The discoloration of waters containing Congo red using Fenton reagent was studied at different pH values and different temperatures. The results reported a significant discoloration after 5 min, at pH = 3.50 and temperature of 55°C. In these conditions, it was obtained a color removal (CR) equal to 75.6 ± 5 and a relative discoloration rate of 14.12 %/min. Apparent activation energy was determined using the Arrhenius equation. The value of E was determined as being equal to 85.9 kJ/mol. The activation enthalpy (ΔH) and the activation entropy (ΔS) were calculated from the diagram of the transition state. The value of the enthalpy (83.44 kJ/mol) indicates an endothermic reaction. Positive values of entropy (30.78 J/mol) suggest that entropy increases upon achieving the transition state, which often indicates a dissociating mechanism.

Keywords: Congo red; Fenton reagent; discoloration process; UV-Vis spectra

Azo dyes are widespread environmental pollutants related to many important industries such as textile, printing, and cosmetic manufacturing. With the increasing production of these dyes, the discharge of dye effluents at high concentration and strong colour has caused serious environmental pollution because many of these dyes are toxic and recalcitrant to biodegradation [1]. Many different approaches have been proposed to remove dyes from aqueous solution such as adsorption and precipitation, chemical and electrochemical oxidation, chemical coagulation and biological anaerobic/aerobic decomposition [2-10]. Recently, advanced oxidation processes have been proposed as offering promise for the treatment of wastewater containing Congo red by Fenton oxidation process.

Experimental part

Materialiale and methods

The azo dye, Congo red, was provided Fluka and used as received. UV-Vis absorption spectrum and molecular structure of Congo red are illustrated in figure 1. Hydrogen peroxide (30% w/w), ferrous sulfate (FeSO₄•7H₂O), sulfuric acid, were purchased from Fluka or Aldrich. All the chemicals were analytical grade and used directly without any further purification. All sample solutions were prepared with deionized water.

Experimental determinations were performed for aqueous solutions of Congo red, with initial concentrations of 3.558×10⁻⁵ mol L⁻¹. The added ferrous sulfate concentration in the system was 4.17×10⁻⁵ mol L⁻¹ and the hydrogen peroxide concentration was 1.76×10⁻³ mol L⁻¹. Experiments were analysed at different initial values of pH such as: 2.51, 3.02, 3.50, 3.93 and at different temperatures: 25, 35, 45, 55°C . For each experiment, Erlenmeyer glass, equipped with refrigerator bottom, which contained 100 mL solution of ferrous sulphate and Congo red subject to degradation were placed in a thermostat water bath with constant temperature and stirred by a magnetic stirrer. The pH value of each reaction solution was adjusted to the desired value by using the prepared 5% sulfuric acid solution, and was measured with a model Consort C533 pH meter. The reactions were initiated by adding calculated amounts of hydrogen peroxide to the reactor. Samples were taken out from the beaker periodically using a pipette and were immediately analyzed by spectrophotometry and then returned back to the beaker.

Analytical methods

The pH value of the solutions was measured by using a digital pH meter. Before the measurement, the pH meter was calibrated with standard buffers of 4.0, 7.0 and 10.0 (25°C). The UV–Vis spectra of Congo red were recorded from 200 nm to 800 nm using a UV–Vis spectrophotometer.
(Varian Cary 50 Bio) with a 1 cm path length spectrometric quartz cell. The absorption spectrum of Congo red in aqueous solution was recorded and it was found that the maximum wavelength was at 497.

**Results and discussion**

UV-Vis spectrum recorded before the addition of hydrogen peroxide is shown in figure 1. It can be observed the presence of two maximum absorption: one in the visible region at a wavelength of 497 nm and the other at 318 nm. The peak at 318 nm was attributed to the absorption of the $\pi \rightarrow \pi^*$ transition related to the aromatic rings bonded to the azo group in the dye molecule. Absorbance at 497 nm is due to the color of dye solution ($n \rightarrow \pi^*$ transition from $\overset{-}{\text{N=}}\text{N}$ group) and is used in order to monitor the compound discoloration. Therefore, the discoloration of azo compound at different reaction times was monitored by registering absorbance at $\lambda_{\text{max}}=497$ nm.

