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ELECTROCHEMICAL TREATMENT OF ACID WASTEWATERS CONTAINING METHYLORANGE

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ABSTRACT. The degradation process of solutions containing Methylorange using electrochemical measurements, on Ti electrode was studied. In order to estimate the contribution of pure adsorption, behavior of Methylorange in open circuit was investigated. The color removal (CR) due to adsorption was estimated at 8.86%. From the anodic polarization, Ti electrode in the blank solution of 0.1 M HCl containing 0.035 M NaCl (ASB) or dye solution of 0.1 M HCl containing 0.035 M NaCl and Methylorange (ASC) a different behaviour was observed. In cathodic polarisation case, the ASC behavior being completely different towards ASB. It can be concluded that the polarisation curve for ASC in the potential range of-426mV to -900mV can be attributed to the dye reduction; thus the color removal was estimated at value of 23.6%. Galvanostatic method to evaluate the effect of current density on solution discoloration process was applied. The color removal at 250min increases of the value of 68.4% calculated at current density of 5mA/cm^2 until the value of 73.4% at current density equal to 15 mA/cm^2. Degradation process of Methylorange follows a first order kinetics reaction. Rate constants increase with the increase of current densities and their values are: 0.0047min^{-1}, in the case of degradation at a current density of 5 mA/cm^2, and 0.006min^{-1}, in the case of degradation at a current density of 15mA/cm^2.

Keywords: Methylorange, electrochemical degradation, titanium electrode, kinetics process

INTRODUCTION

Wastewaters contain a range of organic pollutants (about 10.000 different dyes) such as acids, alkalies, solid particles, toxic compounds and dyes which even in low concentrations must be removed. Synthetic dyes are used in textile industry (60%), paper industry (10%), plastic manufacture (10%) and it is estimated that 10-15% of the dyes is lost during fabrication processes. It is reported that approximately 5 tonnes of dyes discharge from coloration industries every year. Furthermore, some azo dyes, their precursors and a number of their reaction products are carcinogenic.

Due to environmental requirements in recent years, different techniques have been used for removal of such waste as adsorption, oxidation, reduction and electrochemical reactions. To eliminate dyes from aqueous coloured

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effluents and reduce their ecological impact, several biological, physical and chemical methods have been proposed: biological treatment [1-4], physical or chemical flocculation, electrofilteration, membrane filtration, electrokinetic coagulation [5-8], adsorption and precipitation [9-11] and other oxidative/ reductive chemical and photochemical processes [12-17].These methods have individual advantages, but also have some constrains when they are applied individually. Development of the appropriate techniques for treatment of dye wastewater is important for the natural waters protection. Other techniques including radiation and discoloration with ozone in combination with H_2O_2 are also employed [18].

Electrochemical treatments have certain advantages by comparison with other methods, namely: wide application, simple equipment, easy operation, lower temperature requirements and no sludge formation. It is important to select the proper electrode material, because the reaction products strongly depend on those materials as well as the experimental conditions. Selection of a proper electrode material is vital for an efficient and enduring operation of an electrode. Several researchers have tested the feasibility of electrochemical degradation using various electrode materials:glassy carbon, Pt, Pt+Ir, Ti, Al, Co+Pd, Fe, IrO_2, PbO_2, SnO_2, diamond paste doped with boron [19-33].

The objective of this research was to evaluate the electrochemical discoloration process of solutions with Methylorange content by direct electrochemical degradation, with an electrode made of Ti using a synthetic solution with Methylorange disolved in 0.1 M HCl aditivate with 0.035 M NaCl.

RESULTS AND DISCUSSION

The Methylorange was the organic compound studied, whose structure and spectrum are shown in Figure 1. This azo dye was purchased from Fluka and used as received. All others chemical compounds used were of analytical type. As it can be seen from Figure 1, the maximum absorption for dye in the visible region was at 502 nm. Beside the main peak, other two characteristic absorption peaks at the wavelength of 273 and 321 nm in the ultraviolet region, were identified.

