Treatment by Electrocoagulation of Congo red from Aqueous Solution Using Cantor Alloy

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Abstract

Electrocoagulation (EC) is one of the most effective techniques in removing color and organic pollutants from wastewater. This study aims to use a new alloy system, so-called High Entropy Alloys (HEAs), which contains at least five principal elements with 5-35 at. %, as an electrode in the EC process. The well-studied equiatomic CrMnFeCoNi HEA (Cantor alloy) was used as an anode in the treatment of the synthetically prepared wastewater (congo red solution) with EC. In the EC study, COD and color removal were evaluated at different current densities (5-100 mA/cm2) for 15 min electrolysis period. The results showed that removal efficiency of above 80 % was obtained for both parameters of COD and color at the lowest current density of 5 mA/cm². The optimum current density was determined to be 10 mA/cm², and the COD and color removal efficiencies were found to be 84 and 99.4 %, respectively. It was shown that the Cantor alloy possesses an effective removal in the EC process.

Keywords: Electrocoagulation, congo red, high entropy alloy, cantor alloy, COD removal.

Cantor Alaşımı Kullanılarak sulu çözeltiden Kongo Kırmızısının Elektrokoagülasyon ile Arıtımı

Öz

Elektrokoagülasyon (EC) atıksudan renk ve organik kirleticileri uzaklaştırmak için en etkili tekniklerden biridir. Bu çalışmada, en az beş temel element ve herbir element için % at. 5-35 içeren Yüksek Entropi Alaşımları (HEA) olarak adlandırılan yeni bir alaşım sisteminin EC prosesinde elektrot olarak kullanılması hedeflenmiştir. Yoğun şekilde çalışılan eşit atomlu CrMnFeCoNi HEA (Cantor alaşımı), sentetik olarak hazırlanmış congo red çözeltisinin EC ile arıtılmasında anot olarak kullanılmıştır. Yapılan EC çalışması 15 dakika elektroliz süresinde farklı akım yoğunluklarında (5-100 mA/cm²) KOİ ve renk giderimi değerlendirilmiştir. Deney sonucunda, akım yoğunluğu 5 mA/cm², her iki renk ve KOİ parametrede % 80 üzeri arıtım verimi elde edilmiştir. Optimum akım yoğunluğu ise 10 mA/cm² olarak belirlenmiş, KOİ ve renk giderim verimi sırasıyla % 84 ve 99,4 olarak bulunmuştur. Yapılan bu çalışma neticesinde, kullanılan Cantor alaşımının EC prosesinde giderimde etkili olduğu gösterilmiştir.

Anahtar Kelimeler: Elektrokoagülasyon, kongo kırmızısı, yüksek entropi alaşımı, cantor alaşımı, KOİ giderimi.

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1. Introduction

Increasing industrialization and urbanization are increased environmental pollution, and therefore, fresh water resources are depleted (Asghar et al., 2020). Industrial facilities play a critical role due to the discharge of toxic wastes into receiving water bodies and mostly result in dyes. Dyes are annually produced from many industries such as textile, cosmetics, paper, food, leather, and other industries. Therefore, water contaminated with dyes is highly polluted, colored, turbidity and it has high chemical oxygen demand (COD). They cause an important harmful impact on the aesthetics of the aquatic environment and have damaging consequences on organisms (Khan et al., 2014). Thus, it is a necessity to apply conventional or advanced treatments to almost 90 % of the water consumed in the industry prior to discharging into the ecosystem (Silva et al., 2018).

Dyes are refractory pollutants and are treated using advanced treatment technologies (Asghar et al., 2020; Bello et al., 2020; Bahadur & Bhargava, 2019 ; Asghar, Raman, et al., 2017) such as fenton oxidation (Asghar, Abdul Raman, et al., 2017), ozonation (Wang et al., 2019), ultrasound (Asghar et al., 2020), electrochemical oxidation-reduction (Cortés et al., 2007), indirect electro-oxidation using strong oxidants (Liu et al., 2019), electrocoagulation (EC) (Huda et al., 2017), and advanced oxidation processes (AOPs). AOPs show higher efficiency, however, result in high chemical consumption (Buthiyappan & Raman, 2019) and limit their wide applications (Khandegar & Saroha, 2013). In this respect, the EC process has been used to treat wastewater with different characteristics due to its moderate chemical requirement, versatility, safety, selectivity, ease of control, and automation (Thakur et al., 2009).

