TREATMENT OF ACID BLUE 25 CONTAINING WASTEWATERS BY ELECTROCOAGULATION

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În acest studiu, a fost cercetată electrocoagularea colorantului acid Albastru 25 în soluție apoasă utilizând aluminiu ca anod de sacrificiu. Experimentele au fost realizate pentru o concentrație inițială de 5x10-5M. Performanțele procesului de electrocoagulare au fost evaluate pe baza eficiențelor de mineralizare, respectiv decolorare a soluției de Albastru Acid 25. S-a studiat şi influența unor parametri operaționali, cum ar fi: valoarea inițială a pH-ului soluției, densitatea de curent şi timpul de electrocoagulare, asupra eficienței procesului. Rezultatele arată că, după 18 minute timp de electrocoagulare, s-a atins un grad de decolorare de 99.3% pentru i=100 A/m2 şi un grad de mineralizare de 66% pentru i=50 A/m2.

In this study, the electrocoagulation of the Acid Blue 25 dye in aqueous solution using aluminium as sacrificial anode was investigated. Experiments were carried out with 5·10-5M initial concentration. The performance of the electrocoagulation process was analyzed in terms of mineralization, respectively decolorization of the solution of Acid Blue 25. The influence of several operational parameters, such as: the initial value of the solution pH, the current density, and the time of electrocoagulation, on the efficiency of this process was also studied. Results show that, after 18 minutes of electrocoagulation and at a current density of 100 A/m2, a 99.30% decolourization and a 66.6% COD reduction at a current density of 50 A/m2 have been obtained.

Keywords: electrocoagulation, Acid Blue 25 dye, decolorization, COD reduction

1. Introduction

One of the major challenges facing mankind today is to provide clean water to vast majority of the population around the world. Water quality and

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available quantity are being challenged by increased pollution from point and non-point sources such as industry and agriculture. In this context, there is an obvious need to develop inovative, much more effective and inexpensive techiques for wastewater treatment. [1,2]

The large quantity of organic coloured wastewaters generated by textile, leather, plastic or mineral processing industries became a big environmental problem. It was estimated that aproximatively 1-15% of the dye is lost during dyeing and finishing processes and released, generating large amounts of wastewaters.[3] The characteristics of those wastewaters are either high or low pH (alkaline or acidic media, depending on the process used), high temperature, high oxygen demand (COD), high concentration of colouring material. As a consequence, it is a great need to treat dye effluents before discharging to the recieving water stream to comply with the stringent environmental legislation. [4-6]

There are many procedures to remove dyes from coloured efluents such as: adsorption, precipitation, chemical degradation, photodegradation, biodegradation, chemical coagulation and electrocoagulation. Adsorption and precipitation are very time consuming and costly processes, with low efficiency. Chemical degradation with oxidative reagents such as chlorine is the most effective methods, but it generates some toxic products such as organochlorine compounds. Although biodegradation process is cheaper than other methods, it is less effective because of the toxicity of dyes that have inhibiting effect on the bacterial development. [7,8]

Electrocoagulation is a process that consists in creating metallic hydroxide flocs in the wastewater by electrodissolution of soluble anodes, usually made of iron or aluminium. [9]

The processes during electrocoagulation can be described as follows: at the anode, dissolved metal species destabilise and aggregate particles from suspensions; in addion, they contribute to precipitation and adsorption of dissolved contaminants. At the cathode, the evolved hydrogen bubbles entrap the large dispersed entities and ensure their flotation. In particular, electrocoagulation technique has been shown to be efficient for decolourization of wastewaters from textile and dye industries. If aluminium is used as sacrificial anode, the main reactions occuring at the electrode are as follows: [9,10]

$$\text{Anode: } Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \quad (1)$$

$$\text{Cathode: } 3H_2O_{(l)} + 3e^- \rightarrow \frac{3}{2}H_{2_{(g)}} + 3OH^-_{(aq)} \quad (2)$$

Al^{3+} and OH^- ions generated by electrode reactions (1) and (2) react to form various monomeric species such as: $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$, as well as polymeric species such as: $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$. These intermediate species convert

finally into $Al(OH)_{3(s)}$; the overall process of flocks formation may be described as:

$$Al^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + 3H^{+}_{(aq)} \quad (3)$$

The precipitation process has complex reaction kinetics. [11-13]

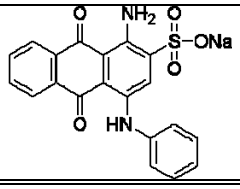
In this study, the efficiency of electrocoagulation for wastewaters containing Acid Blue 25 dye using aluminium as sacrificial anodes and mild steel as cathodes was investigated.

