Degradation of methylene blue aqueous solution using atmospheric pressure dielectric barrier discharge

Zhijiao Ni[1], Hongwei Lu[1,2,*], Yuxuan Han[1], Xuejun Zha[1]

[1]College of Science, Donghua University, Shanghai, 201620, China
[2]Member of Magnetic Confinement Fusion Research Center, Ministry of Education, Shanghai, 201620, China
*Corresponding author: hwlu@dhu.edu.cn

Abstract: Methylene blue (MB) is toxic to humans and aquatic animals, and its removal from aqueous solutions requires high power consumption and long processing times. To improve the effect of dielectric barrier discharge (DBD) treatment of methylene blue and increase the energy utilization rate. In this study, we employed a novel approach, using a cylindrical DBD reactor, to treat MB in aqueous solutions. We found several factors, including input voltage, aqueous solution flow rate, number of high voltage electrodes, electrode size, and inside diameter of the dielectric tube influenced the MB removal rates with DBD. Our experimental results indicate that the change of electrode parameters can effectively improve the removal rate of methylene blue in DBD plasma treatment. At the same time, electrode parameters can lead to medium layer change of energy consumption; hence, the influence of electrode parameters on energy utilization efficiency also has an optimal value.

1. Introduction

MB [1], as a phenothiazine salt, is extensively used in chemical indicators, dyeing, pharmaceuticals, and identification purposes. In recent years, the rapid development of the textile industry [2] has resulted in a significant amount of dye wastewater [3]. This wastewater is difficult to degrade, has a deep color, a wide range of pH values, and a complex composition, which can adversely affect the water environment. It not only harms the ecological environment but also impacts people's daily lives. The traditional wastewater treatment technology has several shortcomings [4~8] and cannot selectively degrade all types of dye wastewater.

As an advanced oxidation technology, DBD [9~12] can generate high-energy electrons, ultraviolet light, ozone, hydroxyl, and other strongly oxidized substances to decompose organic particulate in the water to simpler without causing secondary pollution to the environment. During the DBD reaction process, high-energy electrons are generated and ionize and excite water molecules. The first-order products include ions, excited molecules, and secondary electrons, while the second-order products consist of oxygen atoms, ozone, hydrogen peroxide, and hydroxyl groups with strong oxidation properties. The active substances in the secondary products play a vital role in degrading wastewater. MB molecules react with these active molecules, undergo a series of reactions such as

bond breaking, ring opening, and association, and ultimately degrade into CO_2, H_2O, and other inorganic ions, achieving the purpose of degrading wastewater. Additionally, the local high temperature and ultraviolet light produced during the DBD discharge process also promote the degradation of MB to some extent.

However, DBD plasma still faces issues such as poor discharge stability [13]. Many scholars [14-18] have investigated the media thickness, discharge gap and voltage parameter influence on stability of Dielectric Barrier Discharge, but little has been reported to investigate high voltage electrode parameters of the effect on the removal rate of dye wastewater of the dielectric barrier discharge reactor. Especially the cylinder-type discharge reactor.

In this work, a cylinder-type discharge reactor was applied for removal of MB from aqueous solution, and influence factors such as electrode structure (density and size of high voltage electrodes, dielectric layer thickness) and instrument parameters (level of input voltage, flow rate of aqueous solution, rate of carrier gas) on removal rate of MB and the energy efficiency was discussed. The experimental results show that there are optimal values for the output voltage of the power supply, the flow rate of the solution, the inner diameter of the medium tube, and the characteristic size of the high-voltage electrode, which can improve the degradation effect of methylene blue and stabilize the discharge reaction. Our results suggest that improving reactor parameters of DBD plasma is a promising approach for the degradation of organic pollutants in water treatment processes.