EC is a treatment process that removes pollutants from wastewater using electric current and metal electrodes. The metal electrodes used in the process react electrochemically with pollutants by producing water-soluble hydroxides with the applied electric current. Since the adsorption capacity of metal hydroxides is very high, metal hydroxides form coagulants by adsorbing different pollutant parameters in the water, and the formed coagulants are removed from the water by precipitating. Aluminum (Al^{+3}) and iron (Fe^{+3}, Fe^{+2}) electrodes are commonly used in such processes. However, the passivation and corrosion of the electrodes over time is a disadvantage in the EC process and affects the pollutant removal efficiency along with the treatment cost. Therefore, many different metallic electrodes and alloys have been investigated to be used in EC (Dura, 2013a).

An inspection of the literature shows various alloy electrodes were used in wastewater treatment with EC (Donneys-Victoria et al., 2020; Molano-Mendoza et al., 2019; Dura, 2013b). They pointed out that conventionally alloys provide a more efficient wastewater treatment compared to pure metals (Aitbara et al., 2021). Therefore, the alloys containing more than one element possess better removal efficiency compared to their pure counterparts. The recent studies in materials science show that a novel alloys system, so-called high entropy alloys (HEAs), contains at least five principal elements and compositions of 5–35 at. %. These alloys show higher mixing entropy in a liquid or solid solution to stabilize the expected phases (Murty et al., 2019).

These alloy systems show higher mechanical (Kao et al., 2009), magnetic (Chaudhary et al., 2021), thermal properties (Kukshal et al., 2018) as well as corrosion (Shi et al., 2017), and oxidation (Holcomb et al., 2015) resistance than conventional alloy systems. Thus, they have received much attention due to their potentially desirable properties. The well-studied equiatomic CrMnFeCoNi HEA (Cantor alloy) with a single face-centered cubic (FCC) structure possesses exceptional corrosion behavior than the stainless-steel counterparts (Shi et al., 2017)(Luo et al., 2018). Additionally, the comparable properties of Cantor alloy with Fe and Al-based alloys promise potential applications in many fields like aqueous solutions (Qiu et al., 2017).

In the present study, the removal efficiency of Cantor HEA anodes in the EC process was studied in detail. To date, no study has been investigated the usage and effect of HEAs in the EC process.

2. Material and Method

2.1. Preparation of Cantor Alloy

Indutherm MC 15+ induction melting furnace were used to produce Cantor alloy from high purity raw materials (>99.0 wt. %). The melting process was carried out in an alumina crucible under an argon atmosphere to avoid oxidation. The liquid metal was also stirred by the magnetic field to ensure chemical homogeneity. The homogeneous alloy was cast into a copper mold having a 40 mm x 60 mm x 10 mm rectangular shape (Figure 1a).

2.2. Experiment

The aqueous solution was prepared by taking 1 g of Congo red, whose properties are given in Table 1, in 1 L of distilled water without pH adjustment. The experiments were carried out on Congo red solutions with a concentration of 500 mg/L prepared during the experiment. 2 mg/L NaCl was added to increase the ionic strength of the solution. The EC reactor was made of Plexiglas, with a diameter of 19 cm and a height of 15 cm (Figure 1b). The EC working volume was 250 mL. In the study, Cantor alloy was used as the anode, aluminum as the cathode (4 cm wide, 5 cm high and 0.5 cm thickness) and a distance of 2 cm was set between the electrodes. The total effective electrode area was determined to be 24 cm^2. The reactor was supplied with a direct current power supply. Experiments were conducted in Congo red solution with initial an initial pH value of 7 and a conductivity of 4.02 mS/cm, at different current densities (5–100 mA/cm^2) for 15-minute electrolysis time. A sufficient distance was left between the bottom of the electrodes and the cell for efficient mixing. A homogeneous mixture of the solution was provided using a magnetic stirrer at 250 rpm. The electrodes were washed at least 2 times before each experiment.

