Decolorization of reactive blue 19 from aqueous solutions by electrocoagulation process

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Abstract

Background: Industrial wastewater contains several harmful chemicals, such as textile dyes, that are toxic to human and biological life. Accordingly, the wastewater from textile industry must be treated to minimize hazardous effects, including carcinogenic, mutagenic, teratogenic, coloring agent prior to disposal. The aim of the present study was to investigate the effect of electrocoagulation (EC) process for reactive blue 19 dye removal from aqueous solutions.

Materials and Methods: In the current experimental study the electrocoagulation process was employed to remove reactive blue dye from aqueous solution using laboratory scale batch reactor. The electrodes were positioned vertically and parallel to each other. Two iron and two aluminum electrodes were used as anode and cathode, respectively. Different operating parameters, including current density (0.2, 0.5, 1.3, 2.6, 5.2 mA/cm²), initial pH (3, 5, 7, 9, 11), initial dye concentration (10, 20, 30, 50, 100, 200 mg/l), and reaction time (10, 20, 30, 60 min), were tested with the synthetic wastewater in order to determine the optimal parameters.

Results: The best-operating conditions were achieved at the current density of 0.5 mA/cm², initial pH of 3, and the dye concentration of 30 mg/l. The optimum parameters at the batch-stirred EC system led to 92.26 % and 98.93% of decolorization after 20 and 60 min of operation, respectively.

Conclusions: The results clearly showed that EC was an effective and operational process for reactive blue 19 removals.

Keywords: Decolorization, Electrocoagulation, Reactive blue 19

Introduction

Different types of chemical dyes are used in various industrial applications, such as textiles, dyestuffs, cosmetics, and paper industry (1). Dyes are typically divided into three groups of anionic, cationic, and nonionic dyes, which include subgroups of anionic (direct, acidic, and reactive), cationic (base dyes), and nonionic (scattered dyes). Reactive dyes are used widely due to their high diversity, solubility in water, and ease of use. The reactive blue 19 (RB19) with the chemical formula of C_{22}H_{6}N_{2}Na_{2}O_{11}S_{3} is anthraquinone dye, which has a complex molecular structure.

The disadvantages of blue 19 include low biodegradability, low light, dissolved oxygen transfer, and prevention from photosynthesis (2). Fig 1 illustrates the chemical structure of RB19.

One of the hazards of the reactive blue dye is its mutagenicity and carcinogenicity properties. For example, textile wastewater is one of the main contaminating sources of waters with dyed materials. The entry of dyed and toxic wastewater into the ecosystem affects the chemical and biological changes in aqueous solutions and consumes high amounts of oxygen. Accordingly, it is considered an important source of contamination.
in the aquatic environment (3). As can be inferred from their nature, dyes are characterized as the apparent contaminants. Even in relatively low concentrations, dyes remove the transparency and aesthetic quality of surface water, and prevent the penetration of light into the receiving waters. As a result, they cause serious damages to fish, fauna, and flora in the region.

These dyes are resistant to light, water, and oxidants, and consequently they are hardly collected after entering aquatic environments. Dyes are very resistant to biodegradation and remain stable in the environment due to their artificially constructed (4) and complex molecular structures. Given the new environmental rules, the use of existing and common control methods seems to not be helpful in the control of these contaminations. Moreover, they cannot be considered a factor in the control of entry and achievement of the discharge standards even by spending high cost.

As a result, a wide range of studies has been conducted on the identification and development of low-cost effective methods to control and remove these contaminations (5, 6). Several processes, such as precipitation, chemical coagulation, ion exchange, adsorption (surface adsorption), chemical oxidation, membrane processes, and biological degradation processes, have been employed to remove dye from wastewater.

One of the most important of these processes is electro-coagulation, which is effectively used to remove dye from wastewater. Electro-coagulation process (EC) can greatly remove the organic compounds due to its simplicity, usability in the environment, reliability, its ability in degradation of material at large volume, adaptability, non-toxicity, and less time for treatment, compared to some chemical methods (7, 8).

In the EC method, there is no need to add chemical materials (9), and the power electrical current is supplied from a direct power supply and transferred to the metal electrodes immersed in water. Metal ions are produced during auto-reactions in anode and hydrogen gas is released from the cathode. Metal ions at the appropriate pH level of the solution form a wide range of active coagulants and metal hydroxides, which coagulate the suspended particles of the solution and precipitate the adsorbed contaminants (10).

