Atmospheric pressure diffuse discharge treatment of aqueous solution of methylenum coeruleum

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Abstract. High voltage atmospheric cold plasma is a novel, non-thermal technology which has shown potential for degradation of various toxic components in wastewater. In this study, the degradation of methylene blue in aqueous solution as a model dye using a cold diffuse plasma source at atmospheric pressure has been investigated. Ambient air used as feed gas and aqueous solutions with same concentrations of the dye were treated by runaway electrons preionized diffuse discharge plasma. The removal efficiency from contaminant increased with the time of treatment increased from 5 to 20 minutes. Optical UV-IR spectroscopy was used for gathering information about the transmittance of aqueous solutions before and after treatment. The experimental results illustrated that transmittance of aqueous solution of methylene blue after 20 minutes of treatment by diffuse discharge plasma increased by ~ 30%.

1. Introduction

Until recently the amount of organic pollutants (organic compounds, plastics, organic dyes, etc.) increasing and detected in various water resources, thereby submitting a serious problem for the public health. For example, dye wastewaters from the textile industry are notable widely distributed (over one million of kilograms of dye contaminants are put out into the environment each year) [1] and primarily responsible for numerous issues. Therefore, the removal of color from textile industry wastewaters covers a major environmental goal because it gives a possibility to reuse water for textile processing. However, many of dyes made as very resistant material for degradation and so this it is not easy to clean water from contaminants. New organic dyes have very stable molecular structures and because of this, common wastewater treatment techniques are usually noneffective for dyes degradation. As a result, new technologies for removal of dyes from wastewater investigating.

Recent studies indicate that non-thermal plasma is a very promising process for cleaning wastewaters from dye contaminants. Such plasmas generated by atmospheric pressure discharge can generate various reactive species (OH, H₂O₂, O, O₃, etc.), UV and shock waves. Therefore, atmospheric pressure discharge using in a variety of fields, such as water purification [2, 3], chemical treatment [4, 5] and sterilization [6, 7].

In the present work, we report a new method for cleaning wastewater from organic dyes – runaway electron preionized diffuse discharge (REP DD) treatment. REP DD is a good source of UV, VUV and X-ray radiation [8–11] and allow to generate diffuse discharge in various gases at atmospheric pressure or higher. These features give an opportunity for a new perspective plasma method for wastewater cleaning from dye contaminants.
2. Experimental part

2.1. Chemicals
Methylene blue was selected as the standard organic contaminant dye because of its stable molecular structure. Moreover, water polluted by methylene blue indicates a high color strength and toxicity and has become widely distributed industrial wastewater [12] and its treatment has been actively studied in the last time. In this work, we used methylene blue aqueous solution with 1 to 2 ratio.

2.2. Experimental setup
All experiments in this work were conducted on the set-up presented on the figure 1. For the formation of runaway electron preionized diffuse discharge in our experiments we used a generator NPG18-3500N of negative voltage pulses, which amplitude could reach 22 kV with full width at half maximum 5 ns (1). These pulses were applied to the 8 mm discharge gap with frequency 100 Hz – where cathode (2), covered by insulator (3), made from stainless steel with a tip at the edge and surface of aqueous solution of methylene blue lying into quartz cuvette as anode (4). Capacitive voltage divider (5) and current shunt (6) were used for registration of electrical parameters of the diffuse discharge in the gap. In experiments, diffuse discharge formed at the atmospheric pressure in air, with delivered into discharge chamber through the windows (7).

![Figure 1. Experimental setup: 1 – generator of voltage pulses, 2 – cathode, 3- insulator, 4 – anode, 5 – voltage divider, 6 – current shunt, 7 – windows.](image)

Figure 2 shows typical oscilloscope tracks of voltage and current pulses, measured by Tektronix TDS series oscilloscope with bandwidth up to 1 GHz and sample rate up to 5 GS s⁻¹. Energy absorbed into the discharge in each pulse was calculated and equalled 5.6 mJ.
3. Results and discussion

The UV–IR spectra for an untreated methylene blue aqueous solution and for diffuse discharge plasma treated solutions during different treatment time in the range 5–20 min are shown in figure 3. The methylene blue dye was diluted with distilled water with 1:2 ratio. The transmittance intensity in the UV-IR spectra (230–380 and 560–740 nm) increased with decreasing treatment time and the solution became more colorless after 20 minutes exposure to the plasma. It is seen that in UV region of spectra transmittance in maximum of amplitude increases to 30% after 20 minutes treatment by REP DD and in the visible region of spectra transmittance increases to 35% after treatment.

The degradation efficiency of the organic pollutant depends on the amount of active species during the discharge process. It is well-known that, plasma in contact with water surface produce many chemically active species, such as O, H, H₂O₂ and OH radicals [13, 14]. In addition, REP DD
generated in the air creates ozone, which is the primary agent for chemical actions in gas-liquid diffuse discharge in air. All these species are very active and able to degrade organic pollutants in wastewater. Really, in our experiments it has been observed that amount of methylene blue, acting with active species in strong plasma chemistry reactions, settled out in solid form.

So then, generation of ozone significantly improve cleaning effect by plasma treatment in air. However, in our experiments we didn’t achieve full cleaning effect even after 20 minutes of treatment by REP DD. There are several reasons of this: 1) low exposure time in plasma; 2) low energy deposited into discharge; 3) low ozone generation. Third point may be related with the effects of water vapor on both discharge near the water surface and plasma properties. In [15] was detected that water vapor in air discharge decreasing ozone generation, because water vapor can absorb significant portion of electron energy of the discharge that acted on the ozone formation.

4. Conclusion

In this work, REP DD was used in atmospheric pressure air to study methylene blue degradation in aqueous solution. Dye degradation was investigated by UV–IR spectroscopy. The degradation of the dye methylene blue was the more efficient the more exposure time in plasma. Our plasma source is able to generate chemically active species, which are play significant part in wastewater cleaning from organic pollutants.

Treatment within 20 minutes of aqueous solution of methylene blue by REP DD leads to the increasing of transmittance on ~ 30% in visible and UV area of spectra. It is good result in addition to the studies of degradation of organic pollutants in corona and dielectric barrier discharge [16, 17].

REP DD is a one of the new perspective way for wastewater cleaning and decolorization. However, it’s still need to improve some characteristics for achieving more effective results in those cleaning processes. REP DD may be utilized alongside with another process such as photo-dissociation may be a promising wastewater treatment technology in the textile industry.

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