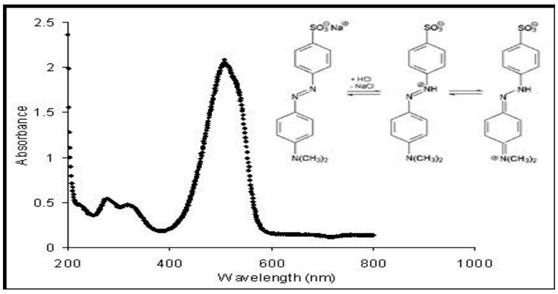


Figure 1. UV-Vis spectrum of initial Methylorange solution and molecular structure of Methylorange in acid medium aditivate with NaCl.

Study of Methylorange adsorption process

In order to estimate the contribution of pure adsorption, behaviour of Methylorange in open circuit was studied. In the open circuit, in ASB solution, the potential is stabilized after approximately 10 min, being of -306 mV at the end of the experiment (Figure 2 as an example). In the dye presence (ASC), within the first 25 minutes, the potential changes are major and can be attributed to a tendency of adsorption-desorbtion of dye on the titanium surface with the formation of a non-adherent and ruggedness film, which is interposed at the metal / solution interface. After 40 min the potential is stabilized, reaching the value of -266mV, at the end of the experiment. The potential shift to less negative values can be associated with the formation of a relative, uniform film, which is due to Methylorange adsorption on the titanium surface. This adsorption has a weak effect on the discoloration and it results from the fact that the titanium surface texture shows affinity for Methylorange, which can be adsorbed on the substrate through free electrons from azot atoms.

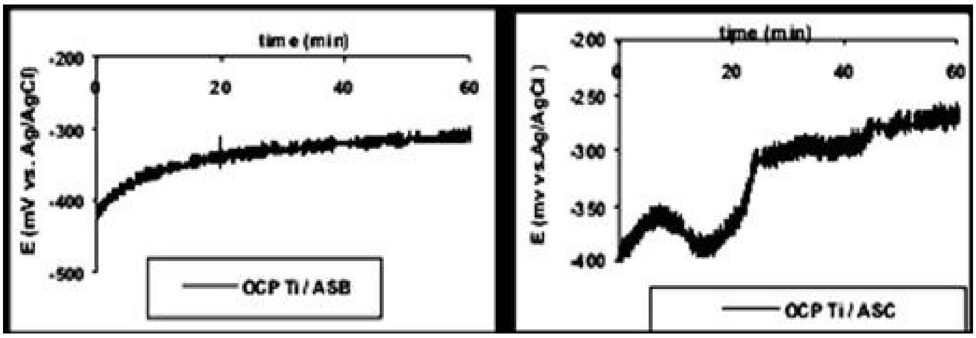


Figure 2. The potential dependence of time registered in open circuit in the absence and in the presence of Methylorange in 0.1 M HCl / 0.035 M NaCl solution.

UV-Vis spectra registered in open circuit, at the initial time and after 60 minutes are shown in Figure 3. A decrease of absorbance value from 2.03 to 1.85 which is attributed of Methylorange adsorption on the titanium surface was observed. Color removal (CR) due to the pure adsorption was determined using the following equation:

$$CR = (1 - A / A_0) \cdot 100 \tag{1}$$

where: A_0 and A represents the initial absorbance and absorbance at a moment “t”, 60 min in this case, respectively.

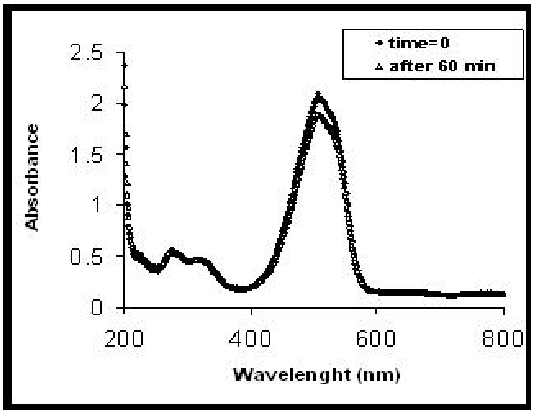


Figure 3. UV-Vis spectrum of Methylorange solution registered in open circuit.

