Study of the Removal Mechanism of Remazol Red RB 133 by Electrocoagulation: Temperature effect.

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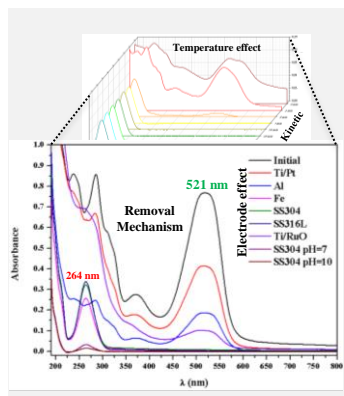
Several factors already studied have proven to interfere in the Electrocoagulation (EC) process efficiency. However, the temperature effect is poorly known. Thus, this work aims to study the temperature effect on the application of the EC process in the removal of Remazol Red RB 133. The kinetics experiments of the effluent containing the dye (500 mg L^{-1}), surfactant Cetyltrimethylammonium bromide (0.75 mM) and NaCl (1000 mg L^{-1}) were performed at temperatures of 298, 308, 318, 328 and 338K with stainless steel 304 and demonstrate that the dye removal mechanism is influenced by oxidative and adsorption processes. The thermodynamic parameters $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ described the process as being endothermic, non-spontaneous and with a tendency to increase the organization of the medium, respectively, and prove the kinetic study assumption of a process with two coexisting mechanisms.

Introduction

The management of the world's water resources is a major concern. Industries are significant polluters of these resources, primarily due to their inadequate waste management [1]. The textile sector utilizes a significant amount of water in all of its processes, resulting in effluents with varying pH levels, high concentrations of organic matter, conductivity, turbidity, total dissolved solids, chemicals, and heavy metals [1]. Among the various existing technologies for treating these wastes, electrochemical technologies such as electrocoagulation (EC) stand out for their versatility, robustness, and ability to remove dissolved contaminants at low concentrations [2]. EC is based on the production of coagulants through the oxidation of metal at the anode and the reduction of water at the cathode, which are capable of disastabilizing and removing contaminants from the aqueous medium. Several factors can affect the EC process, such as the type and density of current applied, the electrode metal, and the solution stirring [2, 3]. However, there are few in-depth studies in the literature on the effect of temperature on the EC process, especially in the removal of dyes. Therefore, this work aimed to investigate the temperature effect on the removal of Remazol Red RB 133 (RRRB 133) in synthetic wastewater containing the surfactant cetyltrimethylammonium bromide (CTABr) and NaCl through kinetic and thermodynamic studies.

Material and Methods

The experiments were performed in duplicate at diferents temperatures (298, 308, 318, 328 and 338K) using a system (see Figure 1) consisting of 304 stainless steel electrodes (5 x 5 x 0.3 cm) supplied with a pulsed current of 0.70 A in 700 mL of solution with stirring at 200 rpm for 45 minutes. The collected samples underwent UV-Visible spectrophotometry analysis at a wavelength of 521 nm to determine the dye removal and rates. This allowed for the calculation of additional kinetic parameters, such as the observed rate constants (k_{obs}) and reaction order (*n*).

The Arrhenius equation is an essential mathematical tool to obtain the relationship between temperature and the rate constants [4]. The Eyring equation is essential for calculating the activation thermodynamic parameters such as enthalpy change ($\Delta H^{\neq}$), entropy change ($\Delta S^{\neq}$), and the Gibbs free energy ($\Delta G^{\neq}$) [5].
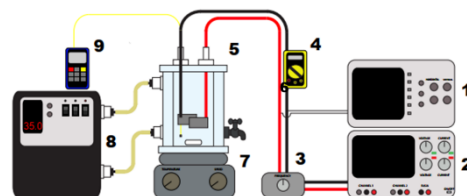

Figure 1. Oscilloscope (1), power source (2), electrical circuit (3), multimeter (4), electrochemical cell (5), sampling point (6), magnetic stirrer (7), thermostatic bath (8) and thermometer (9).

Results and Discussion

As could be observed in Table 1, the reaction orders were practically first order (*n* = 1) and could be considered a pseudo-first order [5]. The k_{obs}, although not suffering a large variation, increase with temperature, demonstrating the positive effect for this variable in relation to the removal of the dye.

Figure 2 show the effect of temperature on dye removal over time. It is evident that, for all temperatures, a new band appears at λ 264 nm as removal occurs at λ 521 nm, indicating a possible modification to the molecule. This is consistent with

1

previous studies on azo dye molecules, such as RRRB133 dye, which are susceptible to oxidation of the nitrogen of the azo group and the amines of the heterocyclic aromatic ring [2]. The temperature 298 K presents a slower kinetics (3.12×10^{-3} s^{-1}) and absorbance decay of the chromophore group in the λ of 521 nm, only with 10 minutes reaches 99.7 % removal, also the appearance of the λ of 264 nm is only seen more expressively at the end of the experiment (45 minutes). The dye concentrations decay initial rates, from 0 to 2 minutes, show a different effect of temperature than expected. In 298 K the absorbance at λ of 521 nm decreased by 77%, while the other temperatures of 308, 318, 328, and 338 K decreased approximately 31, 15, 15, 85 %, respectively. The behavior at 298 K occurred probably because the main mechanism at this temperature is not electrocoagulation, but parallel reactions that produce oxidants that attack the chromophore group [41].

