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Research Article

Contaminant Removal from Drilling Wastewater by Electrocoagulation Method

Muhammed Kamil Oden, Kadriye Ozen*, Emre Midik

Selcuk University, Sarayönü Vocational High School, Department of Environmental Protection Technologies, Konya,Türkiye

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Abstract

In this study, it is aimed to treat the wastewater from drilling operations during the creation of a natural gas storage area by electrocoagulation (EC) method. Boron and sulfate parameters in the wastewater were tried to be eliminated with the help of aluminum electrodes. During the removal of boron and sulfate pollutants, optimization studies were carried out on process time, pH, and current criteria. Boron (B) and sulfate (SO_4) concentrations of wastewater generated during drilling were measured as 1.18 mg/L and 3348 mg/L, respectively. The samples taken after the purification work were placed in the measuring tapes and kept on hold for 24 hours. After the settling time, samples taken from the upper part were analyzed. During boron and sulfate removal, 16 mA/cm^2 current, 30 min contact time, approximately 61% and 36% efficiency were obtained at 7 pH values.

Keywords

Drilling Wastewater, Removal, Electrocoagulation, Aluminum Electrode

1. INTRODUCTION

Water is one of the most basic needs for human beings and all other living things. Easy access to clean water is a critical factor for the continuity of a healthy life. However, with the increase in the population, the annual global water demand has increased and the mixing of wastewater into the existing water resources jeopardizes clean water resources. Researchers predict that

* **Corresponding Author:** Kadriye ÖZEN, kadriyeozenn.1@gmail.com, 0000-0001-8849-8330

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climate changes such as temperature rise due to global warming and adverse changes in the hydrological cycle will increase the pollution of water resources, flood formation, severe droughts, and toxic chemical pollution that negatively affects the natural environment [1]. The reuse of treated water is increasing rapidly in the world. Although reuse rates are different in each country, it reaches up to 40% in some countries [2]. In recent years, electrochemical treatment methods such as electrooxidation and electrocoagulation have attracted attention due to their environmental importance and economic efficiency [3-5]. Compared to conventional coagulation-flocculation applications, electrocoagulation has the advantage of removing the smallest colloid particles due to the presence of an electrical field [6]. Wastewater generated as a result of industrial processes should be treated in a way to bring them to the standards specified in the Water Pollution Control Regulation before they are discharged to the receiving environment. Undesirable effects occur in terms of both aesthetics and human health when textile wastewater containing dyestuffs, even at very low concentrations, is discharged to the receiving environment without treatment. For example, the dyestuff absorbs the sun's rays, and as a result, it causes a decrease in the dissolved oxygen in the environment by preventing photosynthesis in the receiving environment [7]. There are many pollutants that can have a toxic effect. This situation causes extinction and mutation of species in the receiving environment where the wastewater is discharged and limits the reuse of water. It also increases the risk of toxic and carcinogenic substances by creating accumulation in aquatic organisms [8]. The treatment methods commonly used in the treatment of wastewater are generally biological and physicochemical treatment processes. Biological treatment methods are natural processes based on bacteria and small microorganisms. Physicochemical treatment is a method that usually requires the addition of chemicals. Recent studies have focused on the development of promising techniques based on electrochemical technology that does not require chemical additions. These include electrocoagulation, electroflotation, electrodeposition, and others. Electrocoagulation is one of the physicochemical treatment methods that do not require chemicals. The EC process emerges as a preferred process due to its various advantages over the chemical coagulation process [6, 9]. For the development and optimization of the EC unit, characteristics of wastewater such as pH, process variables such as current density and application time, and process configurations such as the type of electrode material and connection type need to be considered in detail [10].

In the electrocoagulation process, if dissolving iron or aluminum electrodes are used as anodes, these electrodes dissolve and give Al^{3+} and Fe^{2+}, Fe^{3+} ions to the solution. These ions combine with the hydroxyl ions in the water and are slightly soluble in $Al(OH)_3$, $Fe(OH)_2$, and $Fe(OH)_3$. It forms metal hydroxides such as. The adsorption properties of metal hydroxide particles formed during electrocoagulation are very high [11]. When aluminum electrodes are used as the anode in the electrocoagulation process, which is one of the electrochemical treatment methods, Al^{3+} ions dissolve and mix with the aqueous environment and combine with the hydroxyl ions in the water to form metal hydroxides with high adsorption properties according to the pH value of the environment, agglomeration of suspended solids and precipitation of dissolved pollutants [12]. Therefore, electrocoagulation in recent years, it has been used successfully in the treatment of paint and textile wastewater, dairy industry wastewater, biodiesel wastewater, and petroleum refinery wastewater, for the removal of different types of pollutants such as organic compounds, heavy metals, anions (such as nitrate, fluoride, and phosphate) and hardness [13].