The electrocoagulation process produces low amounts of sludge and high stability, compared to chemical coagulation. The constant current passes through the inner plates, and the neutral side is charged with the polarization of the electrode, which has different polarity, compared to its side electrode. As a result, outer electrodes become bipolar and inner electrodes become mono-polar. The cell voltage is divided into electrodes based on the number of electrodes. This system is simple and requires low maintenance (11).

The EC method is an alternative technology for wastewater treatment and recovery of valuable chemicals from wastewater (12). Accordingly, the present study aimed to investigate the EC process for RB19 removals from aqueous solution.

Materials and Methods

This research was derived from a research project with the code of 4121 and the ethics code of Ir.bums.REC.1394.124.

Chemical materials

For adjusting the solution pH (using pH-Meter 765 Calimatic) of 11, 9, 7, 5, 3, the researchers applied 1M HCl acid and 1M NaOH. To prepare the synthetic colored wastewater, RB19 was dissolved in one-liter glassy breaker deionized water, which was used as a stock solution. After the determination of the optimal pH in the initial concentration of 30 mg/L, the current density was examined in the values of (0.2, 0.5, 1.3, 2.6, 5.2 mA/cm²). Finally, after the determination of the
current density and optimal pH, different concentrations of the RB19 were adjusted at 10, 20, 30, 50, 100, 200 mg/l.

**Pilot set up and procedures**

This experimental study was conducted in a batch laboratory reactor. This reactor had 4 electrodes (2 iron electrodes and 2 aluminum electrodes), which were employed in one unit simultaneously. Present pilot connected to an external power source alternately.

The EC unit consists of a 500 ml electrochemical reactor with anode and cathode with an effective surface area of 30 cm² for each electrode. Fig 2 illustrates the pilot set up used in this study. The reactor consisted of two iron electrodes as an anode, and two aluminum electrodes as a cathode. The electrodes were connected to electrical power supply (ADS30035-3D). Metal ions were produced in Mechanism1 and metal hydroxides were produced in Mechanism 2 in solution. The produced flocks had wide surface and they were useful in the quick adsorption of organic compounds from solution and imprisonment of colloid compounds. Finally, these flocks were easily removed by flotation or deposition. The mechanism of production of metal hydroxides in iron electrodes as anodes was based on the following mechanisms for the production (13):

**Mechanism 1:** Anode: 4Fe → 4Fe2+ + 8e−
**Mechanism 2:** 4Fe2+ + 10H2O + O2 → 4Fe(OH)3 + 8H+
**Mechanism 3:** Cathode: 8H+ + 8e− → 4H2
**Mechanism 4:**

Overall reaction (13):

4Fe + 10H2O + O2 → 4Fe(OH)3 + 4H2

**Analysis methods**

In the present experiment, the colorimetric method was used to measure the number of RB19 using T80+ UV/V is Spectrometer at 592 nm wavelengths based on the methods presented in Standard methods (14). All the materials were produced by Merck Company. Sampling and experiments were performed in two runs and data were analyzed using Excel software 2010.

The removal efficiency was calculated as follows:

\[ E\% = \frac{C_0 - C_t}{C_0} \times 100 \]

Where, \( C_0 \) (mg/l) is initial concentration and \( C_t \) (mg/l) denotes secondary concentration after reaction time \( t \) (min).

**Results**

**The effect of initial pH**

As shown in Fig 3, the electrocoagulation process is dependent on pH. With the increase of pH from 3 to 11, the removal efficiency of dye decreased. Accordingly, the removal efficiency was 92.93% at pH 3, which decreased to 65.6% at pH of 11.

**The effect of initial concentration of dye**

Fig 4 depicts the effect of RB19 concentration on the removal efficiency. Based on the chart, it is shown that with the increase in dye concentration, the removal efficiency decreased. As a result, the removal efficiency was 93.95% in the concentration of 10 mg/l, which decreased immediately to 17.93% with its increase to 200 mg/l.