Table 1. Congo red properties

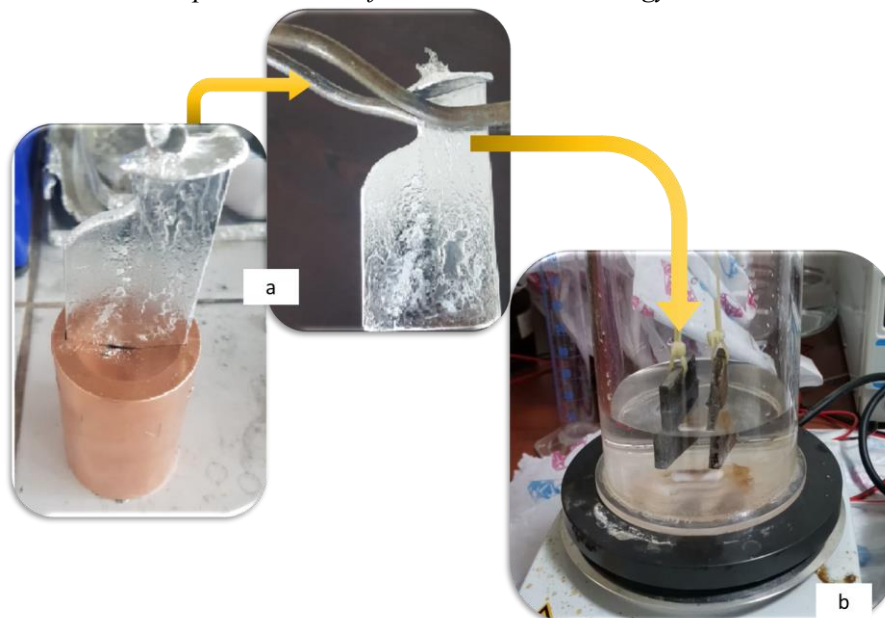| Formula	$C_{32}G_{22}N_6Na_2O_6S_2$
Formula Weight	696.68 g/mol
Brand	ISOLAB
Product Number	911.D01
Appearance	Brownish red powder

Figure 1. Preparation Cantor Alloy (a) EC process (b).

2.3. Analysis

The final pH and conductivity changes were recorded after EC studies at different current densities of Congo red solutions with the same initial pH and conductivity. pH value and the conductivity of the solutions were measured using the Hach Lange/HQ40d kit. The samples obtained after the EC sets were kept for 1 day to obtain the best removal efficiency. Afterward, the Hach UV/Vis DR5000 spectrophotometer was used for the COD and color removal of the supernatants. COD was analyzed according to the Standard Method 5220-D. Congo red starting COD and color concentrations were 500 mg/L and 6350 ADMI. COD and Color removals were calculated according to equations (1) and (2).

$$COD\% = \frac{COD_0 - COD_1}{COD_0} x100 \tag{1}$$

$$Decolorization\ (\%) = \frac{\lambda_0 - \lambda}{\lambda_0} x100 \tag{2}$$

3. Results and Discussion

In EC processes, the current density controls the reaction rate in the reactor since it regulates the coagulation rate and flotation rate. Therefore, it is one of the most critical parameters affecting EC (Mollah et al., 2004; Chen, 2004). EC was performed using different current densities to study its effect on COD and decolorization efficiency.

COD removal at various current densities is shown in Figure 2. It is seen in the figure that the current density was increased systematically from 5 mA/cm² to 50 mA/cm², and the highest COD removal efficiency of 86 % was obtained at 50 mA/cm². It can be due to the higher removal efficiency of pollutants with increasing current density, the higher number of ions produced on the electrodes which support the destabilized pollutant molecules, and thus, the agglomeration of the flocs formed due to the increase in hydrogen formation (Cerqueira et al., 2009). In this case, it can be explained by the accumulation of metal hydroxides in the

environment by increasing the current density that continues to be applied to the alloy. The optimum current density was determined as 10 mA/cm². COD removal efficiency of 84 % was obtained at 10 mA/cm². Although the highest removal efficiency was obtained at 50 mA/cm², the optimum current density was determined as 10 mA/cm² since applying 5 times higher current density for 4 % removal efficiency cause an increase in the energy cost.
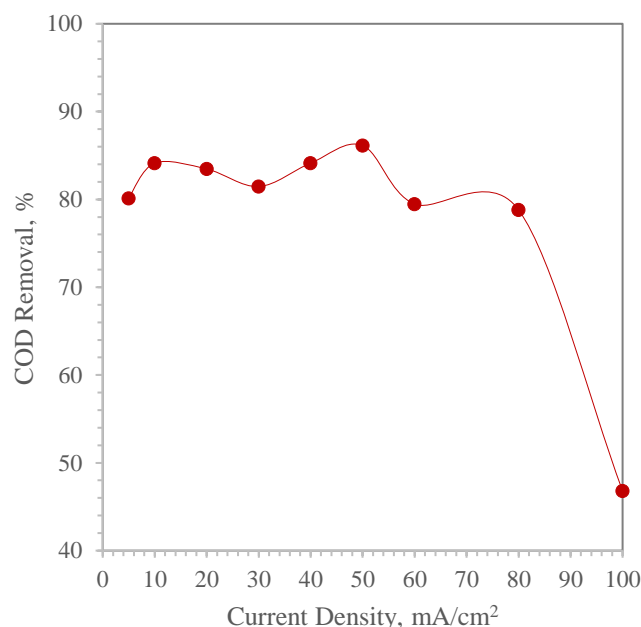

Figure 2. Influence of current density on COD removal

Color removal efficiencies depending on different current densities are given in Figure 3. The removal efficiency was above 90 % at all current densities. Metals ions produced from the CrMnFeCoNi alloy reacted almost all of the congo red molecules.