The quality of well water, artesian, and drill water varies depending on the geology of the basin where the water source is located. Water falling to the earth as precipitation water is polluted both naturally and artificially. For example, limestone environments cause hard waters rich in calcium and magnesium. Precipitation waters in such areas can reach surface waters and underground waters (well water). Artificial pollution, on the other hand, is completely the result of human activities. Industrial wastes, the use of fertilizers and pesticides in agriculture, and domestic wastewater are mixed with underground and surface waters and adversely affect water quality. In parallel with the rapidly increasing world population, there is an increase in the fuel need of human beings, which causes the number of oil and natural gas drillings in the world to increase day by day. Due to the increase in the mentioned drilling activities and the increase in environmental pollution problems caused by the wastes generated during the drilling activities, companies such as Turkish Petroleum Corporation (TPAO) engaged in hydrocarbon drilling have directed the research and development of new methods for the disposal of drilling wastes [14]. Since the beginning of the 2000s, shale gas obtained by using horizontal drilling and hydraulic fracturing methods has led to decreases in natural gas and oil prices worldwide. Today, it has been determined that there are shale gas reservoirs in Turkey, and research continues under the leadership of TPAO [15]. Our waters contain impurities that we cannot see with the naked eye but are harmful to our health. Sometimes we feel them as bad taste, smell, color, scale, and sediment. Sometimes, it may contain various viruses, bacteria, microbiological agents, and heavy metals unknowingly. Generally, treatment technologies are advantageous compared to other disposal methods, as they enable the recovery and reuse of drilling wastewater [14]. The electrocoagulation process is used as an effective method for the treatment of many industrial wastewaters due to its many benefits. In the literature, it is seen that the electrocoagulation process is frequently used in purification. It is also used in the treatment of wastewater containing specific inorganic/organic pollutants such as electroplating wastewater, heavy metal-containing wastewater, mining effluent, textile industry wastewater, garbage leachate, wastewater containing surfactants, agricultural industry wastewater, dairy wastewater, and underground water and drinking water treatment [16].

This study aims to treat the wastewater generated from drilling operations during the creation of a natural gas storage area by electrocoagulation method. Boron and sulfate parameters in the wastewater were tried to be eliminated with the help of aluminum electrodes. During the removal of boron and sulfate pollutants, optimization studies were carried out on time, pH, and current criteria.

2. MATERIALS AND METHODS

2.1. Drilling Wastewater

The drilling wastewater used in this study was obtained from an industry in Aksaray. Wastewater samples were stored at +4 °C. Table 1 shows the characterization of raw wastewater.

Table 1. Raw wastewater characterization**.**

Parameters	pH	Conductivity (µS/cm)	Temperature (Kelvin)	Oil-Gres (mg/L)	Boron (mg/L)	Sulfate (mg/L)
Value	5.47	>100 000	296	9.88	1.18	3348

2.2. Electrocoagulation Process

Two electrodes with 3 cm spacing (an anode and a cathode) were placed perpendicular to the reactor. The electrocoagulation scheme is shown (see Fig. 1). A laboratory scale EC reactor was made of plexiglass with a diameter of 9 cm and a length of 13 cm. Aluminum electrodes consisting of an anode and a cathode, 6 cm wide, 11.5 cm high and 0.1 cm thick equal electrodes were prepared and used in the experiment. Direct current of the reactor was achieved by using Mervesan 305D II brand power supply. The volume of wastewater used is 500 mL.

The electrocoagulation process is effective in removing pollutants from different types of wastewater and is also effectively used in the treatment of ground and surface waters. Some areas where this process is used are groundwater treatment, drinking water treatment, domestic wastewater treatment, and contact cooling towers, and they can be listed as contaminated water.

Aluminum (Al^{3+}) and iron (Fe^{3+}, Fe^{2+}) electrodes are widely used in electrocoagulation. These electrodes react with water during the process to form metal hydroxides such as $Al(OH)_3$, $Fe(OH)_2$, and $Fe(OH)_3$ [17].

