USING SONO-ELECTROCHEMICAL PROCESS FOR DECOLORIZATION AND REMOVAL COD OF DISPERSE-YELLOW-7 DYE IN AQUEOUS SOLUTIONS

Abstract. The performance of using a sono-electrochemical process for decolorization and removal COD *(chemical oxygen demand)* of disperse-yellow-7 (DY7, *4-[4-(Phenylazo)phenylazo]-o-cresol*) in aqueous solutions was investigated in different concentrations electrolytes of NaCl and $CaCl_2$ (0.02, 0.05, 0.1, and 0.2 mol/L), treatment time and DY7 concentration. The combination of electrochemical (EC) and ultrasonic (US) was called the sono-electrochemical (EC_US) process, and it showed the highest treatment DY7 efficiency in comparison with applying EC or US treatment alone (EC_US > EC > US). Using $CaCl_2$ electrolytes had a higher decolor capacity than NaCl electrolytes in the same concentration. At the dose of DY7: 25 ppm, the EC_US method *(NaCl or $CaCl_2$ 0.1 – 0.2 mol/L, frequency 20 kHz, electrodes of TiO_2 and RuO_2–IrO_2–TiO_2)* was totally removal of DY7_25 ppm in aqueous solutions (100% color and 100% COD) within 45 min treatment. This could be a valuable alternative treatment method applying for dyeing wastewater or other refractory organic compounds contained in wastewater.
Keywords: ultrasound, electrochemical, sono-electrochemical, disperse yellow 7

1. Introduction

Textile industry causes considerably higher impacts on water pollution by discharging their effluents into various receiving bodies including ponds, rivers, and other public sewers. Major pollutants loaded from the textile industries are from several of their wet-processing operations like scouring, bleaching, mercerizing, and dyeing [1]. Among these processes, the dyeing process normally uses a large amount of water for dyeing, fixing, and washing processes. Thus, textile wastewater possesses a high COD value, a large amount of suspended solids, broadly fluctuating pH, strong color, high temperature, and low biodegradability caused by varying contaminants within the water environment [2]. Whereas most azo dyes are carcinogenic, other compounds such as aromatic amines must undergo oxidation to form more toxic by-products [2]. Therefore, the removal of azo dyes and other refractory organic contaminants in wastewater has attained much attention in terms of both academic and industrial interest [3-10].

Despite the fact that different biological and physical techniques have been effectively used in the remediation of organic contaminants, these methods have their own advantages and disadvantages. The majority of physical techniques, for example, reverse osmosis, adsorption, and flocculation are capable of transferring primary contaminants into secondary by-products, which results in different environmental issues [2]. Biological remediation methods face significant disadvantages, such as the creation of a large amount of sludge and poor removal efficiency of refractory organic pollutants [2]. Hence, the focus on advanced oxidation processes (AOPs) to overcome the disadvantages of some conventional remediation processes have attached many researchers. The most commonly used AOPs for the remediation of dyeing wastewater are used alone or combining these processes: Fenton-based oxidation [11], ozonation, electro-oxidation [12], and sono-electrochemical (EC_US) [4-10]. Recently, the EC_US technique has been

developed as a green chemistry process that involves the integration of electrochemical (EC) and ultrasound (US) processes for the degradation of a broad range of organic contaminants [13, 14]. Some reviews of the treatment of dyes in aqueous solutions by sono-electrochemical methods are revealed in Table 1.