However, an insignificant but slight decrease in color removal was observed with the increasing current density. The previous studies showed that color removal increased with the increase in the current density (Daneshvar et al., 2006) Pajootan et al., 2012; Mohammadlou et al., 2014), while it created a small but insignificant effect in this study. Considering the final pH of congo red after EC, the increase in pH occurred with the increase in current density. The change in pH affecting the color removal emphasizes that the removal of dyes depends on operating parameters such as pH and current density. It is stated that the use of NaCl as an electrolyte at neutral pH provides anodic oxidation of Cl, and can affect color removal (Brillas & Martínez-Huitle, 2015).
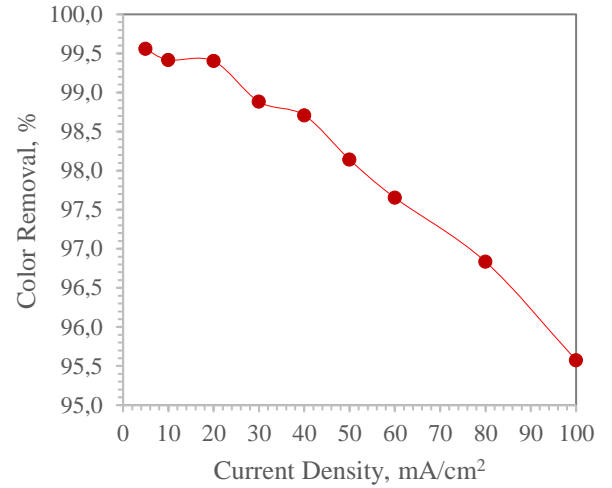

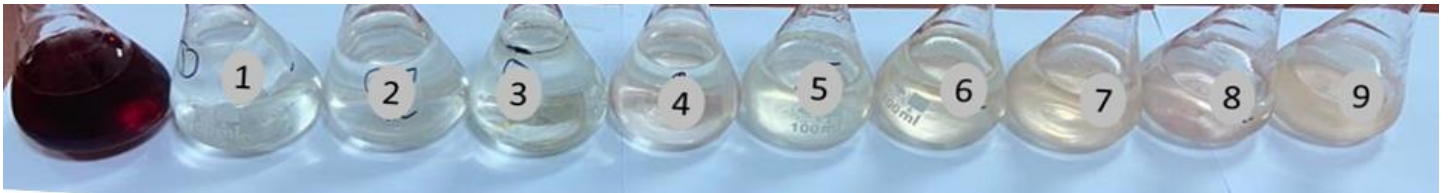*Figure 3. Influence of current density on color removal*

Figure 4. Color change after EC in different current densities (1:5 mA/cm², 2:10 mA/cm²,3: 20 mA/cm², 4:30 mA/cm², 5:40 mA/cm²,6:50 mA/cm²,7: 60 mA/cm², 8:80 mA/cm²,9:100 mA/cm², Electrolysis time:15 min)
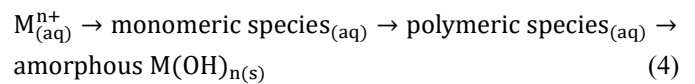
It is stated in the previous studies that the increasing current density increase the color and COD removal efficiencies (Cerqueira et al., 2009; Verma, 2017). However, the increasing current density increases the electricity and energy consumption leading to high costs for the process. Therefore, a treatment study at high current density reveals the disadvantages of the EC process. In addition, different metal anodes were examined and compared in the literature. For example, Armani et al. reported that Fe anode provides a more efficient COD and color removal than Al (Brillas & Martínez-Huitle, 2015). They showed that COD and color removal efficiencies of 84 % and 99.4 % were achieved at 10 mA/cm² for 15 mins using Fe anode.

Increasing the current density caused a change in the final pH and conductivity. This change in pH is a result of the EC mechanism. At the anode, the soluble metal (M) is dissociated into its ions by applying the current as given in Eq. (3).