A.R. Amani-Ghadim et al. found similar behavior in UV-Vis spectra on the treatment of azo dye C.I. Reactive Red 43 using electrocoagulation and proposed mechanism for the formation of these compounds is through electroreduction and oxidation of the chromophore azo group (-N=N-) [2]. In order to investigate this, experiments were conducted with six types of electrodes: iron (Fe), 304 stainless steel (SS304), 316L stainless steel (SS316L), aluminum (Al), titanium/ruthenium oxide (Ti/RuO), and platinum/titanium (Pt/Ti). Two experiments were also performed at neutral (7.0) and basic (10.0) pH with the SS304 electrodes to test the influence of this variable. The results, shown in Graphical abstract, confirm those found in the literature. The band at 264 nm was only observed with the iron-based electrodes (Fe, SS304 and SS316L). Furthermore, the signal for a neutral and basic pH exhibited a lower intensity for this band, indicating that the potential oxidizing species is pH-dependent. Based on the mechanisms found (oxidation and electrocoagulation), it was possible to construct a model for the removal of the concentration of RRRB133 dye:

In this sense, we can describe the system studied in this work as being a hybrid mechanism process, since we have a non-spontaneous process ($\Delta G^{\neq}>0$) and negative entropy ($\Delta S^{\neq}$) as an electro-oxidation [6] and values and sign of $\Delta H^{\neq}$ similar to processes consider electrocoagulation as an adsorption mechanism [7]. Thus, the thermodynamic parameters converge to the kinetic model found that encompasses all these processes.
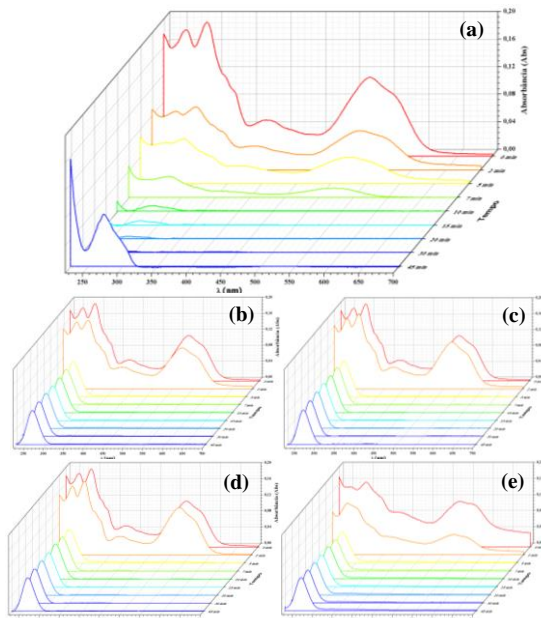

Figure 2. The kinetics of color removal for temperatures of 298 K (a), 308 K (b), 318 K (c), 328 K (d), and 338 K (e).

Table 1. The K_{obs} and n for each temperature.

Temperature (K)	K_{obs}	n	R^2
298	3.12×10^{-3}	1.181	0.9878
308	5.02×10^{-3}	1.093	0.9939
318	5.22×10^{-3}	1.083	0.9936
328	5.68×10^{-3}	1.055	0.9930
338	5.43×10^{-3}	1.079	0.9934

$$-\frac{d[\textbf{RRRB133}\%]}{dt} = 1,337\, e^{-\frac{14736}{RT}}[\textbf{RRRB133}]^1 + \frac{J.A.\varepsilon}{F\,V}\, \varphi\, Q_e (1 - e^{-t(1,379 e^{-\frac{15173}{RT}})})$$

Conclusions

The kinetic and mechanism studies indicate that the dye is primarily removed through the sweep flocculation mechanism, with secondary oxidation reactions of the molecule. The thermodynamic parameters also classify the system studied as a hybrid of adsorptive and oxidative processes.

References
[1] Kabir SMF, Cueto R, Balamurugan. S, Clean Technol 1 (2019) 311–325.
[2] A. Amani-Ghadim, S. Aber, A. Olad, H. Ashassi-Sorkhabi, Chem Eng Process Process Intensif 64 (2013) 68–78.
[3] A. de Oliveira, J. Ribeiro, E. Neto, Water Sci Technol 82 (2020) 56–66.
[4] Ö. Bulca, B. Bulca, S. Atalay, G. Ersöz, J Water Process Eng 40 (2021) 101821.
[5] A. Giwa, I. Bello, A. Olabintan, Heliyon 6 (2020) 4–10.
[6] A. Khan, R. Ahmed, L. Mirza, Port Electrochim Acta 27 (2009) 429–441.
[7] K. Ebisike, A. Elvis, K. Kanayo, O. Jeremiah, Results Chem 5 (2023) 100730.