PLASMA-CATALYTIC DESTRUCTION OF TEXTILE DYEING WASTEWATER USING TITANIUM DIOXIDE

Houria GHODBANE¹,², Oualid HAMDAOUI²

¹ Univ Souk Ahras, Fac. Sci & T Dept. Process Engineering, Souk Ahras, Algeria, hiba_godbane@yahoo.fr
² Laboratory of Environmental Engineering, Faculty of Engineering Sciences, Department of Process Engineering, Badji Mokhtar-Annaba University, P.O. Box 12, Annaba 23000, Algeria.

ABSTRACT

The aim of this work is to study the destruction of Acid Blue 25 dye (AB25), used in the textile industry, by DC glow discharge generated in argon atmosphere in the absence and presence of TiO₂. The effect of operational parameters such as catalyst load and pH of solution on the degradation of AB25 is investigated. It was found that the degradation rate is increased in the presence of TiO₂, in comparison to discharge alone. As shown by the results, the degradation increases with treatment time until the catalyst load reaches 0.5 g L⁻¹. The degradation maximum (90%) is obtained within 1 h of treatment, while the plasmachemical treatment without catalyst only gave 78% AB25 degradation after the same treatment time. The pH has significant influence on the dye degradation.

Keywords: glow discharge, wastewater, non-thermal plasma, advanced oxidation processes, Acid Blue 25

1. INTRODUCTION

Dyeing and finishing of textile goods is a major concern to the environmentalist, due to the introduction of large quantities of color, chemical oxygen demand, nonbiodegradable organics, and other hazardous chemicals into the process effluents [1]. Discharge of such effluents imparts color to receiving streams and affects its aesthetic value. Colors interfere with penetration of sunlight into waters, retard photosynthesis, inhibit the growth of aquatic biota and interfere with gas solubility in water bodies [2–4]. There is a need to develop effective methods for the removal of such organic pollutants, either to less harmful compounds or, to their complete mineralization. Considerable efforts have been made by many researchers to find appropriate treatment systems in order to remove pollutants and impurities of wastewaters emanated from the textile industries. Advanced oxidation processes (AOPs) are considered as themost attractivemethods for the treatment of contaminated water containing toxic and nonbiodegradable pollutants [5–10]. The non-thermal plasma technique is an AOP that combines different physical and chemical effects, such as pyrolysis, UV photolysis, electrohydraulic cavitation, as well the formation of oxidizing species: radicals (H, O, •OH) and molecules (H₂O₂, O₃, etc.) [11,12]. Atmospheric pressure non-thermal plasma recently has attracted a lot of attention for the application of wastewater treatment due to its excellent performance in attacking organic pollutants and the absence of secondary pollution [11,13]. There are many different methods of non-thermal plasma generation, e.g.: DC plasma above liquid, pulsed streamer discharge in liquid, and dielectric barrier discharge. Among various plasma reactors for water treatment, glow discharge above water is attractive as an AOP because of the simplicity of the setup, the easy control of plasma parameters. and the possibility of generating discharge in different gases. Moreover, plasma treatment can be combined with other AOPs. The main problem with using
plasma as an AOPs is its energy cost. The average destruction efficiency of plasma is in the range of 0.03-12 g kWh\(^{-1}\) [14], which is still too high for wide use of this promising technology. One way to overcome this limitation is the use of plasma in combination with a catalyst, where the catalyst is activated directly by plasma, e.g. through UV photons. The combination of glow discharge with other advanced oxidation processes has been suggested as a tactical way to overcome the limitations of the plasma-chemical degradation process on its own. In this study, we have used DC glow discharge for the degradation of a widely used textile dye. This technique is coupled with photocatalysis with titanium dioxide (TiO\(_2\)). TiO\(_2\) is used in mineralization of toxic organic pollutants in wastewater treatment. TiO\(_2\) in solution can be excited by light of a wavelength less than 385 nm and •OH generated on the surface of the TiO\(_2\) is able to oxidize non-selectively a great number of organic pollutants in water, as demonstrated in [15,16].

The objective of this work is to study the degradation of Acid Blue 25 dye (AB25), used in the textile industry, by DC glow discharge generated in argon atmosphere in the absence and presence of TiO\(_2\). The effect of operational parameters such as catalyst load and pH solution on the degradation of AB25 is investigated.

2. MATERIALS AND METHODS

2.1. Materials

Acid Blue 25 (abbreviation: AB25; C.I. number: 62055; chemical class: anthraquinone; molecular formula: \(\text{C}_{20}\text{H}_{13}\text{N}_2\text{NaO}\text{S}\), 1-amino-9,10-dihydro-9,10-dioxo-4-(phenylamino)-2-anthracenesulfonic acid, monosodium salt) is used as a model compound for plasma AOP. The molecular structure of AB25(C.I. 62055) is shown in Fig. 1. The chemical is purchased from Sigma Aldrich and is utilized as received. The aqueous solution of AB25 is prepared by dissolving the required quantity in distilled water. The pH of the solution is adjusted using sodium hydroxide (NaOH) or sulfuric acid (H\(_2\)SO\(_4\)). All reagents utilized in the present work are purchased among the products of high purity.