![UV-Vis spectrum of dye Congo red registered before the addition of hydrogen peroxide](image1)

**Effect of pH value on the discoloration process**

The effect of pH on the discoloration of waters containing azo compound Congo red in the Fenton oxidation process was studied at different values: 2.51; 3.02; 3.50; 3.93 and at temperature of 25°C. The UV-Vis spectra were recorded for 130 min. The UV-Vis spectrum obtained for the discoloration process at the temperature of 25°C and pH = 3.50 is shown in figure 2. For other pH values, similar spectra were obtained.

![UV-Vis spectrum recorded during the discoloration process of waters containing azo dye Congo red at pH = 3.50 and temperature of 25°C](image2)

In all cases, it was observed that the absorbance decreased in time, the most pronounced decrease being recorded at a pH value of 3.50, after 130 min from the initiation of the experiment (fig.3). In order to determine the real absorbance, the baseline was considered to be at a value of 0.45 and the following formula it was used:

$$A_n = A_t - 0.45$$  \hspace{1cm} (1)

where:

$A_n$ is the real absorbance;

$A_t$ is the absorbance registered at reaction time “t”.

![Absorbances variation in time for the discoloration process of waters containing azo dye Congo red at 25°C and different pH values: 2.51; 3.02; 3.50; 3.93](image3)

The color removal (CR) was determined using the following formula:

$$\text{CR} (%) = \left( 1 - \frac{A_r}{A_{r0}} \right) \cdot 100$$ \hspace{1cm} (2)

where $A_r$ and $A_{r0}$ represents the initial real absorbance and respectively the real absorbance at the moment of spectrum registering.

CR variation in time is shown in figure 4. From the inserted graph in figure 4, which represents the CR variation as function of pH, at 130 min, it can be observed that CR reaches the value of 70.6% at pH = 3.50. Thus, this pH value can be considered optimal for the discoloration process of waters containing Congo red at temperature of 25°C.

![Color removal variation of waters containing Congo red depending on time at different pH values: 2.51; 3.02; 3.50; 3.93](image4)

**Determination of discoloration rate**

In order to determine the relative discoloration rate (DR) the values obtained for CR in the time intervals between 0 min - 40 min and 40 min – 130 min were linearized. Thus, from the slopes of straight lines $dy/dx = d(CR)/dt$ obtained, the discoloration rates (DR) were determined as being the percentage of degraded Congo red in a minute (%/min). Relative discoloration rates were obtained from the arithmetic average of the rates values indicated by equations inserted in figure 5. From figure 6a it can be seen that, within the first 40 min, the discoloration rate has the highest value of 0.9529 %/min, at pH = 3.50 and the lowest of 0.455 %/min, at pH = 2.51. At higher time intervals (fig. 6b), a decrease in DR compared with the phytate at the time interval between 0 and 40 min is observed. Therefore, the average values of DR, that satisfy both time intervals were determined (table 1).

Using obtained values for DR, it was calculated the theoretical colour removal at 130 min, obtaining relatively
appropriate values to the experimental results. In order to fit the results in a margin of error accepted in both cases, there were determined the average values of CR (table 1).

Determination of the activation parameters: \((E_a)\); \((\Delta H^0)\); \((\Delta S^0)\)

The UV-Vis spectra were recorded for the discoloration process of waters containing azo dye Congo red, at different temperatures and \(pH = 3.50\) (fig.6). It was found that with the increasing temperature, the time at which it is obtained a value of 75% for CR, decreases significantly from 130 min (at 25 °C) to 5 min (at 55 °C).