In sonochemistry, US can be divided into two classes, high frequency (2–10 MHz) that are mostly used in the medical field, and low frequency (20 kHz–2 MHz), where cavitation is produced in liquids and can be used to influence chemical reactions and chemical processes [13]. When a fluid is exposed to low-frequency US, the liquid *"cavitates"*. The cavitation bubbles produced as a result of exposure to ultrasound undergo extremely powerful collapse inside the fluid, producing "hot spots" of high energy [13]. In an EC process, chemical transformation takes place either spontaneously or non-spontaneously. In an electrolysis cell (non-spontaneously), an external EC potential/cell voltage or current is applied. EC reactions then occur at the interface between the electrolyte solution and the electrodes. The common reaction in electro-chemistry involves redox reactions [13]. The EC_US process is based on a positive synergistic effect, where ultrasound waves with "hot spots" of high energy activate the surface of an electrode, promoting the rate of reaction and consequently, enhancing the efficiency of the electrode [13]. Turning to practice, the combination of US and EC processes in the degradation of COD and color of dyeing wastewater would be a good approach for enhanced treatment efficiency and minimizing waste. In this study, the sonolysis was performed at a frequency of 20 kHz. Two different supporting electrolytes, (NaCl, $CaCl_2$) and a typical dye: disperse yellow 7 (DY7) were used to investigate the effects of electrolytes concentration, treatment time, DY7 concentration under EC_US, EC, and US treatment conditions.

2. Materials and methods

2.1. Materials and reagents

The effects of US_EC, EC, and US on decolorization and COD treatment of DY7 dye in aqueous solutions were studied. Details of the DY7 dye are shown in Table 1. The DY7 dye has maximum absorbance (λ_max) at 430 nm. The treatment solution was prepared by dissolving DY7 dye at the dose of 100 ppm in distilled water and using it as the stock.

Table 1. Dye class, chemical structure, molecular weight, and concentration of DY7

Dye	IUPAC Name	Molecular Formula	Molecular Weight	Class structure	Maximum absorbance	Study concentration
			g/mol		nm	mg/L or ppm
DY7 (*)	*4-[4-(Phenylazo)phenylazo]-o-cresol*	$C_{19}H_{16}N_4O$	316.4	Di-azo	430	10 – 50

(*) *The compound identifier (CID) is 22736*

2.2. Experimental setup

2.2.1. Ultrasonic, electrochemical, and sono-electrochemical setup

In this study, a reactor cup of 250 mL working volume was used. The glass cell had a cylindrical body, containing electrodes of TiO_2 and RuO_2–IrO_2–TiO_2.

The electrodes made from TiO_2 and RuO_2-IrO_2-TiO_2 offer several advantages, including high stability, durability, conductivity, potential range, catalytic activity, and low cost. These properties make them suitable for use in various electrochemical applications, including water treatment [15]. These electrodes have high stability and durability in various harsh chemical environments. They are resistant to corrosion and can withstand high temperatures and pressures, making them ideal for use in electrochemical processes that require long-term stability. These electrodes have high electrical conductivity, which makes them efficient in transferring charge between the electrode surface and the electrolyte solution. This results in faster reaction rates and higher current densities, leading to improved electrochemical performance. In addition, these electrodes have a wide potential range, high catalytic activity which means they can be used for a variety of electrochemical reactions. TiO_2 electrodes are relatively low cost compared to other electrode materials, such as platinum or gold. The combination of RuO_2 and IrO_2 provides a synergistic effect, where the two materials work together to enhance the catalytic activity. The addition of TiO_2 helps to improve the stability and durability of the electrode.

The voltage source applied to the electrode is a direct current power source with a voltage of 12 volts (Figure 1). The electrodes had an effective electrode area of 7 cm^2 and an electrode gap of 4 cm in the dyeing solution. The ultrasonic maximum power is 200 watts and the frequency is 20 kHz (Tomy Seiko CO., Ltd, Japan), and the output nozzle hole area was 0.2 cm^2. An ampere meter was connected to measure the electrical current (mA). In this study, the performance of three methods: ultrasonic (US), electrochemical (EC), and sono-electrochemical (EC_US) in the treatment of DY7 was tested with the presence of different concentrations of electrolyte (pure salts: NaCl and $CaCl_2$: 0.02, 0.05, 0.1, and 0.2 mol/L) during 60 minutes' treatment time. All experiments are triplicates.

Figure 1A. ultrasonic, electrochemical, and sono-electrochemical experiments setup.