2. Materials and methods

The dye containing aqueous solution having $5 \cdot 10^{-5}$M Acid Blue 25 concentration was prepared using Acid Blue 25 reagent provided by Sigma-Aldrich and double distilled water. Several chemical data about this antraquinone dye are shown in Tabel 1.

Tabel 1.

Chemical data of Acid Blue 25 dye

Dye	Chemical structure	Chemical formula	λ_{max}(nm)	M.W.	C.I.
Acid Blue 25		$C_{20}H_{13}N_2NaO_5S$	600	416.38	62055

λ_{max} - the wavelength where the maximum in the absorption uv-vis spectra is recorded.
C.I. – Color Index

Experiments were carried out at laboratory scale in an electrocoagulation reactor made of theromoresistent glass equipped with four electrodes, two anodes and two cathodes with identical dimensions. Both aluminium anodes and mild steel cathodes were made from plates with dimensions 4.5×5.5×2 cm and the distance between the electrodes was 2.5 cm. At the begining of the each run, the electrodes were placed in 700 mL dye solution. The current density was kept constant using a Mastech HY3005D DC power supply.

At the end of the electrocoagulation experiments, the solutions were filtred and their colour and COD were analysed. The dye concentration was determined using a UV-Vis spectrophotometer (Jenway 6400) at 600 nm wavelength. For COD determination "open reflux method" was applied. Most types of organic matter are oxidized by boiling by a boiling mixture of chromic and sulfuric acids. The sample is refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulphate to determine the amount of $K_2Cr_2O_7$

consumed and the oxidizable organic organic matter is calculated in terms of oxygen equivalent. [14]

The acid blue 25 removal efficiency after electrocoagulation treatment was determined using the following equation:

$$R(\%) = \frac{C_0 - C}{C_0}$$

Where: C_0 and C represent the concentrations of dye or COD before and after electro coagulation respectively.

3. Results and Discussions

3.1. Effect of initial pH

The pH represents an important parameter that influences the efficiency of the electro coagulation process. To examine its effect, the pH of the samples was adjusted to the desired value for each experiment by adding sodium hydroxide or sulphuric acid solution. [14]

Fig. 1 shows the effect of initial pH on decolorization efficiency for aluminium electrodes, as it can be seen, the decolorization efficiency decreases slowly with the increase of the pH value in the range of 2-10. At pH values above 9, the efficiency decreases rapidly. The maximum value (99.3%) for color removal was obtained at pH=2, and the minimum (87.7%) for pH=10. Increasing the initial pH from 2 to 4 and keeping the electro coagulation time constant at 18 minutes leads to a decrease of the decolorization from 99.3% to 95.9%.

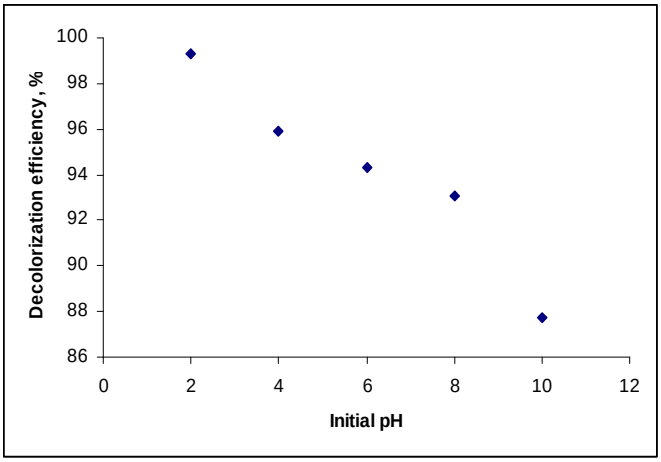


Fig. 1. Effect of initial pH on decolorization efficiency, *electro coagulation time* = 18 min, C_0 =5*10^{-5} M, *i* = 100A/m^2, *stirring rate* 200 rpm, *aluminium anode*, initial *pH*=2-10