2. Materials and methods

2.1 Experimental

Batch experiments were conducted to investigate the effects of aperture size of high voltage mesh electrode size, and dielectric tube inside diameter on the performance of MB degradation using DBD. A custom-made water treatment reactor was used in this study, as shown in Figure 1.
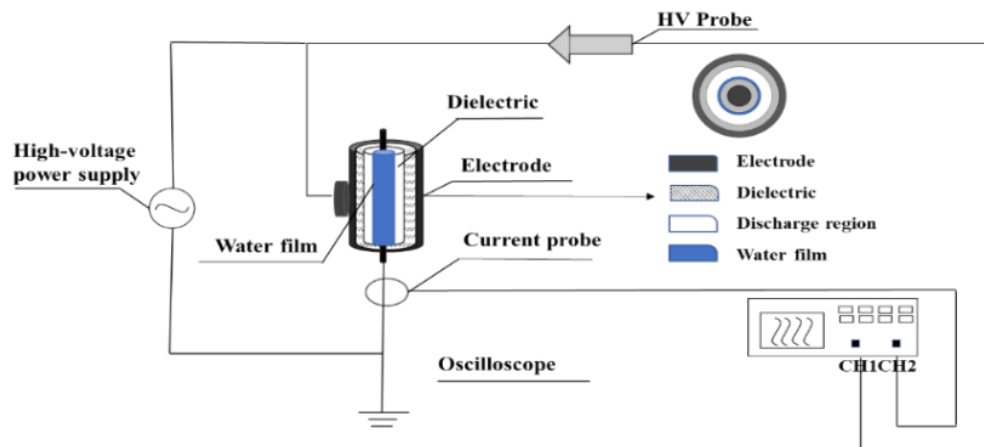

Figure 1. Schematic diagram of the dielectric barrier discharge (DBD) reactor.

The experimental setup comprised a high-voltage AC power supply, a water treatment reactor, and a constant current pump. An AC power supply of 10 kHz (CTP-2000K, Nanjing Suman Electronic Co., Ltd) was utilized. The water treatment reactor was a cylindrical double DBD reactor measuring 581 mm in height and 202 mm in width. It had a grounded electrode inside and a layer of quartz medium with a diameter of 8 mm wrapped around the outer layer. The MB aqueous solution flowed along the inner layer of the quartz medium as a film. The constant current pump (Shanghai Qingpu Huxi Instrument Factory) controlled the flow rate of the aqueous solution. Air was used as the reaction gas, and the flow rate was controlled by a flowmeter (D08-1F flow indicator, Beijing Sevenstar Flow

Co., Ltd.) into the inner and outer mediums. The outer layer was a quartz medium with an outer diameter of 25 mm and an adjustable inner diameter ranging from 20 to 22 mm. The high-voltage electrode was a stainless-steel mesh wrapped in the quartz outer medium, and its size determined the length of the section that could generate plasma discharge. For each batch of experiments, the total volume of the system was 500 ml of 100 mg/L MB aqueous solution prepared with tap water, and the critical conductivity was 494 μs/cm. A fixed volume of 5 mL of the aqueous solution was sampled at regular intervals.