The colour removal was 8.86% at an initial Methylorange concentration of 0.15 M.

Study of anodic and cathodic processes

The polarization curves of ASB and ASC on Ti electrode are shown in Figures 4 and 5. From the anodic polarization (Figure 4), it can be observed that Ti has a different behaviour in the blank solution and dye solution, respectively.

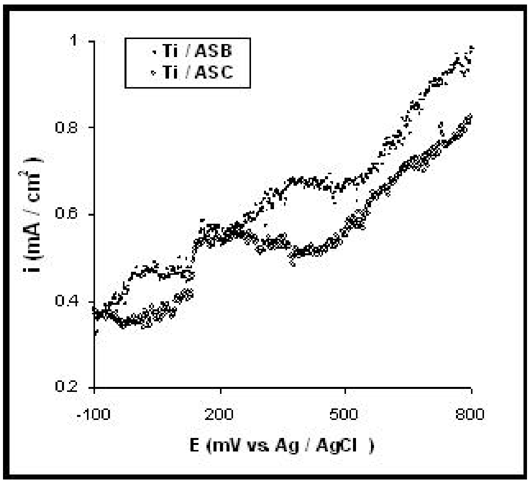
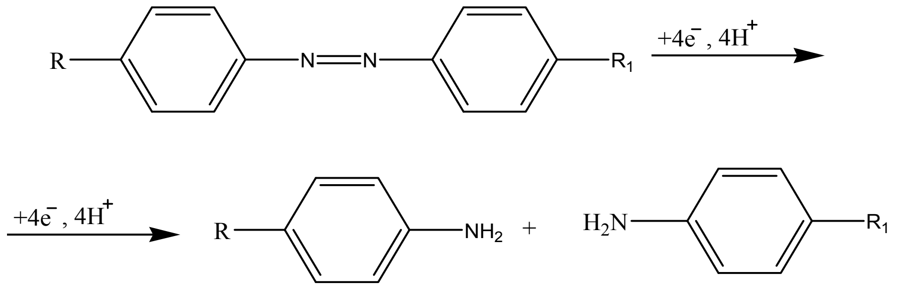


Figure 4. Anodic polarization curves of ASB and ASC on Ti electrode.

For the titanium electrode ASC has a major effect on the reaction in the range of positive potential; thus the potentials were shifted to less negative values, and current densities decreased. These changes may be associated with the formation of a film on the titanium surface, which modified the electronic change at metal / electrolyte interface. The anodic peak which appears at 200 mV is not attributed to an electro-oxidation, but to a tendency of titanium passivation. In spectrum UV-Vis the absorbance level was maintained on the initial value of 2.03. From cathodic polarization curve, a different behaviour of titanium electrode in ASC solution, by comparison with the ASB solution was observed. In the presence of Methylorange the current densities increased from a value of potential equal to -430 mV to -556 mV. This evolution could be attributed to the fact that the cathodic process is too slow to be controlled, therefore no characteristic peaks are obtained. Literature data [33] mentioned on glassy electrode the existence of two reduction peaks of azo group, first bielectronic at ε = - 425 mV / Ag, AgCl, with the formation of hydrazoderivate (according to Scheme 1), and the second tetraelectronic, at more negative potentials, up to -875 mV / Ag, AgCl leading to adequate amines according to Scheme 2:

$$—N{=}N— \xrightarrow{+\,2e^-,\ +\,2H^+} —NH—NH—$$

Scheme 1



Scheme 2

Therefore, the ASC behaviour being completely different towards ASB, it can be concluded that the polarisation curve carriage for ASC in the potential range of -426 mV to -900 mV can be attributed to dye reduction.