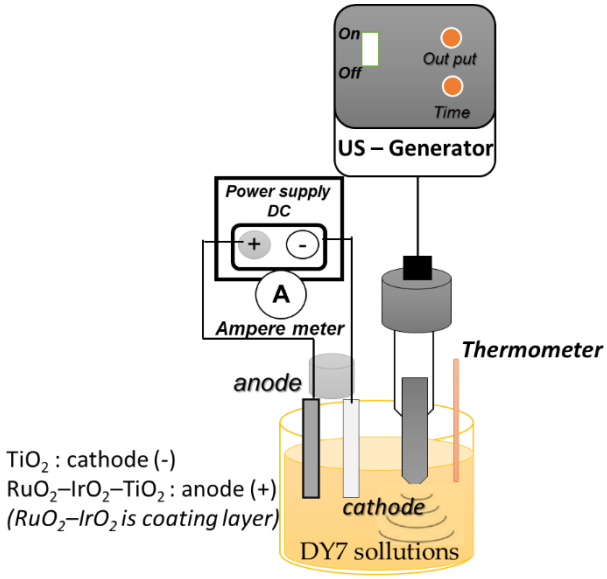

Figure 1B. Diagram of experiments setup

2.2.2. Color and COD analysis

The percentage of decolorization was determined according to the following equation:

$$\text{Decolorization (\%)} = [(A_o - A_t) \times 100\%]/A_0 \quad (1)$$

Where: A_0 is the absorbance value at 430 nm at the beginning (0 min).

A_t is the absorbance value at 430 nm at the treatment time (t min, t: from 0 – 60 min).

The percentage of COD removal was determined according to the following equation:

$$\text{COD removal (\%)} = [(COD_o - COD_t) \times 100\%]/COD_0 \quad (2)$$

Where: COD_o is the COD value at the beginning (0 min).

COD_t is the COD at the treatment time (t min, t: from 0 – 60 min).

The COD values were analyzed following the standard method [16]. In this experiment, it was found that in the range COD of 0 – 90 mg/L, at 420 nm, the standard curve obtained is $y = -0.0017x + 0.1998$, and $R^2 = 0.9968$. Where: y is the absorbance value and x is the COD value.

3. Results and discussion

3.1. Relationship between DY7 concentration and COD or absorbance at 430 nm

The Pearson correlation coefficient (R^2) was calculated at 0.9998 and 0.9859 for relationships between the concentration of DY7 and COD, concentration of DY7 and absorbance at 430 nm, respectively. The data from Table 2 show that the DY7 concentration value increases, the COD value increases accordingly. As the concentration of DY7 increased from 5 ppm to 25 ppm, the ratio of COD and DY7 concentration was about 1.5 ± 0.1 and the ratio of absorbance at 430 nm and DY7 concentration was 0.035 ± 0.001.

Table 2. Relationship between DY7 concentration and COD or absorbance at 430 nm

DY7 concentration (mg/L or ppm)	COD (mg/L)	Absorbance at 430 (nm)	COD: DY7 concentration	Absorbance at 430 nm : DY7 concentration
0	0	0.000		
5	8	0.173	1.60	0.035
10	15	0.350	1.50	0.035
25	35	0.896	1.40	0.036

3.2. Effect of ultrasonic power in the removal of DY7

At first, the COD and the absorbance at 430 nm of all input samples were analyzed and shown in Figure 2. There is a small fluctuation of COD and absorbance at 430 nm of adding $CaCl_2$ or NaCl into 25 ppm DY7 solutions. The effect of ultrasonic power in the treatment of DY7 was tested for all of the samples (Figure 2) for 60 min. In fact, using only US treatment (20 KHz, 500 w/cm^2) was not effective in the removal of color, and COD of the DY7 dye in aqueous solution.