2.2 Analytical methods

The discharge voltage and current were measured using a 500 MHz digital oscilloscope (TDS 2012B, Tektronix, USA) equipped with an HV probe (P6015, Tektronix, USA) and a current probe (TCP303, Tektronix, USA). The voltage and current waveform are obtained by the TDS1000C-SC Oscilloscope (Tektronix, USA). The voltage and current waveform diagram of dielectric barrier discharge is shown in Figure 2(a), and the discharge power was calculated based on the Lissajous figure. All figures are approximate parallelograms with different areas. The calculation method of discharge power refers to the paper published by Mu et al. [19]. Except for the study on the effects of input voltage, the input voltage was 70V.As shown in Figure 2(a), it can be clearly seen that the applied voltage and the breakdown current have the same frequency, but the current waveform has more obvious fluctuations compared to the voltage waveform, which is caused by uneven discharge. Specifically, when the applied voltage is high, the ions in the dielectric layer and discharge layer are not sufficient to provide a stable current carrier for the voltage, resulting in non-steady discharge effects. When the applied voltage is low, the discharge current has a good alternating waveform, indicating that the methylene blue solution in the experiment can indeed be studied by the DBD method. The plasma current spikes are densely distributed during the rising and falling stages of the voltage, but relatively sparse during the stage with a low rate of voltage change. Keeping other conditions constant, the steeper the rising and falling edges of the voltage, the more favorable it is for the generation of discharge channels, resulting in a better pollutant removal effect.
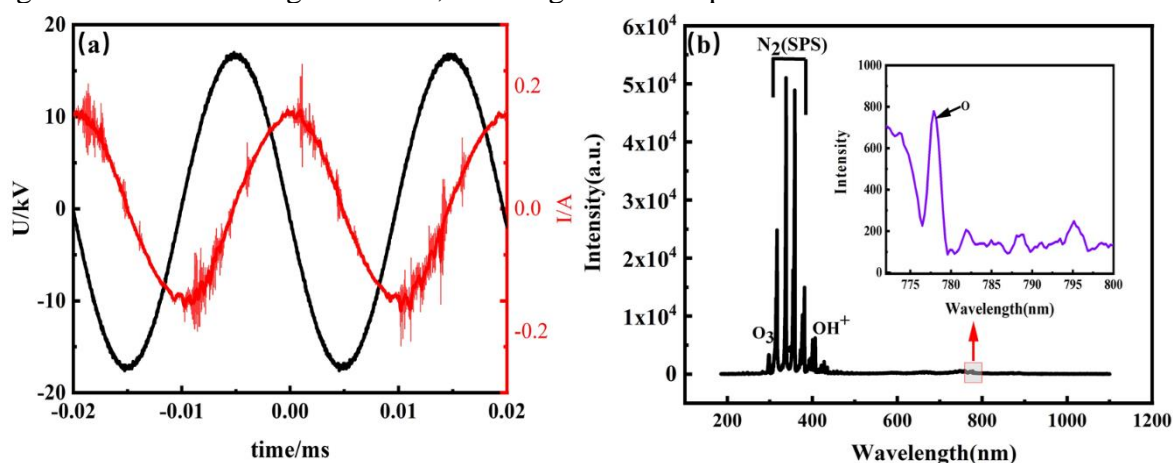

Figure 2. (a) Voltage and current waveforms of the dielectric barrier discharge at 70V.(b) The typical plasma OES of DBD at 70V.

A pH meter (PHSJ-3F, Shanghai INESA＆Scientific Instrument Co., Ltd, China) was used to measure variations in pH during the treatment. A conductivity meter (DDSJ-308F Shanghai MQK Industrial Co., Ltd, China) was used to measure the change in conductivity during degradation. The Ultraviolet visible spectrophotometer was monitored as a function of treatment time and quantified using a UV–vis Spectrophotometer (UV-2600, Shimadzu, Japan). The relationship between MB

concentration and measured absorbance was linear. Methylene blue concentration was determined by the standard curve method. Optical Emission Spectrometer (OES) of the DBD plasma was investigated using an AvantesAvaSpec-ULS4096CL-EVO spectrometer, as shown in Figure 2(b). From the graph, it can be clearly seen that lots of species was produced in the discharge space during the DBD process. The main components are O_3, OH^+, N_2O^+, NO, and H_2O^+. MB molecules are oxidized and decomposed into small molecules by these strong oxidizing species. Ozone survives longer and has a more stable energy state than the other components. By its concentration reflects the amount of all substances produced in the gas phase.

The degradation rate of MB is calculated as:

$$\eta = \frac{c_0 - c_t}{c_0} \times 100\%$$

c_0 and c_t are the concentrations of MB without treatment and after treatment time t, respectively. Through $-\ln\left(\frac{c_t}{c_0}\right) = k * t$ calculate the first order reaction kinetics of MB rate constant k, on behalf of the degradation rate of MB aqueous solution, namely the same time the amount of MB aqueous solution concentration changes much.