**The effect of Current density**

Fig 5 illustrates the effect of the current density on the removal efficiency. Based on the chart, it is shown that with the increase of the current density from 0.2 to 5.2 mA/cm², the removal efficiency elevated from 51.26% to 97.6%.

**The effect of reaction time**

The effect of contact time on the removal efficiency is shown in Fig 6. Based on this chart, it is shown that with increasing contact time from 10-20 min, the removal efficiency increased from 38.6-92.2% and with increasing the contact time to 60 minutes, removal efficiency increased to 98.93%.
Fig 3. Effect of initial pH of the solution on the removal efficiency of the reactive blue 19 (initial concentration=30 mg/l, current density=0.5 mA/cm², contact time=20 min)

Fig 4. Effect of changes in the concentration of reactive blue 19 on its removal efficiency (pH = 3, current density =0.5 mA/cm², contact time= 20 min)

Fig 5. Effect of current density on the removal efficiency of the reactive blue dye 19 (pH=3, initial concentration=30 mg/l, contact time=20 min)
Discussion

According to Fig 3, the identification of the optimal pH of the solution has an important role in the efficiency of the EC process and the contaminant removal mechanism. Experiments were performed for different pHs and the highest removal efficiency was obtained at pH of 3. It was also found that the pH of the solution after the EC process elevated with the increase of electrolysis time due to the production of hydroxide (15). The results showed that the removal efficiency of the dye decreases with the increase of pH. The formation of bivalent and trivalent iron ions depends on the soluble pH (16).

The bivalent ions of iron were in the forms of Fe$^{2+}$, Fe(OH)$^+$, Fe(OH)$_2$ and Fe(OH)$_3^-$: The dominant concentration of these species depended on the pH conditions. At pH less than 11, all bivalent ions were in the form of Fe$^{2+}$. Additionally, Fe(OH)$^+$, Fe(OH)$_2^-$, Fe(OH)$_3^-$ forms at pH less than 11, pH between 1.5 and 11 and pH over 1.5 were in the dominant forms in the solution, respectively. Trivalent ions Fe$^{3+}$, Fe(OH)$_2^+$, Fe(OH)$_3^-$ and Fe(OH)$_4^-$ at pH less than 3, 3-4, 4-6, 6-9.5, and above 9.5 were dominant, respectively. The increase of pH reduced the concentration of Al(OH)$_3$ and elevated the concentration of Al(OH)$_4^-$, leading to reduced removal efficiency of the contaminant (16).

Based on Fig 4, the effect of different concentrations of dye on the removal efficiency showed that with the increase in concentration, the removal efficiency was strongly reduced. At low concentrations, the number of iron hydroxide compounds was higher, compared to the number of dye molecules and the removal efficiency was better for the lower concentrations of dye. In constant current density for all concentrations of dye, a constant value of aluminum ion entered the solution. As a result, based on the Faraday’s law, constant values of flocks would be produced in solution. As a result, the produced flocks at high concentrations of dye were insufficient to absorb all molecules of soluble dye. In other words, by the increase of dye concentration, the removal percentage of dye was significantly reduced (17).

Hussin et al. (2017) examined the lead removal efficiency at a concentration range of 5-30 mg/l in a research conducted by on lead removal by photovoltaic electrocoagulation using a perforated lead electrode. The results showed that the increase of the lead concentration led to the decrease of the removal efficiency. The reason is that the increase in lead concentration caused an increase in concentration polarity through adsorption on the anode and cathode and led to reduced anode dissolution and gas production in the cathode (18).

In addition, in a research conducted by Bayramoglu et al. (2003) on the degradation of reactive blue dye from aqueous solution using aluminum electrodes, they concluded that with the increase of the concentration from 100 to 1000 mg/l, the dye degradation was reduced from 100% to 70% (19). Carvalho et al. also tested the removal efficiency of dye using electrocoagulation method for concentrations of 50 to 300 mg/l. The results showed that with the increase of dye concentration, the adsorption capacity of the flocks decreased. This led to the reduction in the removal efficiency of dye, given that the coagulant value was kept constant (20).