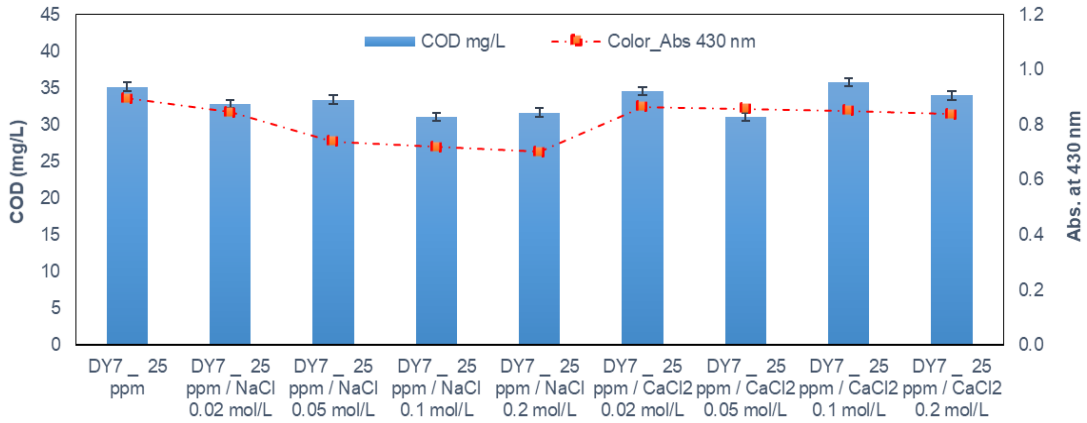

Figure 2. COD and absorbance at 430 nm values after adding $CaCl_2$ or NaCl to 25 ppm DY7 solutions

3.3. Effect of different supporting electrolytes on DY7 removal by electrochemical process

Supporting electrolytes play an important role in electrochemical processes because they allow the flow of current through the solution and facilitate electrochemical phenomena such as oxidation, reduction, and conduction. Specifically, the supporting electrolyte facilitated the removal efficiency of color and COD in wastewater (Table 3 and Table 4). Under two supporting electrolytes, the experimental results showed that $CaCl_2$ (Table 3) electrolytes had higher efficiency than NaCl (Table 4). Under supporting 0.05 mol/L $CaCl_2$ electrolyte, the COD removal efficiency was 70.3%, and the color removal efficiency was 65.6% after 60 min treatment time.

Table 3. Percentage removal COD and color of DY7_25 ppm in 0.05 mol/L $CaCl_2$ by EC process

Time, min	COD, mg/L	COD removal efficiency, %	Absorbance at 430 nm	Color removal efficiency, %	Electric current, mA
0	35.2	0.1	0.896	0	170
5	26.4	25.2	0.663	26	
10	23.4	33.5	0.428	52.2	
20	19.9	44	0.386	56.9	
30	14.6	58.6	0.324	63.8	
45	14	60.3	0.327	63.5	
60	10.5	70.3	0.308	65.6	230

Table 4. Percentage removal COD and color of DY7_25 ppm in 0.05 mol/L NaCl by EC process

Time, min	COD, mg/L	COD removal efficiency, %	Absorbance at 430 nm	Color removal efficiency, %	Electric current, mA
0	35.2	0.1	0.896	0	100
5	26.4	25.2	0.732	18.3	
10	21.6	38.5	0.634	29.2	
20	21.1	40.2	0.594	33.7	
30	16.4	53.6	0.524	41.5	
45	16.4	53.6	0.478	46.7	
60	15.8	55.3	0.428	52.2	150

3.4. Effect of electrolytes (NaCl and $CaCl_2$) on DY7 removal by EC_US process

The efficiency of COD removal in 0.05 mol/L NaCl of the EC process showed that after 10, 30, and 60 minutes, the efficiency of COD removal increased by 38.5%, 53.6%, and 55.3%. (Table 4). In 0.05 mol/L $CaCl_2$ of the EC process showed that after 10, 30, and 60 minutes, the efficiency of COD removal increased by 33.5%, 58.6%, and 70.3%. (Table 3). In 0.05 mol/L NaCl of the EC_US process showed that after 10, 30, and 60 minutes, the efficiency of COD removal increased by 38.5%, 58.6%, and 77%. Similarly, in 0.05 mol/L $CaCl_2$ of the EC_US process showed that after 10, 30, and 60 minutes, the efficiency of COD removal increased by 40.2%, 75.3%, and 85.4%. The efficiency of color removal was also well achieved under the EC_US treatment process (Figure 3). Although EC degradation is considered a clean process for removing organic contaminants, it has a few drawbacks of low degradation efficiency and the electrode is passivated because of frequent electrode fouling [13, 14]. The use of the EC_US process can resolve the issues experienced using EC processes alone [8]. In fact, after 60 min EC_US process treatment time, the surface of electrodes used in this study (TiO_2 and RuO_2–IrO_2–TiO_2) is very clean. In addition, there was a significant increase in temperature (°C) during the EC_US treatment time (from 0 to 60 min). The temperature of all EC_US experiments was gradually increasing from 21.5 ± 1.0°C to 42.0 ± 1.0°C, by contrast, there was a very small change in temperature in the EC treatment process (Figure 3).