3. Results and discussion

3.1 MB degradation by DBD under different inside diameters of medium and different input voltage
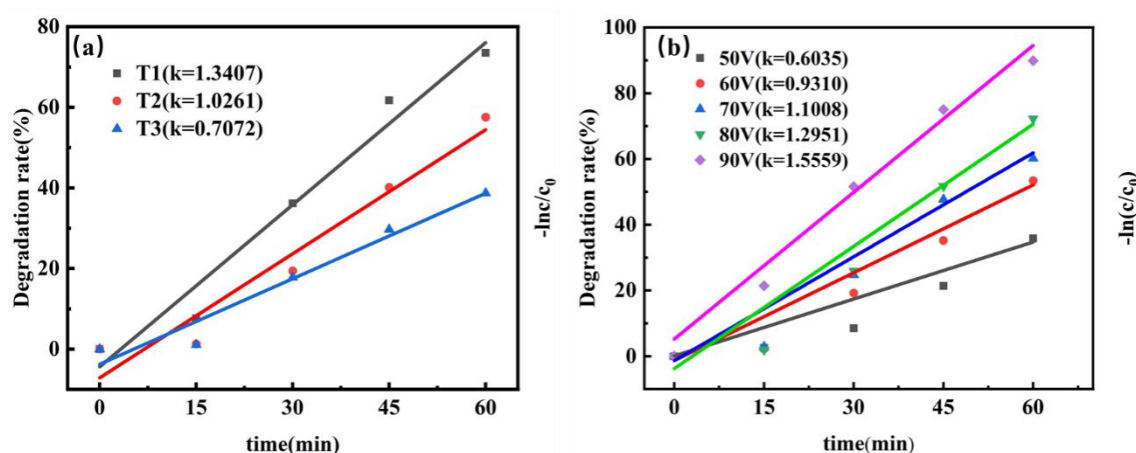

Figure 3. (a) The reduction of MB with varying inner diameters of the medium tube: The inner diameter of the medium tube was changed to 20mm (T1), 21mm (T2) and 22mm (T3) respectively. (b) MB degradation by DBD under different input voltage.

When keeping all other parameters of the reactor constant, the only variable is the inner diameter of the medium, the results are presented in Figure 3(a). The breakdown field strength of gas is determined by gas type and pressure, so for the same gas, voltage, and reactor structure, the breakdown field strength should remain consistent. However, as the thickness of the dielectric plate reduces, the gap discharge and accumulated charge on the dielectric surface increase, along with the expansion of the discharge channel. A decrease in dielectric thickness also leads to a rise in the discharge gap, which can cause an increase in gas breakdown field strength and discharge instability. As demonstrated in Figure 3(a), a medium diameter of T1 (20 mm) yields the most effective plasma degradation of MB and is also the most stable discharge process. Therefore, the experiment maintained an inner diameter of 20 mm.

Figure 3(b) illustrates the MB decomposition efficiencies as a function of treatment time for varying discharge voltages. Increasing the input voltage resulted in the removal of more MB. After 60 minutes, 90 V achieved a degradation rate of 89.9%, compared to only 35.8% at 50 V. Higher discharge voltages lead to greater electric field strength, larger discharge areas, more gas molecules being ionized to generate additional free radicals, and consequently, a higher removal rate of MB. Several studies [20] have shown a positive correlation between MB removal rate and discharge voltage. However, considering factors such as energy efficiency, reactor lifespan, plasma heating effect, and discharge stability, the input voltage was maintained at 70 V throughout the experiment.