During the electro coagulation process, pH varies as can be seen in Fig. 2. The pH changes during electro coagulation depends on the initial pH value. For

initial pH values between 4 and 9, the solution stabilizes at nearly constant value around 9 due to buffering capacity of complex nature of aqua $Al^{3+}/Al(OH)_3$ system. [16]

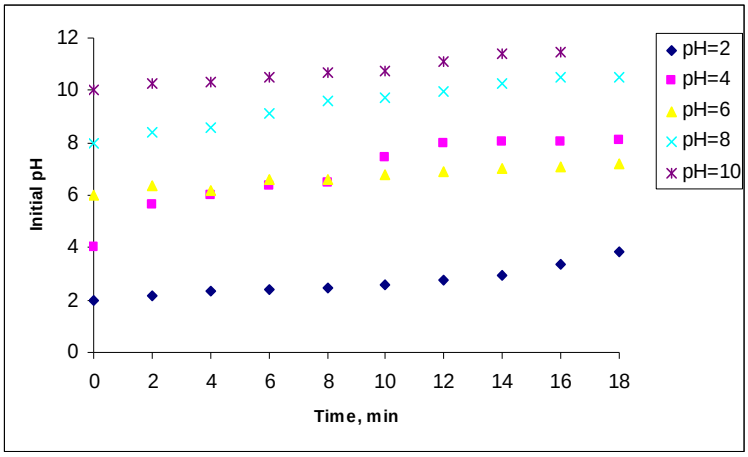


Fig. 2. Change of the pH value during electro coagulation, *electro coagulation time* = 18 min, $C_0 = 5*10^{-5}$ M, $i = 100 A/m^2$, *stirring rate* 200 rpm, *aluminium anode*

3.2. Effect of electro coagulation time on color removal

The electro coagulation time is another parameter that has influence on the treatment efficiency on the electro coagulation process. Fig. 3 presents the relationship between decolorization efficiency and electro coagulation time. According to experimental results, after 2 minutes of operating time was achived a 31% color removal efficiency and after 18 minutes was achieved a nearly complete decolorization (91.70%) of Acid Blue 25 solution.

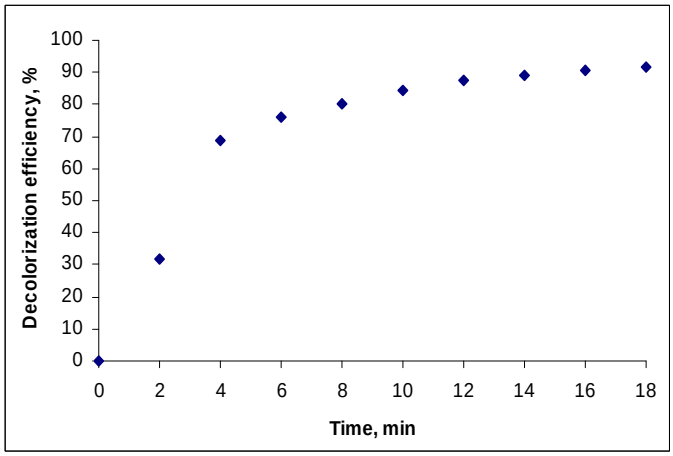


Fig. 3. Effect of electro coagulation time on color removal efficiency $C_0 = 5*10^{-5}$ M, $i = 50 A/m^2$, *stirring rate* 200 rpm, *aluminium anode*, *pH*=2

3.3. Effect of current density on color removal efficiency

The current density is the most important parameter in all electrochemical processes. The current density determines the amount of Al^{3+} ions released from the electrodes.[16] In order to investigate the effect of this parameter on color removal efficiency, the experiments were performed at different current densities in the range of 50-200 A/m^2.

As it can be seen from Fig. 4, as the current density increased from 100 to 200 A/m^2, the decolorization efficiency did not change significantly. At 100 A/m^2 the efficiency was 99.3%, and at 200 A/m^2 was 99.8%. Thus, it may be considered that a minimum value of 50 A/m^2 is required for good decolorization efficiency, of 91.7%.