The effect of EC_US in the treatment of DY7_ 25 ppm, using NaCl or $CaCl_2$ in different concentrations of NaCl: 0.02, 0.05, 0.1, and 0.2 mol/L or $CaCl_2$: 0.02, 0.05, 0.1 and 0.2 mol/L are showed in Figure 4. While using ultrasonic treatment alone cannot remove COD and color of DY7

solutions (Figure 2). According to the results shown in Figure 3 and Figure 4, it could be concluded that the treatment efficiency of combined EC-US is much better under electrolyte using (NaCl or $CaCl_2$). Interestingly, the combination of EC_US is performed the highest treatment COD and color (DY7_25 ppm) after 30-mins treatment time with the using of NaCl or $CaCl_2$ 0.1 to 0.2 mol/L.

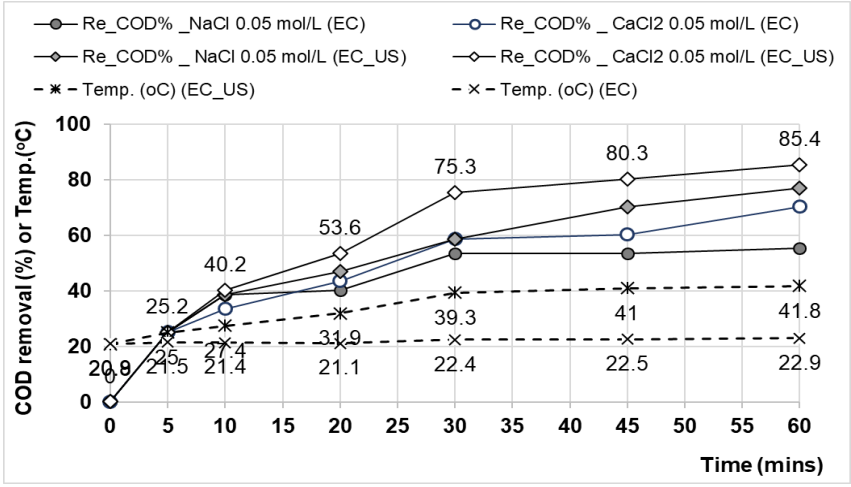

Figure 3. Percentage of COD and color removal efficiency in 0.05 mol/L NaCl and 0.05 mol/L $CaCl_2$ during 60 min treatment by EC or EC_US processes.

Changing the concentration of DY7 (10 ppm, 25 ppm, and 50 ppm), and investigating of EC_US treatment these samples, using 0.05 mol/L $CaCl_2$, the highest removal efficiency was DY7 10 ppm (98%), followed by DY7 25 ppm (85%) and the lowest removal was DY7 50 ppm (72%) after 60 minutes treatment time. The performance of using EC_US in the degradation of color and COD of dying DY7 (10 – 50 ppm) have done in the study. The EC_US process was totally removal of DY7, with the presence removal 100%, after 30 - 60 min treatment time, and much higher than the EC process or US process (EC_US > EC > US). In previous research, Barros et al. (2014) also studied the degradation of amaranth dye using an integrated EC_US technique, with using of a fabricated boron-doped diamond thin film as the anode, a platinum net as the cathode, and saturated calomel as the reference electrode. The sonolysis was also performed at a frequency of 20 kHz. It was noted that the EC_US got a higher degradation efficiency (95%, 90 min) than that of EC (80%) or sonolysis (8%) processes alone [6].