3.2 MB degradation by DBD under the different solution flow rate and mesh of electrode
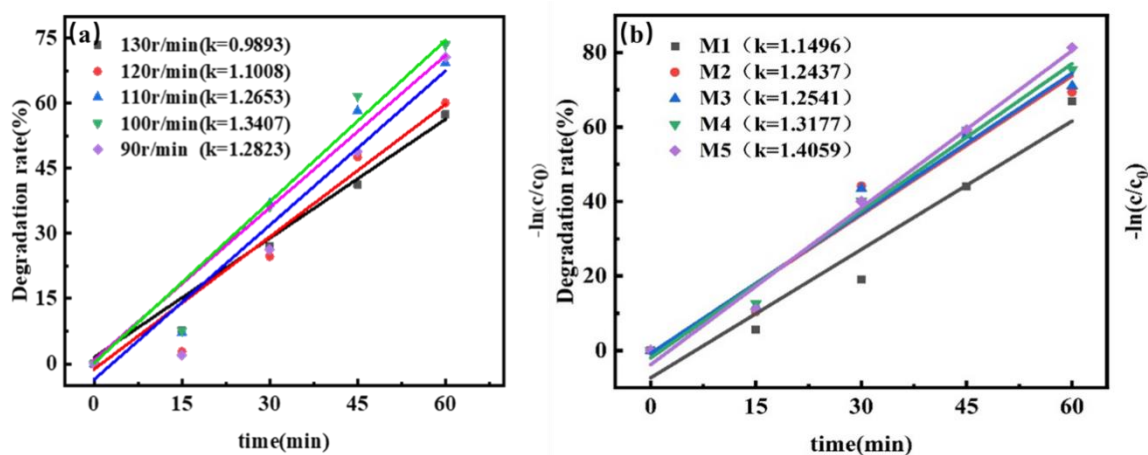

Figure 4. (a) MB degradation by DBD under the different solution flow rate. (b) MB degradation by DBD under different high voltage electrode stainless steel mesh

Figure 4(a) depicts the time course of MB degradation with an aqueous solution circulation flow rate ranging between 90 r/min and 130 r/min. Under the same conditions, MB degradation initially increased and then decreased with an increase in the aqueous solution flow rate. The MB removal rate was highest at 100 r/min, and the kinetic constants of the first-order reaction were also the highest. One of the primary goals of changing liquid rate in aqueous solution treatment is to increase the likelihood of collision between water and MB molecules with plasma and improve the gas-liquid mass transfer coefficient. A too-fast or too-slow liquid flow rate can result in discharge instability, reduced discharge channels, and high-energy particles generated by a discharge that cannot fully contact with MB molecules, leading to a reduced removal rate and energy utilization efficiency. Therefore, the aqueous solution circulation flow rate was maintained at 100 r/min during the experiment.

Keeping other characteristic parameters of the discharge tube unchanged, different high-voltage electrodes with a stainless-steel mesh aperture of 830 μm (M1, 20 mesh), 250 μm (M2, 60 mesh), 150 μm (M3, 100 mesh), 106 μm (M4, 150 mesh), and 74 μm (M5, 200 mesh) were used in the experiments. The results are presented in Figures 4(b).

The experimental results indicate that the aperture size of the high-voltage electrode has a significant impact on the removal of MB. The highest MB removal rate and first-order kinetic constant value were observed when the M5 electrode was used, suggesting that the DBD treatment effect on MB was better with a smaller electrode aperture, assuming other reactor characteristics remained unchanged.