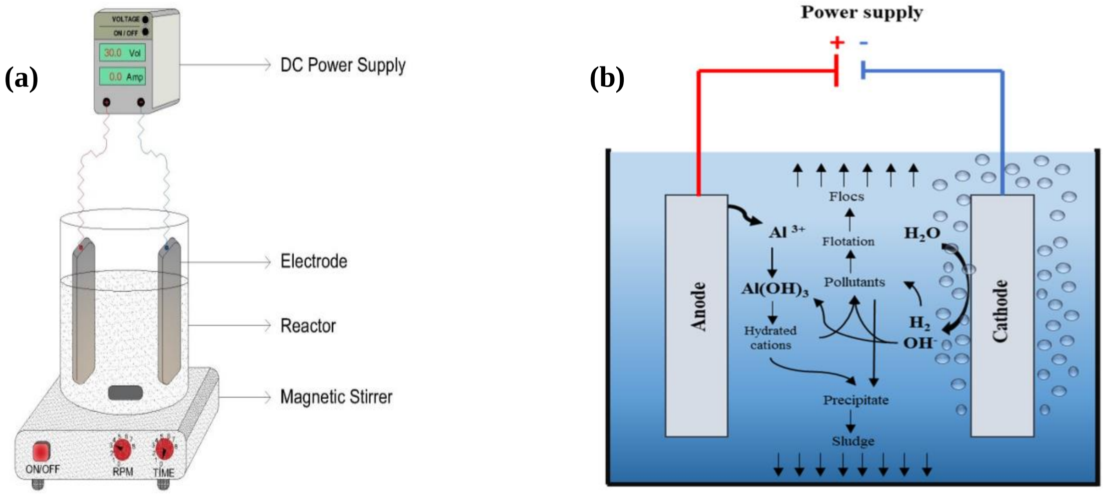

Figure 1. (a) Schematic representation of EC process[18] **(b)** Some Systematic Diagram of the Electrocoagulation process [19]

During the experimental work, the wastewater in the reactor was mixed using a magnetic stirrer at a speed of 0-300 rpm. Prior to EC experiments, the surfaces of the electrodes were cleaned with acetone and maintained in a cleaning solution (100 mL of 35% HCl and 200 mL of 2.8% $C_6H_{12}N_4$) for at least 5 minutes and then rinsed with distilled water and dried in a disinfector at 105 ^{0}C. The current density (16-48 mA/cm^2), the reaction time (10-30 min) and pH (3-10), which affect the EC process. After a few hours of precipitation period after each experimental set, the purified samples were pipetted and analyzed according to Standard Methods.

3. RESULTS AND DISCUSSION

Drilling wastewater treatment with the electrocoagulation method using aluminum metal anodes, changes in the drilling wastewater with different pH, time and current experiments in the laboratory environment using aluminum metal parts were observed. During the experimental study, the pollution load of boron (B) and sulfate (SO_4) parameters was investigated.

2.3. Time optimization

While taking the time optimization values, 16 mA/cm^2 electricity was applied in the electrocoagulation device with the help of an aluminum metal electrode, and the study was carried out at the times determined for the time optimization study (10, 20, 30, 40, 50, 60, 90 minutes). The sedimentation process was ensured by keeping the wastewater passing through this process for 24 hours. Then, boron (B) and sulfate (SO_4) analyses of the supernatant (caliper topwater), respectively, were performed in a spectrophotometer device. The time optimization scheme is shown (see Fig. 2).