The current density of the EC process had an important impact on the degradation efficiency [13]. The effect of wastewater conductivity on dye removal and specific electrical energy consumption, various experiments were performed using NaCl as the electrolyte. With an increase in salt concentration from 0.1 to 1.0 g/L, a drastic improvement in solution conductivity (from 0.38 to 1.94 mS) was observed by Nandi, B. K., et al., 2017 [10]. Thus, in this investigation of EC_US processes, there was a significant increase in the electric current (mA) and temperature (°C) during the treatment time (from 0 to 60 min). The temperature of all experiments gradually increased from 21.5 ± 1.0 °C to 42.0 ± 1.0 °C, and the increase of electric current (mA) after the treatment depending on the initial and type of electrolyte (Table 5).

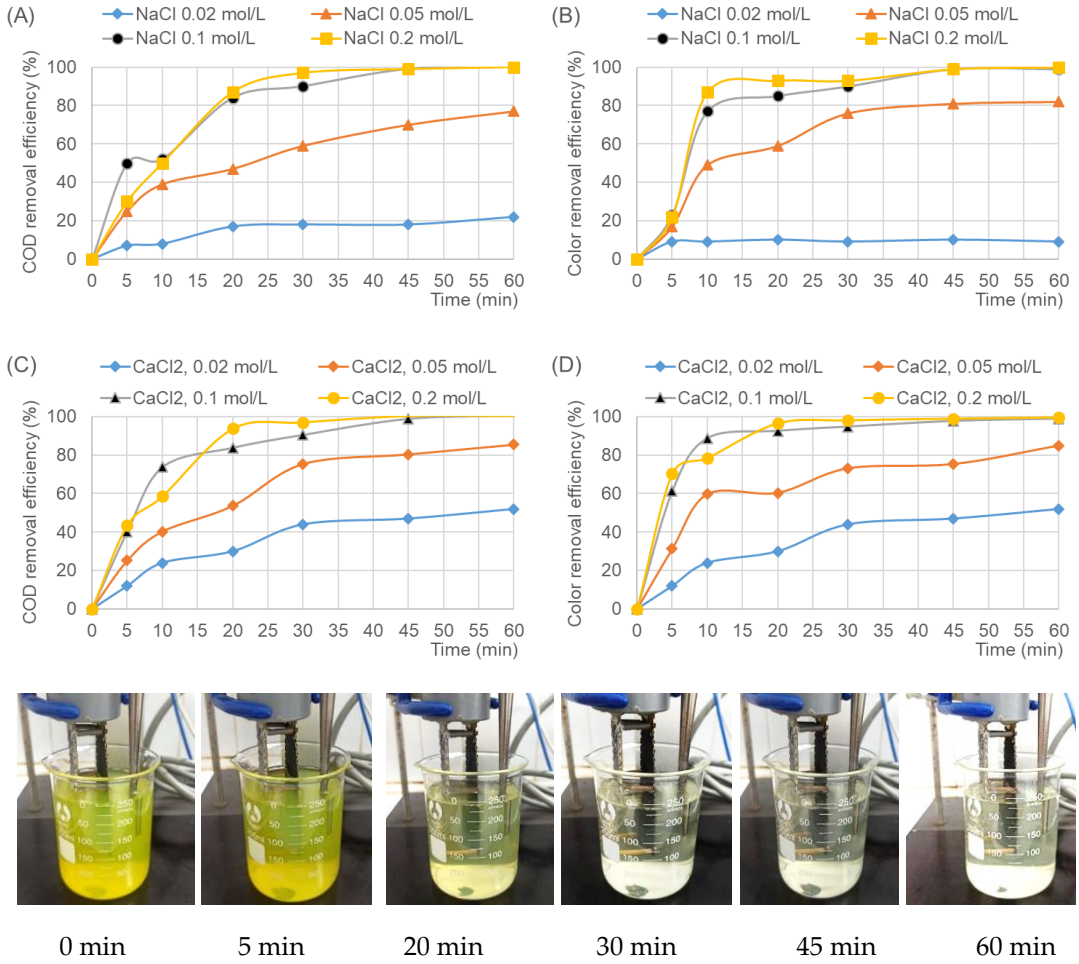

Figure 4. Percentage of COD and color removal efficiency (DY7_25 ppm) by EC_US processes, using electrolyte NaCl (A, B) or $CaCl_2$ (C, D), treatment time: 0 – 60 min). Photos of the EC_US experiment using electrolyte 0.1 mol/L $CaCl_2$.