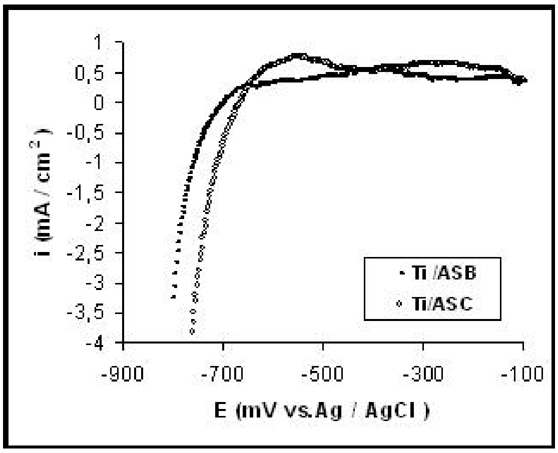


Figure 5. Cathodic polarization curves of ASB and ASC on Ti electrode.

UV-Vis spectrum of Methylorange solution registered at the end of the cathodic process is shown in Figure 6. A decrease of the absorbance from the 2.03 to 1.55 was observed, therefore the color removal calculated using the equation (1) has been calculated 23.6%.

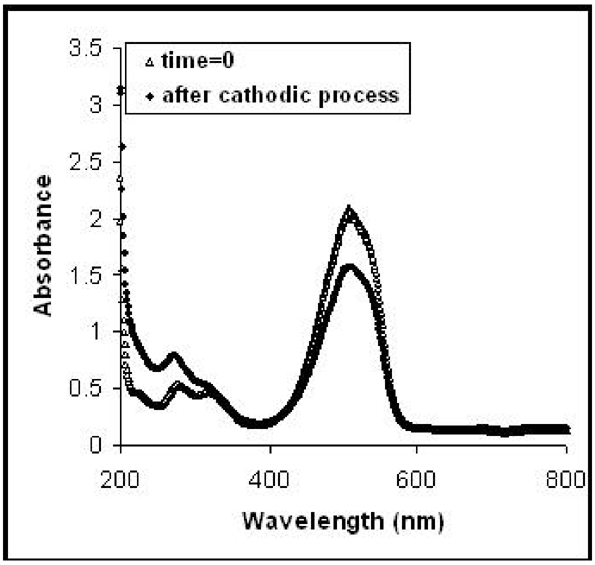


Figure 6. UV-Vis spectrum of Methylorange solution registered after cathodic process.

Study of discoloration process at different current densities

Galvanostatic technique was applied to evaluate the current density effect on discoloration process of dye solution. Electrochemical measurements, for two different current densities 5 mA/cm^2 and 15 mA/cm^2, respectively, were carried out. Each experiment ran for a time of 250 min, samples being analysed at certain time intervals, namely: 20 min, 40 min, 60 min, 80 min, 100 min, 150 min, 200 min, 250min. At specified time intervals absorbances values were evaluated. The degradation process of dye was followed by means of color removal (CR) values, which were calculated using equation (1). UV-Vis spectra of discolorated Methylorange at different current densities, 5 mA/cm^2 and 15 mA/cm^2 respectively, applied for 250 min, at room temperature are shown in Figures 7 and 8.

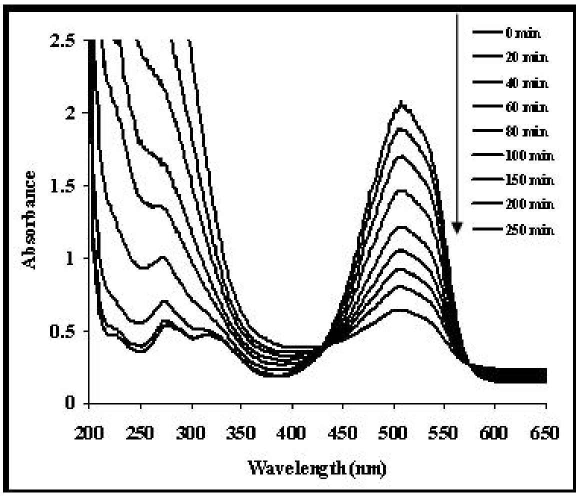


Figure 7. UV-Vis spectrum of Methylorange solution registered for current density of 5 mA/cm^2, for 250 min.