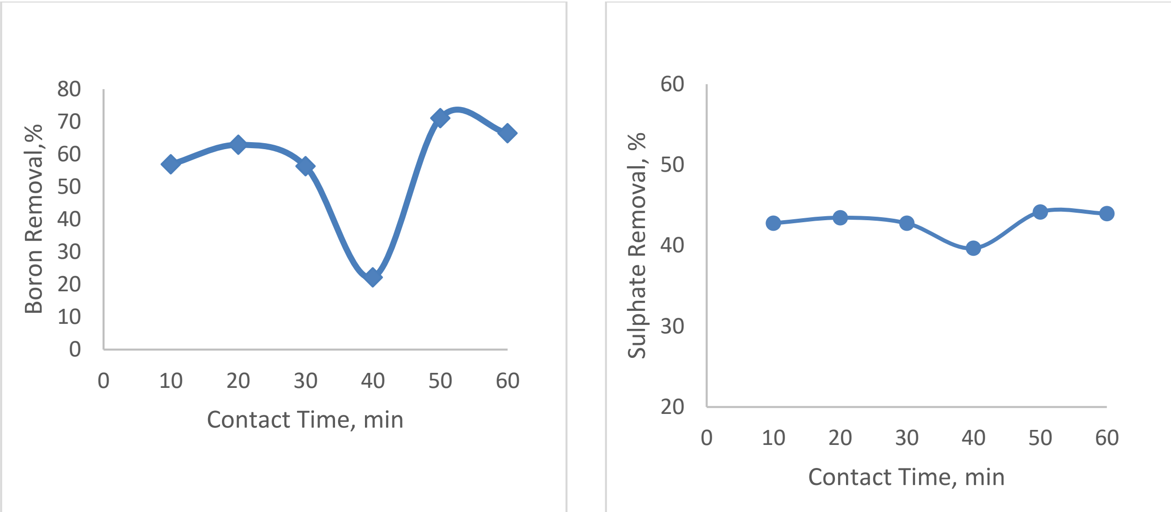

Figure 2. Time optimization in the application of the electrocoagulation process.

2.4. pH Optimization

While determining the pH optimization, the contact time was taken as 30 minutes and the current constant of 16 mA/cm^2 was applied. The pH values used for the pH study were determined as (3, 5, 7, 9), respectively. After the pH of the drilling wastewater was adjusted by adding acid or base, the application was started in the wastewater electrocoagulation process. The applied wastewater was taken into a measuring tape for waiting. Boron (B) and sulfate (SO_4) analyzes were made in these samples, and measurements were made in the spectrophotometer device. The pH optimization scheme is shown (see Fig. 3).

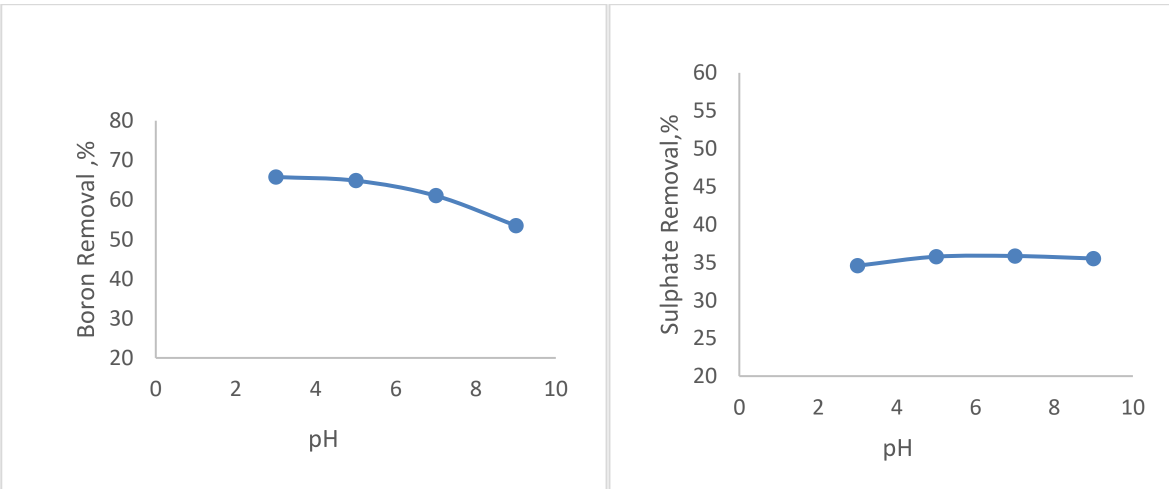

Figure 3. pH optimization in the application of the electrocoagulation process.

2.5. Current Optimization

After the optimization was determined as the original pH of the raw wastewater and the contact time of the pH value as 30 minutes, a trial study was started in the drilling wastewater to determine the other variable flow. For flow optimization, the study has been started on the treatment of drilling wastewater with flows in the range of 0-16-32-48 mA/cm^2. The current density optimization scheme is shown (see Fig. 4).