Table 5. The electric current (mA) before and after the EC_US treatment processes.

EC_US process DY7_ 25 ppm	**0.02 mol/L NaCl**	**0.05 mol/L NaCl**	**0.1 mol/L NaCl**	**0.2 mol/L NaCl**
Electric current (mA) from 0 to 60 min	60 → 60	100 → 150	250 → 320	370 → 470
EC_US process DY7_ 25 ppm		**0.05 mol/L $CaCl_2$**	**0.1 mol/L $CaCl_2$**	**0.2 mol/L $CaCl_2$**
Electric current (mA) from 0 to 60 min		170 → 230	360 → 440	450 → 530

4. Conclusions

Performance of using the EC_US system for color and COD removal from DY7 dyeing water was successfully investigated using supporting electrolytes NaCl and $CaCl_2$ in different concentrations (0.02, 0.05, 0.1, and 0.2 mol/L). Using only the US treatment process (20 KHz, 500

w/cm^2) was not effective in the treatment of DY7 dye water. However, the combination of EC_US is performed the totally removal COD and color (DY7_25 ppm) after 30-mins treatment time with the using of NaCl or $CaCl_2$ 0.1 to 0.2 mol/L, and it could be concluded that the performing of process EC_US > EC > US treatment alone. This is the first investigation of using electrolytes $CaCl_2$ in EC and EC_US processes, and interestingly $CaCl_2$ electrolytes had a higher pigmentation capacity than NaCl in the same treatment condition. Moreover, after the treatment of the EC_US process, the surface of the electrodes used in this study (TiO_2 and RuO_2–IrO_2–TiO_2) is very clean. According to these results, the EC_US process could be a valuable alternative to conventional physicochemical methods for the treatment of textile wastewater and/or other refractory organic compounds contained in wastewater.

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SỬ DỤNG QUÁ TRÌNH SIÊU ÂM-ĐIỆN HÓA ĐỂ LOẠI MÀU VÀ COD CỦA CHẤT NHUỘM MÀU VÀNG PHÂN TÁN 7 TRONG DUNG DỊCH

Tóm tắt. Nghiên cứu về hiệu quả sử dụng quá trình siêu âm-điện hóa để loại bỏ màu và COD (nhu cầu oxy hóa hóa học) của phẩm màu vàng phân tán (DY7, 4 - [4 - (phenylazo) phenylazo] - o-cresol) trong dung dịch đã được thực hiện ở các nồng độ điện li khác nhau của NaCl và $CaCl_2$ (0,02, 0,05, 0,1 và 0,2 mol/L), thời gian xử lý và nồng độ DY7. Sự kết hợp của điện hóa (EC) và siêu âm (US) được gọi là quá trình siêu âm-điện hóa (EC_US) cho thấy hiệu quả xử lý DY7 cao nhất so với việc áp dụng EC hoặc US riêng lẻ (EC_US > EC > US). Sử dụng điện li $CaCl_2$ có khả năng loại màu cao hơn NaCl ở cùng nồng độ. Ở liều DY7: 25 ppm, phương pháp EC_US (NaCl hoặc $CaCl_2$ 0,1-0,2 mol/L, tần số 20 kHz, điện cực TiO_2 và RuO_2-IrO_2-TiO_2) đã hoàn toàn loại bỏ DY7_25 ppm trong dung dịch (100% màu sắc và 100% COD) trong vòng 45 phút xử lý. Đây có thể là một phương pháp xử lý thay thế có giá trị áp dụng cho nước thải nhuộm hoặc các hợp chất hữu cơ khó phân hủy khác có chứa trong nước thải.

Từ khóa: Siêu âm, điện hóa, siêu âm-điện hóa, Disperse Yellow 7.