Difference between color removal efficiency obtained at 50 A/m^2 and the one obtained at 100 A/m^2 can be explained as follows: by increasing the current density, the amount of dissolved aluminum increases and consequently, it produces more the hydroxy polymers; thus, the attraction of the dye impurities is also increased. [15]

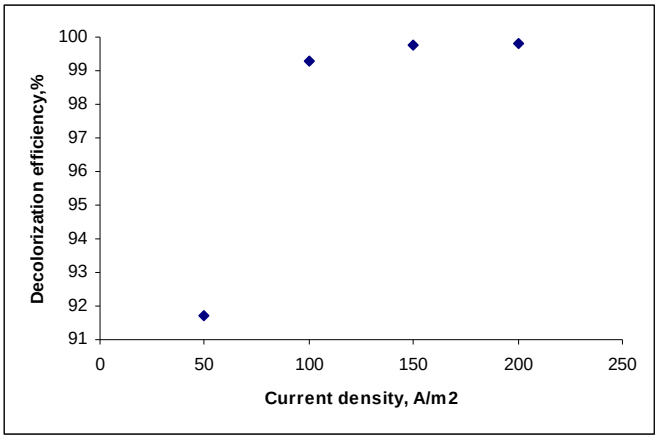


Fig. 4. Effect of current density on the decolorization efficiency, C_0 = 5*10^{-5} M, *stirring rate* 200 rpm, *aluminium anode*, *pH*=2

3.4. COD removal efficiency

The diminution of color does not necessary imply reduction of COD values. The color of solution may be removed by dye degradation, formation of organic/organometallic complexes, and/or a combination of two procedures. Complete degradation of a dye is expected to reduce the COD most effectively. [3] In order to establish electro coagulation efficiency regarding COD reduction a

300 mgO_2/L solution was prepared.. In Fig. 5 the variation of COD reduction efficiency during electro coagulation process is shown. It can be observed that after 2 minutes of electro coagulation with 50 A/m^2, a 33.3% COD removal efficiency was obtained, while after 18 minutes was already achieved a 66.6% COD removal efficiency.

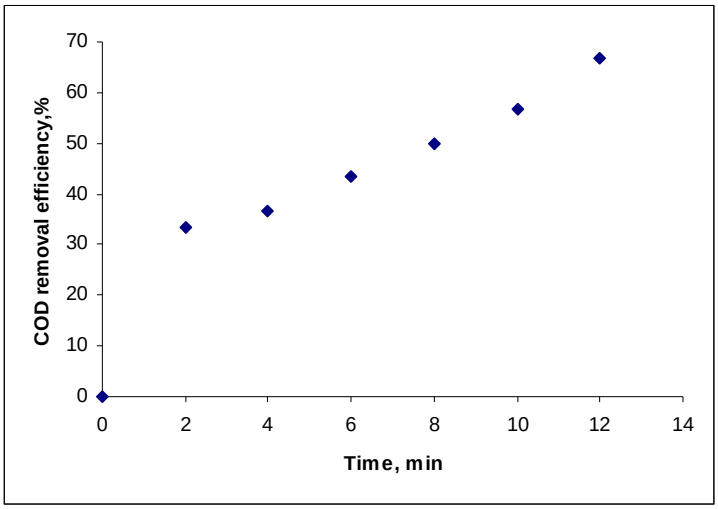


Fig. 5. COD removal efficiency variation during electro coagulation process, C_0 =300 mgO_2/L, *stirring rate* 200 rpm, *aluminium anode*, *pH*=2

4. Conclusions

The electro coagulation process was successfully applied to treat a wastewater containing Acid Blue 25 dye. Our experiments have demonstrated that parameters like: initial effluent pH, current density applied, electro coagulation time, have significant influence on color removal efficiency.

During the study of the electro coagulation process efficiency regarding COD reduction it was found that COD values drop from 300 to 100 mgO_2/L after 12 min. of processing,. The best conditions in order to achieve a 99.3% decolorization efficiency were: current density 100 A/m^2, initial pH=2, operating time 18 minutes.

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