Figures 7 and 8 show that absorbance decreases in time, on the same current density, which demonstrates Methylorange degradation and discoloration. Absorbance values, at the same reaction time, present a significant decrease, hence a greater rate of degradation, with the current density increase. This may be shown by determining the colour removal (CR) using the equation 1, at time values when the spectral recordings were performed. Dependence of colour removal of time, at different current densities, is shown in Figure 9. Thus, the color removal at 250 min increases from 68.4% calculated at current density of 5 mA/cm^2 to the value of 73.4% at a current density equal to 15 mA/cm^2.

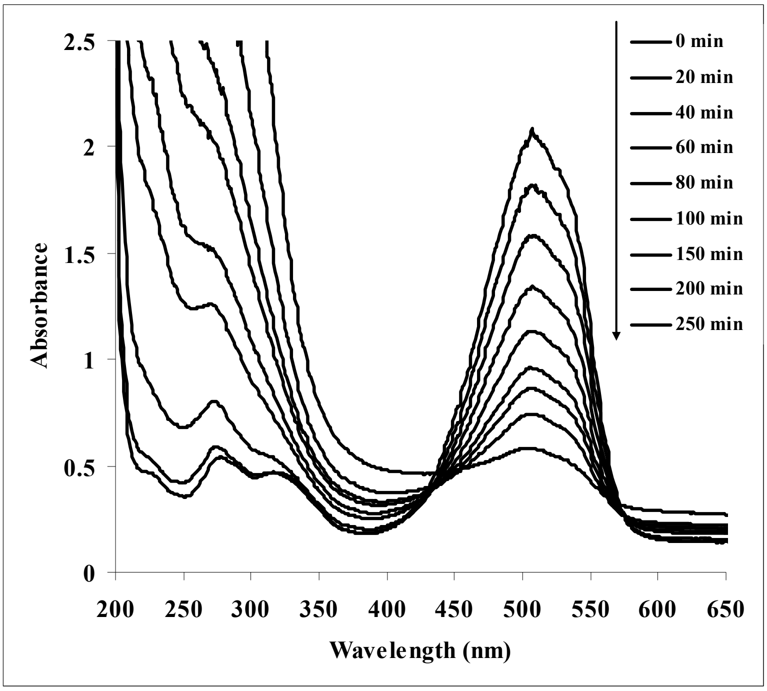


Figure 8. UV-Vis spectrum of Methylorange solution registered for current density of 15 mA/cm^2, for 250 min.

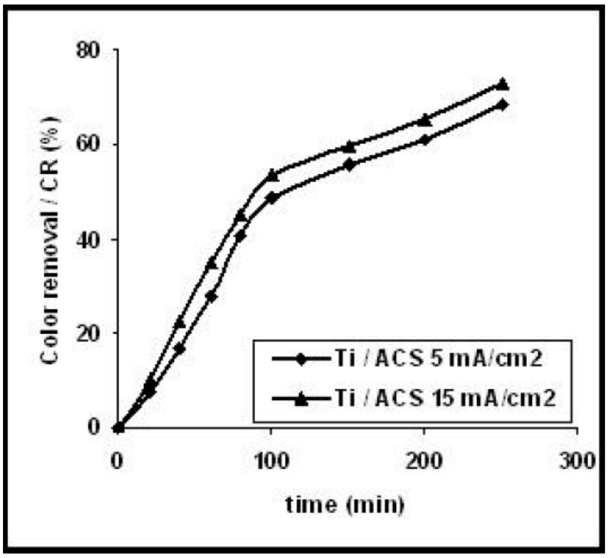


Figure 9. Dependence of color removal on time at different current densities.