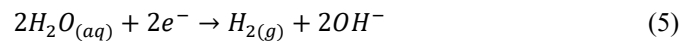$$M_{(s)} \rightarrow M_{(aq)}^{n+} + ne^- \tag{3}$$

Metal ions form coagulant species and metal hydroxides at a suitable pH (Eq. 4). During the EC, the large surface area of metal hydroxides causes rapid adsorption of soluble organic compounds and captures the colloidal particles. The forming heaps could be easily removed from the aqueous environment by precipitation or flotation (Feng et al., 2007). The elements in the CrMnFeCoNi HEA dissolved into metal ions with the applied current and formed metal hydroxides. It is stated that all elements have unique corrosion and adsorption capacities

(Vargel, 2020). Accordingly, COD and color removal efficiencies revealed that the pollutant adsorbing capacity of the CrMnFeCoNi HEA could be increased due to the presence of different metals.

$$M_{(aq)}^{n+} \rightarrow \text{monomeric species}_{(aq)} \rightarrow \text{polymeric species}_{(aq)} \rightarrow \text{amorphous } M(OH)_{n(s)} \tag{4}$$

The following reaction occurs at the cathode.

$$2H_2O_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2OH^- \tag{5}$$

It is seen in Eq. 5 that hydrogen is produced at neutral or alkaline pH. In addition, it was observed that the final pH increased with increasing current density. It can be interpreted that this situation is caused by the increase of OH^- ions dissolved in the cathode based on Eq. 5. On the other hand, the conductivity remained constant up to 30 mA/cm², after which it showed a tendency to increase (Figure 6). It can be interpreted that this situation was caused by the accumulation of ions in the water after the pollutant removal was completed. The increase in conductivity of water caused the formation of electro-corrosion. Although the conductivity remained constant up to 30 mA/cm², above which the increasing rate showed a smooth trend. Thus, it can be concluded that the electrode shows a corrosion-resistant property.
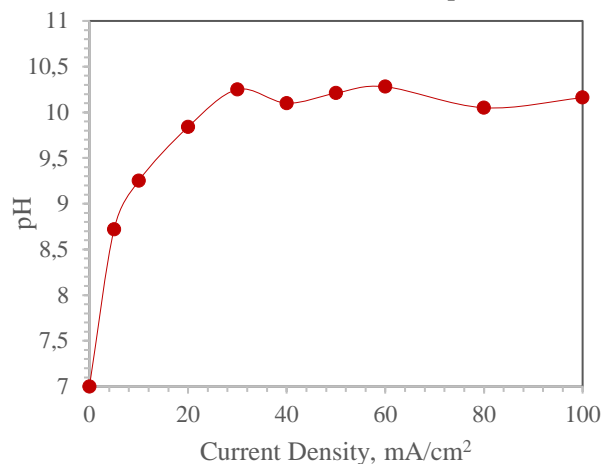
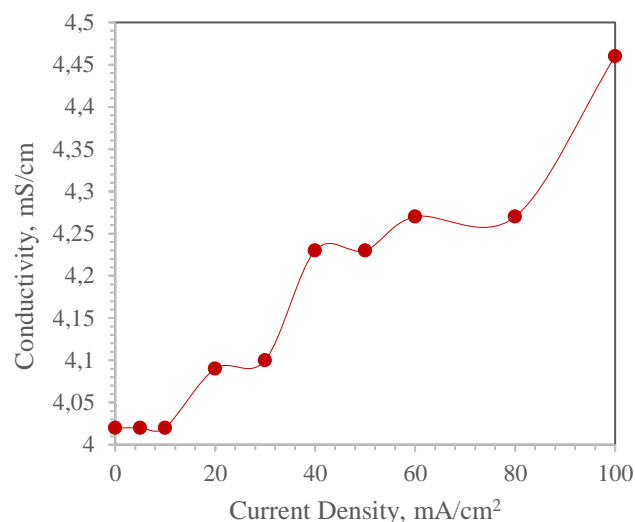*Figure 5. Change pH after EC in different current densities*

Figure 6. Change conductivity after EC in different current densities

4. Conclusions and Recommendations

In this study, the performance of a novel alloy system, so-called high entropy alloys (HEAs), which exhibit high corrosion behavior, in the treatment of wastewater with EC was evaluated. The well-known CrMnFeCoNi HEA (Cantor alloy) was used as an electrode the investigate its effect on COD and color removal efficiencies of synthetic dye solution at different current densities. pH and electrolysis time were kept constant during the process, and the best COD and color removal were obtained at 10 mA/cm^2, with values of 84 and 99.4 %, respectively. Since the Cantor alloy is effective at low current density, it can reduce the energy cost. Since HEAs are novel engineering materials, it is worth investigating their effect on the COD and color removal with various parameters.

Acknowledgment

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