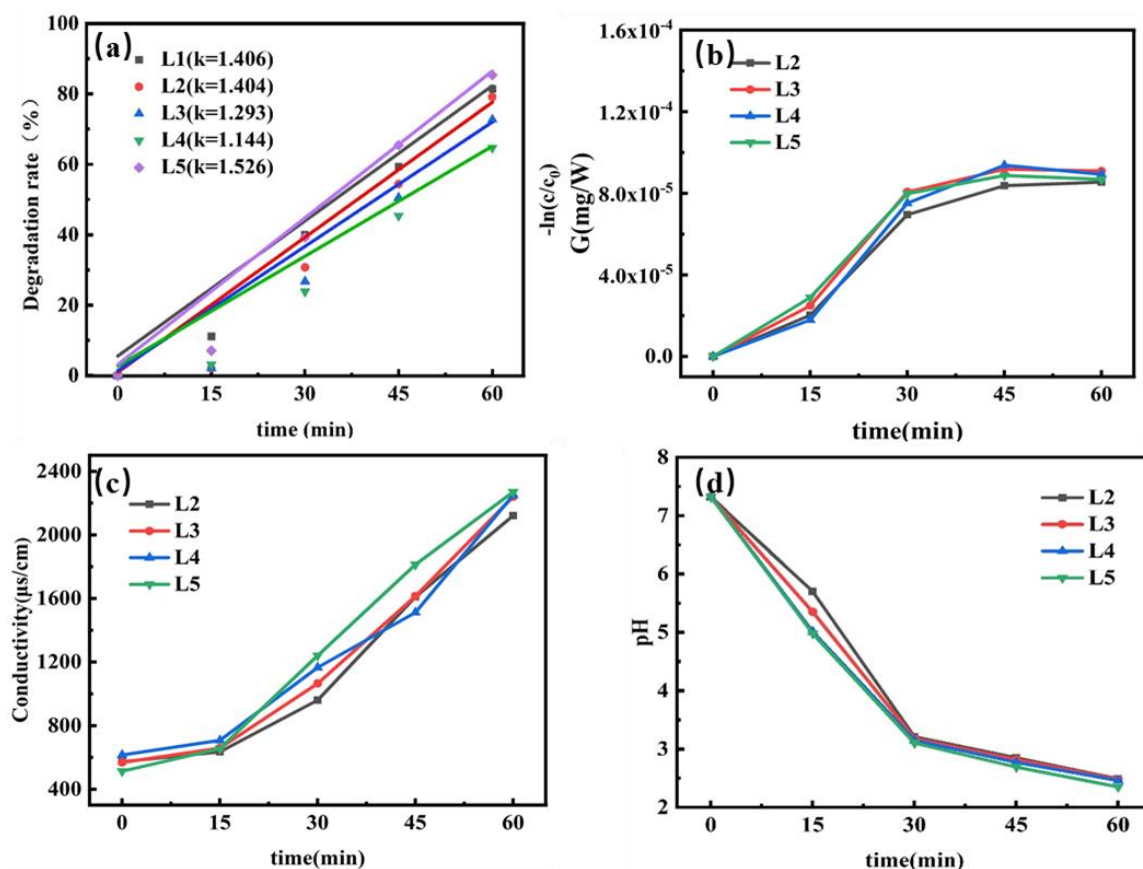## 3.3 MB degradation by DBD under different lengths of electrode

Figure 5. Variation of the parameters of aqueous solution under DBD treatment by different lengths of high voltage electrode. (a) MB degradation; (b) Energy efficiency; (c) conductivity; (d) PH.

In the discharge tube, with other parameters held constant, experiments were conducted using high voltage electrodes of different lengths of stainless-steel mesh: 72.5 mm (L1), 117 mm (L2), 132 mm (L3), 145 mm (L4) and 165 mm (L5). The results are presented in Figures 5 (a), (b), (c) and (d), which show the variation of MB degradation rate, variation of energy efficiency and conductivity of reactors with different high voltage electrode lengths within 60 min.

As shown in Figure 5, the length of the high-voltage electrode has a significant effect on the removal of MB. The highest removal rate and first-order kinetic constant of MB were obtained with the L5 electrode, indicating that a longer electrode length leads to better DBD treatment of methylene blue when other reactor characteristics are constant. The length of the high-voltage electrode directly affects the equivalent capacitance of the circuit. A longer electrode increases the area of the ground electrode, leading to increased U_g and I_g under the same input voltage.

Although the equivalent capacitance and average discharge power of the DBD reactor increase with the increase in high-voltage electrode length, the energy consumed by the dielectric layer also increases. Therefore, the high-voltage electrode length has an optimal value for energy utilization efficiency. As shown in Figure 5(b), the energy utilization efficiency is the highest when the high-voltage electrode length is L3(132mm). The conductivity and degradation rate are positively correlated, as shown in Figure 5(c), because the higher the degradation rate, the more unbound ions in the aqueous solution, leading to higher conductivity.