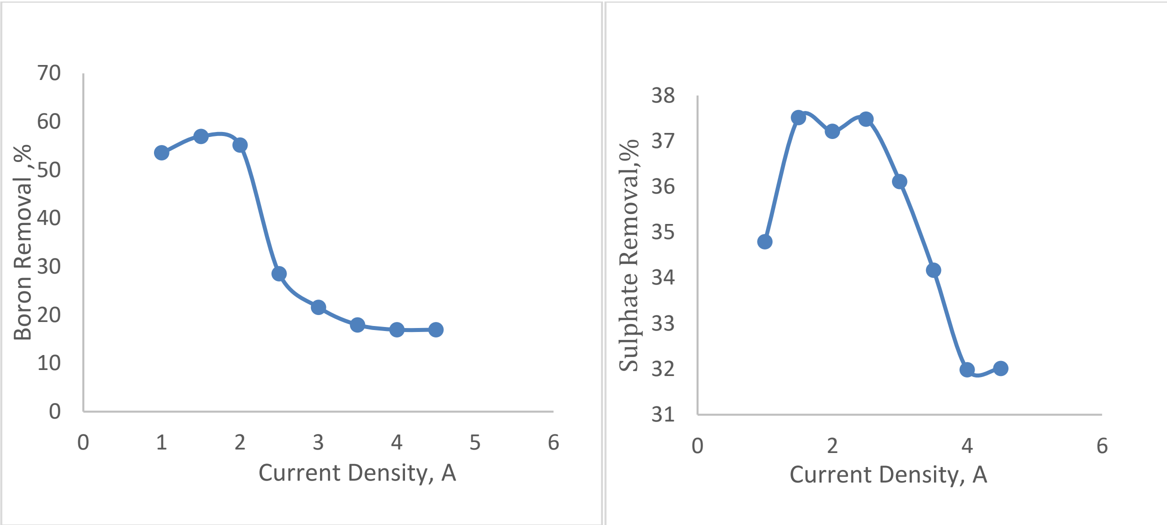

Figure 4. Current Density optimization in the application of the electrocoagulation process.

In this sense, cost-effective process such as EC to recover them from wastewater and reuse in recent years has attracted the attention of researchers. In different studies, by applying various electrode materials as cathode and anode, high pollutant removal efficiencies were achieved.The electrocoagulation process performs very good treatments on aluminum and iron electrodes [20]. Comparison the results of this study with some studies is shown (see Table. 2).

Table 2. The obtained results for real water type with available data in the literature. (Initial concentration (C_0 in mg/L), Electirical Conductivity (E.C in mS/cm), current density (j in mA/cm^2), acidity (pH_i) and reaction time (t in min)).

Electrode	*Pollutants*	*Operating parameters*					*R_e (%)*	*Refs.*
		C_0	*E.C.*	*j*	*pH_i*	*t*		
Al	B and Sulphate	1.18, 3348	>100 000	16	7	30	61, 36	This Study
Fe-Fe	COD, color, Ni, Zn, total Cr	475.8, 5983, 8.1, 149.25, 358	17.14	30	5	30	76.2, 99.8, 96, 99.7, 98.5	[18]
Al, Steel	nitrate-N	10-31.7	7.73-31.36	20, 20	8-9	300-360	>90	[21]
Fe, Al	Cu, Cr, Ni	45, 44.5, 394	2.0	10	3	20	100	[22]
Al	oil and grease	35	6.19	20–80	3.6–8.7	20	98	[23]
Fe&Al	COD, oil-grease, chloride	560, 125, 150	0.98	3	8	30	88, 90, 50	[24]

3. CONCLUSION

In this study, boron and sulfate removal from drilling wastewater by electrocoagulation method was investigated. Efforts were made to purify the wastewater generated during drilling from the Aksaray region by using aluminum electrodes. According to the data obtained, the most appropriate contact time was determined as 30 minutes. Boron (B) parameter input value (C_0) was measured as 1.18 mg /L and Sulphate input value (C_0) was measured as 3348 mg /L. First, time optimization was applied, and pH and current optimization were performed, respectively.

As a result of these measurements, the most suitable pH value was determined as the original pH. During boron and sulfate removal, 16 mA/cm^2 current, 30 min contact time, approximately 61% and 36% efficiency were obtained at 7 pH values.

It should not be forgotten that raw wastewater trials should be carried out in order to be used in heavy metal removal studies from wastewater. Due to the fact that the electrode material used in the study is a waste material, it does not have any cost other than the cost of transportation and can be easily supplied, and it is thought that environmental protection is realized in many ways thanks to the use of aluminum metal waste, which is an environmentally waste material, in wastewater treatment. It has been demonstrated that the wastewater generated during drilling operations can be treated by the electrocoagulation process without changing the original pH and conductivity values. With this study, more than 37% removal of boron and sulfate parameters from drilling wastewater was obtained. It is important to study both the first usage of wastewater from the Aksaray industry. It is also valuable that the data obtained have been acquired as a result of the treatment of real wastewater. These data will shed light on the treatment of drilling industry wastewaters and help design industrial type treatment plants. As a result, the electrocoagulation process is an effective method in the treatment of drilling industry wastewater.

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