Kinetics of Methylorange degradation

1). Determination of apparent rate constant

In general, degradation curves of dyes follow a first order kinetics reaction. The first order kinetic can written as follows:

$$-d[dye] / dt = k_{ap}[dye] \quad (2)$$

where: k_{ap} is apparent rate constant.

Integrating the equation (2), a first order kinetics equation was obtained:

$$\ln [dye]_0 / [dye]_t = k_{ap} \times t \quad (3)$$

Straight line plots $\ln [dye]_0 / [dye]_t = f(t)$ allow us to obtain the apparent rate constants for Methylorange, at both current densities. The absorbance is directly proportional with the concentration of Methylorange degraded; equation (3) can be written as:

$$\ln A_0 / A_t = k_{ap} \times t \quad (4)$$

where: A_0 and A represent the initial absorbance and absorbance at a given “t” time, respectively.

2) Verification of first order kinetics

a) Absorbance variation in time

The variation of absorbances resulted in the given experimental conditions were be evaluated, in time and as a function of the current densities whereat the degradation process of Methylorange had been studied. Absorbance versus time evolutions are shown in Figure 10.

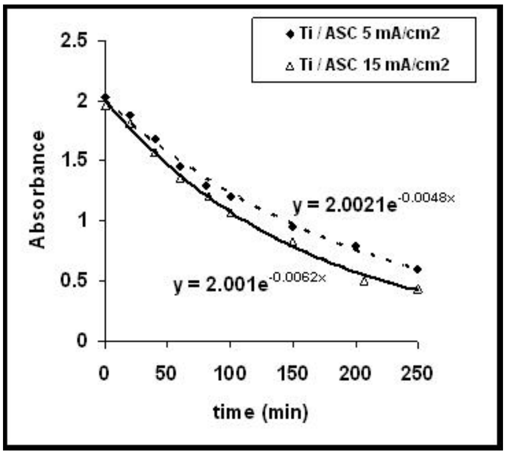


Figure 10. Absorbances variation during Methylorange degradation at different current densities applied.

It was noticed that, for the same current density, absorbance decreases exponentially with time, according to a relation $A = A_0 \exp(-kt)$, which corresponds to a first order kinetics, related to Methylorange degradation. From Figure 10, it can be seen that apparent rate constants values are: 0.0048 min^{-1}, in the case of degradation at a current density of 5 mA/cm^2, and 0.0062 min^{-1}, in the case of degradation at a current density of 15 mA/cm^2.

b) Integrated equation constant rate verification. Rate constants determination

The curves $\ln A_0 / A = f$ (time) obtained from experimental data during the degradation process of Methylorange are shown in Figure 11. From Figure 11, it can be noticed that straight lines were obtained, passing through the origin and whose slope is $dy / dx = k_{ap}$;it can be observed that the value of R^2 is approximately equal 1;this proves that the degradation of ASC respects the first order kinetic. Rate constants (k_{ap}) increase with the increasing of current densities and have values ranging of 0.0047min^{-1}, in case of degradation at a current density of 5 mA/cm^2 and 0.006 min^{-1}, in case of degradation at a current density of 15 mA/cm^2, respectively.

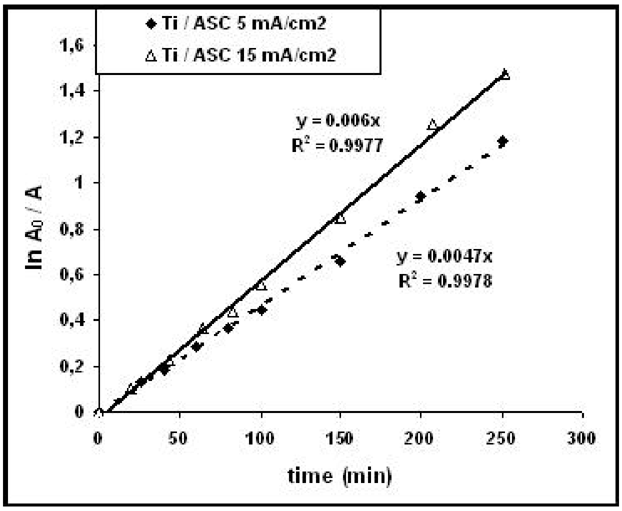


Figure 11. Diagrame corresponding with the first order kinetics in case of Methylorange degradation at different current densities.