![Chemical structure of AB25](image)

Fig. 1. Chemical structure of AB25.

2.2. Reactor

The scheme of the reactor is shown in Fig. 1. The reactor chamber is a cylindrical vessel with a diameter of 100 mm and height of 150 mm. The DC discharge system consists of a high voltage power supply connected through a ballast resistor to the reactor chamber. The power supply can provide a voltage of 15 kV and current at the range of 0-100 mA. The polarity of the HV electrode is positive through all the experiments. A cone-shaped stainless steel metal electrode with a top angle of approximately 40° and a rounded, polished tip is attached to a
micrometer screw above the liquid reservoir. The distance between the electrode and the water surface can be adjusted with the micrometer screw with a precision of 0.1 mm. In all experiments, this distance is fixed to 10 mm and treatment is carried out for 2 hours. The glow discharge degradation of AB25 is studied in the reactor for a constant solution volume of 500 mL, while stirring the liquid medium in order to achieve a uniform treatment of the whole volume. The efficiency of the discharge has been examined by measuring the decolorization of the dye solution with a UV/VIS spectrophotometer UV mini-1240 “SHIMADZU”, (SBN – SPEC-91). The concentration of the dye was determined from the measured UV–VIS spectrum, using the maximum of AB25 absorption at 602 nm. In the present study, plasma is generated in the closed reactor chamber, where argon gas is pumped through at flow rate of 300 sccm. Before the start of each experiment, the system has been purified with argon flow of 1 sLm for 10 minutes, in order to remove residual air from the chamber.

Fig. 2. The scheme of the reactor of glow discharge above water used for AB25 degradation with Ar gas flow.

3. RESULTS AND DISCUSSION

3.1 Determination of the optimal concentration of TiO$_2$

The determination of the optimum catalyst concentration is carried out by varying the catalyst load for the AB25 destruction process. Fig. 3 represents the reduced AB25 concentration C/C$_0$ with C$_0$ = 20 mg L$^{-1}$ for TiO$_2$ concentrations from 0 to 1 g L$^{-1}$. The results show that the degradation increased with treatment time until the load reaches 0.5 g L$^{-1}$. The maximum of degradation (90%) is obtained within 1 h of treatment. On the other side, the plasmachemical treatment without catalyst gave only 78% AB25 degradation during the same treatment time. Beyond this optimal catalyst concentration, the treatment efficiency decreases. These results show that for any concentration higher than 0.5 g L$^{-1}$, other factors can affect the degradation. Probably, increasing the TiO$_2$ concentration leads to the aggregation of the catalyst particles reducing the contact surface between the solution and catalyst. This decreases the number of active sites on the surface, making the UV activation of TiO$_2$ difficult and resulting in a loss of catalyst efficiency.
3.2. Effect of pH

TiO$_2$ has an optimal pH where the best performance of the catalyst can be achieved. This optimal pH value depends on the solution temperature, catalyst structure and solution composition. In order to investigate the influence of initial pH on AB25 degradation by DC glow discharge in the presence of 0.5 g L$^{-1}$ of TiO$_2$, the experiments were carried out at different solution pH values adjusted by H$_2$SO$_4$ and NaOH admixing. The results are shown in Fig. 4. AB25 degradation by DC glow discharge in the presence of TiO$_2$ is enhanced at low pH and monotonically decreases with an increase of the solution pH to 10. This behavior is different than the observed case of treatment without catalyst, where an increase of efficiency of AB25 degradation is observed at low as well as high pH. This fact leads to the conclusion that the best performance of the plasma reactor with catalyst TiO$_2$ can be achieved only at low pH. Therefore, it may be desirable to work in ambient air atmosphere instead of in argon, because of HNO$_3$ and HNO$_2$ production in the solution during treatment. HNO$_3$ and HNO$_2$ formation will lead to an artificial decrease of pH and so will enhance the photocatalyst process efficiency. Nevertheless, investigation of reactor operation in ambient air is out of scope of the present study.

**Figure 3:** Kinetics of AB25 degradation process for different initial concentrations of TiO$_2$ (treated volume 500 mL; initial dye concentration 20 mg L$^{-1}$; pH 6.7).

**Figure 4:** Initial degradation rate of AB25 at various pH values in the presence of 0.5 g. L$^{-1}$ of TiO$_2$ (treated volume 500 mL, initial dye concentration 20 mg L$^{-1}$).
4 CONCLUSION

Non-thermal glow discharge at atmospheric pressure is used as AOP to decompose the widely used Anthraquinonic dye Acid Blue 25 in liquid medium. The process is carried out with and without photocatalyst TiO$_2$ in order to combine the plasma effect with TiO$_2$ activation by UV radiation from the discharge. It was found that the degradation rate is increased in the presence of TiO$_2$, in comparison to discharge alone. As shown by the results, the degradation increases with treatment time until the catalyst load reaches 0.5 g L$^{-1}$. The degradation maximum (90%) is obtained within 1 h of treatment, while the plasmachemical treatment without catalyst only gave 78% AB25 degradation after the same treatment time. Beyond this optimal catalyst concentration, a reduction in the treatment efficiency is observed. The pH has significant influence on the dye degradation and fast AB25 destruction is observed at pH < 3.

REFERENCES