, hence $HO^\bullet$ radical reactions dominate the oxidation process [35]. Nevertheless, carbonates could be generated during MO degradation under alkaline conditions. $HO^\bullet$ radicals are unselective and react readily with carbonate ions, reducing the efficiency of the oxidation process [32]. This is a possible explanation for the higher COD removal at pH 4. Because of ozonation, the MO molecules decompose into organic acids and aldehydes, resulting in a decrease in pH values. In the case where the initial pH was 10, the pH was changed from 10 to 7.2 after the reaction. As a result, the carbonate ions in solution were decreased and $HO^\bullet$ radicals increased. This is a possible reason for the increase in COD removal after 12 min in alkaline solution. It can be seen in Table 2 that the dissolved ozone concentrations was lower at pH 10 than that at pH 4 after reaction, which related to the radical-type chain reaction of ozone under alkaline conditions.

Fig. 2b shows that the effect of the initial pH value on COD removal was not significant in the combined treatment. It can be seen in Table 2 that the dissolved ozone concentration at various pH was also not significantly different in the combined treatment. The COD removal under alkaline conditions was only slightly higher than that under acidic conditions. The reason for this is that the adsorption of MO on ACF/TiO_2 was relatively high at alkaline pH values. By comparing Fig. 2a and b, it can be seen that the effect of pH on COD removal was negligible so pH adjustment is not required in the combined treatment. This is because COD removal from the MO solution can be attributed to MO degradation in the bulk phase induced by pulsed discharges and the photocatalysis of TiO_2 loaded ACF, as well as the adsorption of ACF on MO in the combined treatment of pulsed discharge and ACF/TiO_2.

4. Conclusions

Synergistic effect existed in a combined pulsed discharge/ACF/TiO_2 system. Compared with pulsed discharge alone, the energy efficiency of the combined system increased by 58.2%. Moreover, ACF/TiO_2 could be regenerated *in situ* during the combined treatment. The solution conductivity had a major effect on COD removal in the combined treatment, while the initial solution pH value had a minor effect on COD removal. ACF/TiO_2 contributed in two ways in the combined treatment: by acting as an adsorption center that assembled the reactants in its surface contiguous zone by adsorption; and by acting as a decomposition site that accelerated the transformation of ozone into $HO^\bullet$ radicals and decomposed MO and its byproducts to CO_2 and H_2O.

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References

[1] T.E. Agustina, H.M. Ang, V.K. Vareek, A review of synergistic effect of photocatalysis and ozonation on wastewater treatment, J. Photochem. Photobiol. C: Photochem. Rev. 6 (2005) 264–273.
[2] L. Zou, B. Zhu, The synergistic effect of ozonation and photocatalysis on color removal from reused water, J. Photochem. Photobiol. A: Chem. 196 (2008) 24–32.
[3] S. Wang, F. Shiraishi, K. Nakano, A synergistic effect of photocatalysis and ozonation on decomposition of formic acid in an aqueous solution, Chem. Eng. J. 87 (2002) 261–271.
[4] L. Li, W. Zhu, L. Chen, P. Zhang, Z. Chen, Photocatalytic ozonation of dibutyl phthalate over TiO_2 film, J. Photochem. Photobiol. A: Chem. 175 (2005) 172–177.
[5] Y. Li, X. Li, J. Li, J. Yin, Photocatalytic degradation of methyl orange by TiO_2-coated activated carbon and kinetic study, Water Res. 40 (2006) 1119–1126.
[6] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Catalytic ozonation of sulfonated aromatic compounds in the presence of activated carbon, Appl. Catal. B: Environ. 83 (2008) 150–159.
[7] E. Carpio, P. Zúñiga, S. Ponce, J. Solis, J. Rodriguez, W. Estrada, Photocatalytic degradation of phenol using TiO_2 nanocrystals supported on activated carbon, J. Mol. Catal. A: Chem. 228 (2005) 293–298.
[8] R. Yuan, R. Guan, J. Zheng, Effect of the pore size of TiO_2-loaded activated carbon fiber on its photocatalytic activity, Scripta Mater. 52 (2005) 1329–1334.
[9] W.-C. Oh, F.-J. Zhang, M.-L. Chen, Y.-M. Lee, W.-B. Ko, 1 Characterization and relative photonic efficiencies of a new Fe-ACF/TiO_2 composite photocatalysts designed for organic dye decomposition, J. Ind. Eng. Chem. 15 (2009) 190–195.
[10] P.F. Fu, Y. Luan, X.G. Dai, Preparation of activated carbon fibers supported TiO_2 photocatalyst and evaluation of its photocatalytic reactivity, J. Mol. Catal. A: Chem. 221 (2004) 81–88.
[11] J. Shi, J. Zheng, P. Wu, X. Ji, Immobilization of TiO_2 films on activated carbon fiber and their photocatalytic degradation properties for dye compounds with different molecular size, Catal. Commun. 9 (2008) 1846–1850.
[12] R. Yuan, R. Guan, W. Shen, J. Zheng, Photocatalytic degradation of methylene blue by a combination of TiO_2 and activated carbon fibers, J. Colloid Interface Sci. 282 (2005) 87–91.
[13] T. Guo, Z. Bai, C. Wu, T. Zhu, Influence of relative humidity on the photocatalytic oxidation (PCO) of toluene by TiO_2 loaded on activated carbon fibers: PCO rate and intermediates accumulation, Appl. Catal. B: Environ. 79 (2008) 171–178.
[14] S.H. Mushrif, A.D. Rey, H. Tekinalp, Effect of metal salt on the pore structure evolution of pitch-based activated carbon microfibers, Ind. Eng. Chem. Res. 47 (2008) 3883–3890.