It can be seen from the experimental results that with the increase of discharge time, the pH of the solution gradually decreases, which indicates that in the process of degradation of methylene blue by

dielectric barrier discharge, acidic substances are generated in the solution. There are two sources of acidic substances: nitrogen and oxygen in the air during discharge react to produce nitrogen oxides (as shown in Figure 2(b)), and nitrogen oxides dissolve in water to produce nitric acid [21]; Organic and inorganic acids are generated during the degradation of methylene blue, making the solution acidic [22].

As shown in Figure 5(d): the larger the electrode size, the more acidic the solution with the increase of treatment time, indicating that the larger the high-voltage electrode size, the higher plasma discharge intensity, better uniformity, higher methylene blue degradation rate, more nitric acid, organic acid, inorganic acid and other intermediate products, resulting in more acidic solution, lower pH value.

4. Conclusions

The experiments in this paper demonstrate that the removal rate of MB by DBD is not only influenced by the power supply voltage, liquid rate, and medium tube diameter but also significantly impacted by the characteristic size of the discharge tube. The positive promotion effect of decreasing the dielectric layer thickness is smaller than the negative effect of increasing the gas gap distance. The smaller the thickness of the medium layer, the better the treatment effect. The discharge voltage determines the number of active particles produced, and the voltage is positively correlated with the degradation rate. However, the excessively high voltage will result in unstable discharge, significant heat loss, and reduced reactor lifespan.

The liquid flow rate has an optimal value; when it is too fast or too slow, discharge instability occurs, gas-liquid mass transfer efficiency is reduced, and ultimately the removal rate of MB is decreased. The aperture size of the high-voltage electrode has a significant effect on the removal of MB. A smaller aperture size results in higher degradation efficiency of methylene blue. Additionally, the length of the high-voltage electrode has a pronounced effect on the MB removal rate. The longer the electrode length, the better the MB degradation effect. However, the energy consumed by the dielectric layer also increases with the high voltage electrode length, so there is an optimal value for energy utilization efficiency.

Acknowledgment

References

[1] Peter Olusakin Oladoye, Timothy Oladiran Ajiboye, Elizabeth Oyinkansola Omotola, Olusola Joel Oyewola, Methylene blue dye: Toxicity and potential elimination technology from wastewater, Results in Engineering, Volume 16, 2022, 100678.

[2] Zhezhova Silvana, Sonja Jordeva, Sashka Golomeova-Longurova, Stefan Maksimov, and Vanga Dimitrijeva-Kuzmanoska. "The Development of Textile Industry in Shtip." Tekstilna Industrija 69.4 (2021): 14-19.

[3] Varjani Sunita, Parita Rakholiya, Toral Shindhal, Anil V. Shah, and Huu Hao Ngo. " Trends in dye industry effluent treatment and recovery of value added products." Journal of Water Process Engineering 39 (2021): 101734.

[4] DUTTA K, MUKHOPADHYAY S M, BHATTACHARJEE S, et al. Chemical oxidation of methylene blue using a Fenton like reaction[J]. J. Hazard Mater, 2001, 84(1): 57-71.

[5] Rania Al-Tohamy, Sameh S. Ali, Fanghua Li, Kamal M. Okasha, Yehia A.-G. Mahmoud, Tamer Elsamahy, Haixin Jiao, Yinyi Fu, Jianzhong Sun. A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety, Ecotoxicology and Environmental Safety, Volume 231, 2022, 113160,

[6] Wang Shaobin, Huiting Li, Sujuan Xie, Shenglin Liu, and Longya Xu. "Physical and Chemical Regeneration of Zeolitic Adsorbents for Dye Removal in Wastewater Treatment." Chemosphere (Oxford) 65.1 (2006): 82-87.

[7] Didier De Vasconcelos, Grazielly Maria, Jéssica Mulinari, Selene Maria De Arruda Guelli Ulson De Souza, Antônio Augusto Ulson De Souza, Débora De Oliveira, and Cristiano José De Andrade. "Biodegradation of Azo Dye-containing Wastewater by Activated Sludge: A Critical Review." World Journal of Microbiology & Biotechnology 37.6 (2021): 101.