From Figures 10 and 11, it can be observed that are obtained values of apparent rate constants approximately equal, for the same values of current densities; so it can be concluded that in the case of ASC degradation on Ti, it is respected the first order kinetics.

CONCLUSIONS

Electrochemical degradation process of a synthetic solution with Methylorange disolved in 0.1 M HCl solution aditivate with 0.035 M NaCl was studied.

In order to estimate the contribution of pure adsorption, behaviour of Methylorange in open circuit was studied. UV-Vis spectra registered in open circuit, at the initial moment and after 60 min had shown a decrease of the absorbance from t2.03 to 1.55, which was atributed to Methylorange adsorption on the titanium surface. The color removal (CR) due to adsorption was calculated to be 8.86% for a concentration of 0.08 mM Methylorange in ASB.

For the anodic polarization, observed that Ti in the blank and dye solution has a different behaviour. The anodic peak that appeared at 200 mV was not attributed to an electro-oxidation, but to a tendency passivation of titanium. In spectrum UV-Vis the absorbance level was maintained at the initial value of 2.03.

In cathodic polarisation case, the ASC behavior being totaly different towards ASB, it can be concluded that the polarisation curve carriage for ASC in the potential range of -426mV to -900mV can be atributted to the dye reduction. UV-Vis spectrum of Methylorange solution registered at the end of cathodic process had shown a decrease of the absorbance from 2.03 to 1.85; thus, the color removal was calculated to be 23.6%.

Galvanostatic technique was applied to evaluate the current density effect on discoloration process of dye solution. Thus, the color removal at 250 min increases from 68.4% calculated at current density of 5 mA/cm^2 to the value of 73.4% at a current density equal to 15 mA/cm^2.

The degradation process of Methylorange in ASB at studied current densities, 5 mA/cm^2 and 15 mA/cm^2, respectively, follows the first order kinetic reaction. Rate constants (k_{ap}) increase with the increase of current densities and their values are: 0.0047 min^{-1}, in the case of degradation at a current density of 5 mA/cm^2, and 0.006 min^{-1}, in the case of degradation at a current density of 15 mA/cm^2.

EXPERIMENTAL SECTION

Electrochemical measurements were carried out using a standard cell, with a working electrode made of Ti (the surface area of 2 cm^2), an auxiliary electrode in the form of glossy platinum plate (the surface area of 1 cm^2) and an Ag/AgCl electrode was used as a reference electrode. The electrode made of titanium was polished with very fine metallographic paper, washed with distilled water, degreased with acetone and dried. By electrochemical measurements azo dye Methylorange was degraded using a titanium electrode. The electrochemical behaviour of Methylorange was evaluated by potentiostatic method using computerized electrochemical equipment VoltaLab 40 with software. The electrochemical degradation process was examined at positive and negative polarization, respectively, including open circuit condition, in a range of potential between -200mV and 800mV for the anodic process, and between -200 mV and -1000mV for the cathodic process, applying a scan rate of 10 mV/s. Galvanostatic technique was applied to evaluate the effect of current density on dyeing solution discoloration process. A SourceMeter 2420 3A potentiostat / galvanostat was used to controll the current density. The experiments were performed for two different current densities, 5 mA/cm^2 and 15 mA/cm^2, respectively. Each experiment ran for 250 min, samples being collected at certain time intervals. At specified time intervals absorbance values were assessed using an UV-Vis spectrophotometer, Varian Cary 50 with software.Temperature was maintained at 20ºC. Electrochemical solutions tested contained: acid blank solution composed of 0.035M NaCl, 0.1M HCl (ASB) and dye solution, which had the following components: 0.08mM Methylorange, 0.035M NaCl, 0.1M HCl (ASC).

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