The discoloration rates (DR % / min), whose values are presented in table 1, were also determined. It is noted that DR increases exponentially with the temperature (fig. 7a).

Thus, the apparent activation energy \((E_a)\) was determined using the logarithmic form of Arrhenius equation:

\[
\ln DR = \ln A - \frac{E_a}{RT}
\]

where:
- DR – relative discoloration rate (% / min);
- A – preexponential factor;
- \(E_a\) – apparent activation energy (kJ/mol);

From the graphical representation of \(\ln DR = f (1/T)\), a straight line with the slope \(d(\ln DR) / d(1/T) = E_a / R\) was obtained (fig.7b); thus, the value of the apparent activation energy was determined as being equal to 85.9 kJ/mol.

This value of activation energy is much greater than other azo dyes oxidized with Fenton reagent. For example, in case of metilorange, in similar experimental conditions, an activation energy value equal to 22.09 kJ/mol has been reported [13]. Hence, it is concluded that the oxidation process of Congo red in the presence of Fenton reagent with difficulty occurs at low temperatures. However, the method can be more effective by raising the temperature to 55 °C, when the discoloration time decreases of 26 times.

**Table 1**

<table>
<thead>
<tr>
<th>Temperature 25 °C</th>
<th><strong>pH = 3.50</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH</strong></td>
<td><strong>Time = 130 min</strong></td>
</tr>
<tr>
<td>2.51</td>
<td>54.1 ± 1.3</td>
</tr>
<tr>
<td>3.02</td>
<td>69.2 ± 4</td>
</tr>
<tr>
<td>3.50</td>
<td>75.6 ± 5</td>
</tr>
<tr>
<td>3.93</td>
<td>61.2 ± 3</td>
</tr>
</tbody>
</table>

**Fig. 5.** Fitting of experimental data for the DR determination (% / min): a – for the time interval between 0 and 40 min; b - for the time interval between 40 and 130 min

**Fig. 6.** UV-Vis spectra recorded for the discoloration process, at pH = 3.50 and the different temperatures: a - 35°C; b - 45°C; c - 55°C
The activation enthalpy ($\Delta H^0$) and the activation entropy ($\Delta S^0$) were calculated from the diagram of the transition state using the following equation:

$$\ln \frac{DR}{T} = \ln \frac{R}{N_A} + \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (4)$$

On the other hand, the plots of $\ln (DR/T)$ against $1/T$ Eqn (4) also gave straight lines, as shown in figure 8. The slopes of these lines represent $\Delta H^0/R$ and the intercepts are $[\ln R/N_A h + \Delta S^0/R]$, from which the values of $\Delta H^0$ and $\Delta S^0$ were calculated. It can be noticed that the reaction enthalpy has a great value equal to 83.44 kJ/mol.

The sign of the enthalpy indicates an endothermic reaction. Positive values of entropy (30.78 J/mol) suggest that entropy increases upon achieving the transition state, which often indicates a dissociating mechanism.

**Conclusions**

In case of Congo red oxidation with Fenton reagent, the optimum pH was 3.50; the colour removal is aprox. 75%, at temperature of 55°C, the discoloration time being of 5 min. The discoloration rate has the higher value at pH = 3.50 and increases exponentially with temperature.

The apparent activation energy value is equal to 85.9 kJ/mol. This value of activation energy is much higher than other azo dyes oxidized with Fenton reagent. Thus, the discoloration process of Congo red, in the presence of Fenton reagent, occurs with difficulty at low temperatures. However, the method can be more effective by raising the temperature to 55°C, when the discoloration time decreases of 26 times.

The activation enthalpy ($\Delta H^0$) and the activation entropy ($\Delta S^0$) were calculated from the diagram of the transition state. The value of the enthalpy (83.44 kJ/mol) indicates an endothermic reaction. Positive values of entropy (30.78 J/mol) suggest that entropy increases upon achieving the transition state, which often indicates a dissociating mechanism.

**References**


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