[8] Ding C-M, Q-P Song, and C-X Wang. "Adsorption Performance of Chitosan in Printing and Dyeing Wastewater Treatment." Huan Jing Yu Jian Kang Za Zhi 25.8 (2008): 688-90.

[9] Demeestere K, Gago-Ferrero P, Langenhove H V, et al. Ozonation as an Advanced Treatment Technique for the Degradation of Personal Care Products in Water[M]// Personal Care Products in the Aquatic Environment. 2014.

[10] Fang Cao, Changsheng Shao, Shenhao Wang, Yahui Wu, Chao Liu, and Qing Huang. "Simultaneous Removal of Levofloxacin and Sulfadiazine in Water by Dielectric Barrier Discharge (DBD) Plasma: Enhanced Performance and Degradation Mechanism." Process Safety and Environmental Protection 171 (2023): 459-69.

[11] Kim Kil-Seong, Churl-Shin Yang, and Y.S. Mok. "Degradation of Veterinary Antibiotics by Dielectric Barrier Discharge Plasma." Chemical Engineering Journal (Lausanne, Switzerland: 1996) 219 (2013): 19-27.

[12] Jin Donghan, Lu Hongwei. Effect of electrode materials on degradation of methylene blue wastewater by DBD plasma under parallel magnetic field [J]. China Environmental Science, 2020, 40(4): 1570~1576.

[13] Huang F-M, H-L Wang, Z-C Yan, L. Chen, and T-Z Feng. "Degradation of Methylene Blue by Dielectric Barrier Discharge Plasma." Huanjing Kexue Yu Jishu / Environmental Science & Technology 33.2 (2010): 35-38.

[14] Ghomi H.,Safa N.N, Ghasemi S. Investigation on a DBD Plasma Reactor. IEEE Transactions on Plasma Science 2011, 39 (11), 2104-2105.

[15] Malashin M. V., Moshkunkov S. I.,KhomichV. Y. Shershunova, E. A. Study of spatiotemporal dynamics of a nanosecond atmospheric-pressure dielectric barrier discharge in millimeter-long air gaps. Plasma Physics Reports 2017, 43 (2), 170-174.

[16] Malashin M. V., Moshkunov S. I.,Khomich V. Y. Shershunova E. A., Yamshchikov V. A. On the possibility of generating volume dielectric barrier discharge in air at atmospheric pressure. Technical Physics Letters 2013, 39 (3), 252-254.

[17] Soloviev V. R., Selivonin I. V., Moralev I. A. Breakdown voltage for surface dielectric barrier discharge ignition in atmospheric air. Physics of Plasmas 2017, 24 (10).

[18] Lee H., Lee Y., Chang H. The discharge condition to enhance electron density of capacitively coupled plasma with multi-holed electrode. Physics of Plasmas 2012, 19 (9).

[19] R. Mu, Y. Liu, R. Li, G. Xue, S. Ognier.Remediation of pyrene-contaminated soil by active species generated from flat-plate dielectric barrier discharge, Chem. Eng. J. 296 (2016) 356–365.

[20] Aggelopoulos, Christos A. et al. "Degradation of antibiotic enrofloxacin in water by gas-liquid nsp-DBD plasma: Parametric analysis, effect of H2O2 and CaO2 additives and exploration of degradation mechanisms." Chemical Engineering Journal 398 (2020): 125622.

[21] Fan Yangyang, Jiushan Cheng, and Qiang Chen. "Degradation of Metronidazole Simulated Water by Nanosecond Pulsed DBD Plasma." IOP Conference Series: Earth and Environmental Science 687.1 (2021): 12074.

[22] CHANDANA L, MANOJ KUMAR REDDY P, SUBRAH- MANYAM C H. Atmospheric pressure non -thermal plasma jet for the degradation of methylene blue in aqueous medium[J]. Chemical Engineering Journal, 2015(282): 116-122.