In a research conducted by Kumar Nandi et al. (2013), the same results were obtained so that after 30 min of the process, with the increase of the concentration from 50 mg/l to 200 mg/l, the
removal efficiency was reduced from 98.87% to 67.78%. The reason is that in constant time and density, a constant value of iron hydroxide compounds was produced in all dye solutions. As a result, the flocks produced at high concentrations were insufficient to absorb all the soluble dye, while the number of iron hydroxide compounds were higher than the number of dye molecules at lower concentrations (10).

The current density was an important parameter in the electrocoagulation process, which determined the value of coagulant, the value of bubble produced, the size and growth of flocks, which can affect the efficiency of the electrocoagulation process. As shown in Fig 3, the anode dissolution rate of anode elevated with the increase of the current density, leading to an increase in the number of metal hydroxide flocks, and thus increased the removal efficiency of contaminants (15).

Accordingly, based on the results of the effect of current density on the removal efficiency, it was found that the increase of the current density from 0.05 mA/cm² to 1 mA/cm², the removal efficiency increased from 51.26% to 97.6%. The current density determined the value of metal ions released from the electrodes. In general, the dissolution of metal ions was directly associated with the applied current density.

However, the excessive increase of current density leads to condition, in which the electrical energy is wasted during increased water temperature and the efficiency of current density decreases. With the increase of the current density from a certain value, there is no change in the removal efficiency (15).

Likewise, in a study carried out by Bellebia et al. (2009) the increase of current density from 0.94 mA/cm² to 4.12 mA/cm², the removal efficiency of the acidic dye increased from 70.66% to 93.48% (21). Vasudevan (2014) conducted a study on the removal of phenol from aqueous solution using electrocoagulation method, indicating that the increase of the current density from 0.22 A/dm² to 0.1 A/dm² led to a significant increase in the removal efficiency. The obtained results revealed that the value of phenol removal was related to the value of adsorbent production (ferric hydroxide), which was related to the time and current density.

With the increase of current density, more bubbles with smaller sizes were produced, which resulted in more phenol removal through flotation. Accordingly, the concentration of hydroxyl production and current density directly affected the removal efficiency. Increase in the current density led to more dissolution of the iron and production of more hydroxyl radicals (22). The results showed that with the increase of the contact time, the removal efficiency of the dye increased, and in the first 20 min of the EC process, more than 90% of solution dye was removed with a concentration of 30 ppm. One of the important parameters in the removal efficiency of contaminants during the electrocoagulation process was the effect of contact time, which determined the value of ion produced from the ion electrolyte.

The reaction time affected the electrolysis process efficiency. During the dissolution process, the anionic electrode produced a coagulant. The dye removal efficiency was associated directly to the concentration of metal ions produced in the electrodes. In the current research, the electrolysis time was examined at a constant current density of 8 mA/cm² and pH of 12. The results showed that with the increase of the reaction time from 10 to 60 min, the removal efficiency increased from 68% to 92%. After 20 min, only 10% removal efficiency increased, which led to considering the contact time of 10-20 min as the optimal time (23).

The reaction time influenced the efficiency of electrolyte process. During electrolysis, anionic electrolytic dissolution led to the production of different coagulants. The dye removal efficiency was directly affected by the concentration of metal ions produced in the electrodes (11). As the electrolysis process time increased, the concentration of metal ions and hydroxides flocks increased (24). In a study conducted by Aoudj et al. (2010) on the treatment of dyed wastewater resulting from industries using electrocoagulation, it was found that the increase of the reaction time from 10 to 60 min, the removal efficiency of dye increased from 52.2% to 98.28% (11).

**Conclusion**

Electrocoagulation is a promising technology, which can play a key role in water treatment. However, this method offers several disadvantages over conventional coagulation/flocculation methods. The types and amounts of produced species depend on the metal concentration and pH. Although the present study did not investigate the treatment cost of dye, the obtained results revealed that the optimum parameters (pH=3, initial dye concentration=30 mg/l) led to the 98.93% of decolorization after 60 min of operation with the lowest consumption energy at the current density of 0.5mA/cm².

The current study benefited from bipolar
configuration by using 4 electrodes (alternative arrangement) for dye removal because in bipolar connection there is a higher surface area compared to that of monopolar connection (25). It was found in the literature that reactive blue dye can be removed from wastewater via their reaction to hydroxide precipitates generated from methods and released by the electrodes.

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Conflicts of Interest
The authors declare no conflicts of interest.

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