[15] B.R. Locke, M. Sato, P. Sunka, M.R. Hoffmann, J.-S. Chang, Electrohydraulic discharge and nonthermal plasma for water treatment, Ind. Eng. Chem. Res. 45 (2006) 882–905.

[16] M.A. Malik, Water purification by plasmas: which reactors are most energy efficient? Plasma Chem. Plasma Process. 30 (2010) 21–31.

[17] B. Sun, M. Sato, J.S. Clements, Optical study of active species produced by a pulsed streamer corona discharge in water, J. Electrostat. 39 (1997) 189–202.

[18] P. Šunka, V. Babický, M. Člupek, P. Lukeš, M. Šimek, J. Schmidt, M. Černák, Generation of chemically active species by electrical discharges in water, Plasma Sources Sci. Technol. 8 (1999) 258–265.

[19] P. Šunka, Pulse electrical discharges in water and their applications, Phys. Plasmas 8 (2001) 2587–2594.

[20] P. Lukes, M. Clupek, P. Sunka, F. Peterka, T. Sano, N. Negishi, S. Matsuzawa, K. Takeuchi, Degradation of phenol by underwater pulsed corona discharge in combination with TiO_2 photocatalysis, Res. Chem. Intermed. 31 (2005) 285–294.

[21] X.-L. Hao, M.-H. Zhou, Y. Zhang, L.-C. Lei, Enhanced degradation of organic pollutant 4-chlorophenol in water by non-thermal plasma process with TiO_2, Plasma Chem. Plasma Process. 26 (2006) 455–468.

[22] H. Wang, J. Li, X. Quan, Y. Wu, Enhanced generation of oxidative species and phenol degradation in a discharge plasma system coupled with TiO_2 photocatalysis, Appl. Catal. B: Environ. 83 (2008) 72–77.

[23] J.-w. Shi, S.-h. Chen, S.-m. Wang, P. Wu, G.-h. Xu, Favorable recycling photocatalyst TiO_2/CFA: effects of loading method on the structural property and photocatalytic activity, J. Mol. Catal. A: Chem. 303 (2009) 141–147.

[24] Y. Zhang, S. Deng, B. Sun, H. Xiao, L. Li, G. Yang, Q. Hui, J. Wu, J. Zheng, Preparation of TiO_2-loaded activated carbon fiber hybrids and application in a pulsed discharge reactor for decomposition of methyl orange, J. Colloid Interface Sci. 347 (2010) 260–266.

[25] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, New York, 1998.

[26] Y. Zhang, J. Zheng, X. Qu, H. Chen, Effect of granular activated carbon on degradation of methyl orange when applied in combination with high-voltage pulse discharge, J. Colloid Interface Sci. 316 (2007) 523–530.

[27] Y. Zhang, J. Zheng, X. Qu, H. Chen, Design of a novel non-equilibrium plasma-based water treatment reactor, Chemosphere 70 (2008) 1518–1524.

[28] Y. Zhang, B. Sun, S. Deng, Y. Wang, H. Peng, Y. Li, X. Zhang, Methyl orange degradation by pulsed discharge in the presence of activated carbon fibers, Chem. Eng. J. 159 (2010) 47–52.

[29] L.R. Grabowski, E.M.v. Veldhuizen, A.J.M. Pemen, W.R. Rutgers, Breakdown of methylene blue and methyl orange by pulsed corona discharge, Plasma Sources Sci. Technol. 16 (2007) 226–232.

[30] O. Gimeno, F.J. Rivas, F.J. Beltrán, M. Carbajo, Photocatalytic ozonation of winery wastewaters, J. Agric. Food Chem. 55 (2007) 9944–9950.

[31] H. Wang, J. Li, X. Quan, Decoloration of azo dye by a multi-needle-to-plate high-voltage pulsed corona discharge system in water, J. Electrostat. 64 (2006) 416–421.

[32] A.T. Sugiarto, S. Ito, T. Ohshima, M. Sato, J.D. Skalny, Oxidative decoloration of dyes by pulsed discharge plasma in water, J. Electrostat. 58 (2003) 135–145.

[33] A.T. Sugiarto, T. Ohshima, M. Sato, Advanced oxidation processes using pulsed streamer corona discharge in water, Thin Solid Films 407 (2002) 174–178.

[34] J. Feng, Z. Zheng, Y. Sun, J. Luan, Z. Wang, L. Wang, J. Feng, Degradation of diuron in aqueous solution by dielectric barrier discharge, J. Hazard. Mater. 154 (2008) 1081–1089.

[35] S. Irmak, O. Erbatur, A. Akgerman, Degradation of 17β-estradiol and bisphenol A in aqueous medium by using ozone and ozone/UV techniques, J. Hazard. Mater. 126 (2005) 54–62.