

Removing of the Dye Pollutant Acid Red 1 from Contaminated Waters by Electrocoagulation Method Using a Recirculating Tubular Reactor with Punched Anode

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Summary: In the present study the removal of Acid red 1 (AR1), as a pollutant of contaminated waters, was investigated by the electrocoagulation method using a recirculating tubular reactor with punched anode. The role of the parameters affecting removal efficiency including current density, electrolysis time, electrolyte concentration and type, pH, the flow rate of the solution, and dye concentration was studied. Spectrophotometric results indicated that for 2500 ml of the dye solution containing 30 mg L⁻¹ AR1 more than 95% of the dye was removed under the following conditions: current density of 1.3 mA cm⁻², electrolysis time of 20 min, pH of 6, electrolyte dosage of 0.08 g L⁻¹, and the flow rate of 2 L min⁻¹. Results showed that with an increase the electrolyte concentration and current density, color removal efficiency increases. Increasing of the flow rate of solution in the reactor due to decrease the retention time, decreases the removal efficiency. According to nature of electrocoagulation process, neutral range of pH is suitable for decolorization process.

Keywords: Acid red 1, Electrocoagulation, Decolorization, Recirculating tubular reactor, Punched anode.

Introduction

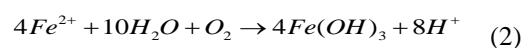
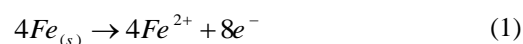
Due to the existence of different industries in this modern and developed world and as a result of human being's rapid breakthrough in different aspects of science, it is necessary to consider environmental pollution as a phenomenon which destroys our habitats and environments gradually and subtly. Indeed, it can be argued that environmental pollution can be rightly regarded as one of the greatest threats to human beings in the 21st century. Hence, in the future, preserving water for human survival and health is considered to be an issue which must be definitely addressed [1]. Most common colors which is used in the industries dealing with dyeing and textile include azo dyes. They have one or more azo groups (-N=N-) in their structures which can cause mutation and cancer in animals and human beings. Furthermore, due to their aromatic structures, azo dyes are highly stable compounds which make them resistant to biodegradation and other treatment methods. Acidic colors are regarded as a significant category of azo dyes. Most of the members in this category are mono-azo or di-azo dyes [2]. In recent years, many physico-chemical methods such as sedimentation, chemical coagulation, ion exchange, adsorption on a variety of adsorbents, photocatalytic oxidation, membrane processes like nano-filtration, and reverse osmosis and biodegradation have been mainly used for treatment of dye wastewaters [3, 4]. In the last decade, electrocoagulation has attracted the attention of many researchers to treat

wastewaters. Today, it is mainly used for treatment of wastewaters produced in food and oil industry, dye and textile industry, chemical and mechanical polishing. It has also been greatly useful in removing detergents and heavy metals from wastewater [5]. In this process, the removing agent of the pollutants (iron or aluminum hydroxide clots) is produced by the electrochemical reactions which use an electrochemical cell. Hence, wastewater treatment is conducted according to the following three major processes:

1. Electrochemical reaction on the surface of the electrode followed by coagulant formation in the aqueous media.
2. The pollutants which are soluble or colloidal are adsorbed on coagulants.
3. Removing via sedimentation or floatation [6].

In case of the use of iron as an electrode, the following reactions are observed:

At the anode:

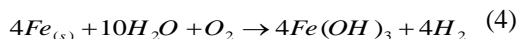


At the cathode:

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Overall reaction:



The obtained $Fe(OH)_3$ stays in the aqueous solution in the form of gelatinous suspension; it can remove pollutions from wastewater by complexation or electrostatic attraction after which coagulation phenomenon takes place. In complex formation mechanism which happens on the surface, the pollutants are attracted to the hydrated iron in the form of ligand [7].

The present study aimed at investigating the removal of AR1 dye pollutant from aqueous-based solutions using electrocoagulation which utilizes a recirculating tubular reactor having punched anode. Moreover, the role of some important parameters including current density, electrolysis time, concentration and type of electrolyte, pH, flow rate of the solution, and the concentration of dye was investigated.

Experimental

Design of reactor

As Fig.1 shows, the electrocoagulation system consists of a DC power supply (ADAK-PS808), a reactor including an iron pipe as the cathode and another iron punched pipe inside it as the anode, and a pump and a plastic tank for storage of solution. The cathode was made of a pipe with a length of 21.1 cm and a diameter of 7.2 cm, and anode was made of a pipe with a length of 21.1 cm and a diameter of 2.8 cm, that were parallel with the anode electrode inside the cathode tube.

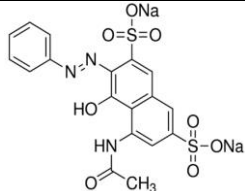
Chemicals and the Analysis

All the chemicals used in the study, including NaCl, NaOH and H_2SO_4 were provided by Merck; Acid Red 1 used in the study was obtained from Sigma-Aldrich. The structure and characteristics of the AR1 are given in Table-1.

All tests were performed in a recirculating tubular reactor at room temperature (298 K), and the solution volume was set to 2.5 liters. Due to the low electrical conductivity of the sample, to increase the electrical conductivity of aqueous solution sodium chloride, potassium chloride, sodium sulfate, and

sodium bromide were used as an electrolyte. A total amount of 2.5 liters of solution containing 30 mg L^{-1} of the dye were prepared, and the appropriate amount of electrolyte was added to them; after turning on the pump, while passing the solution from the reactor, the desired current density was established between the electrodes. After interrupting the flow, the dye solution was transferred into the test tube and to encourage the clot was centrifuged (Hettich EBA20) for 5 minutes with 600 rpm. In order to assess the efficiency of electrocoagulation method for the removal of the dye AR1, the absorbance of the solution before and after the electrolysis was measured by a spectrophotometer (UNICO 2100) at $\lambda_{max} = 506$ nm to determine the concentration of color remains. After each test, the reactor for cleaning and removal of oxide layers from the anode surface was washed for 5 minutes with a solution of hydrochloric acid 0.1 M. Then, the reactor was washed several times with water to prepare it for the next test. To adjust the pH level of the experiment for the purpose of evaluating the effect of pH of the solution, 0.1 M HCl and NaOH solutions were used. The solution pH was measured using a pH meter (Metrohm).

Table-1: Structure and characteristics of C.I. Acid Red 1.

Features	Values and data
Structural formula	
Color type	Anionic
Molecular formula	$C_{18}H_{13}N_3Na_2O_8S_2$
Commercial name and C.I. number	C.I. Acid Red 1, C.I.118050
Molecular weight (g mol ⁻¹)	509.42
Name of product company	Sigma
CAS.No.	3734-67-6

Results and discussion

Effect of current density on the dye removal efficiency

Fig. 2 shows that according to Faraday's law, if the time of electrolysis and the amount of the clots increase, there will be an increase in the efficiency of dye removal. Fig. 3 also shows that with an increase in the current density, the dye removal efficiency will increase. Moreover, with an increase in the rate of clots in the solution, the efficiency of coagulation increases leading to greater removal efficiency of dye. In addition, with an increase in the production of hydrogen as a result of higher currents, the flocculated matter is floated more easily [8-11].

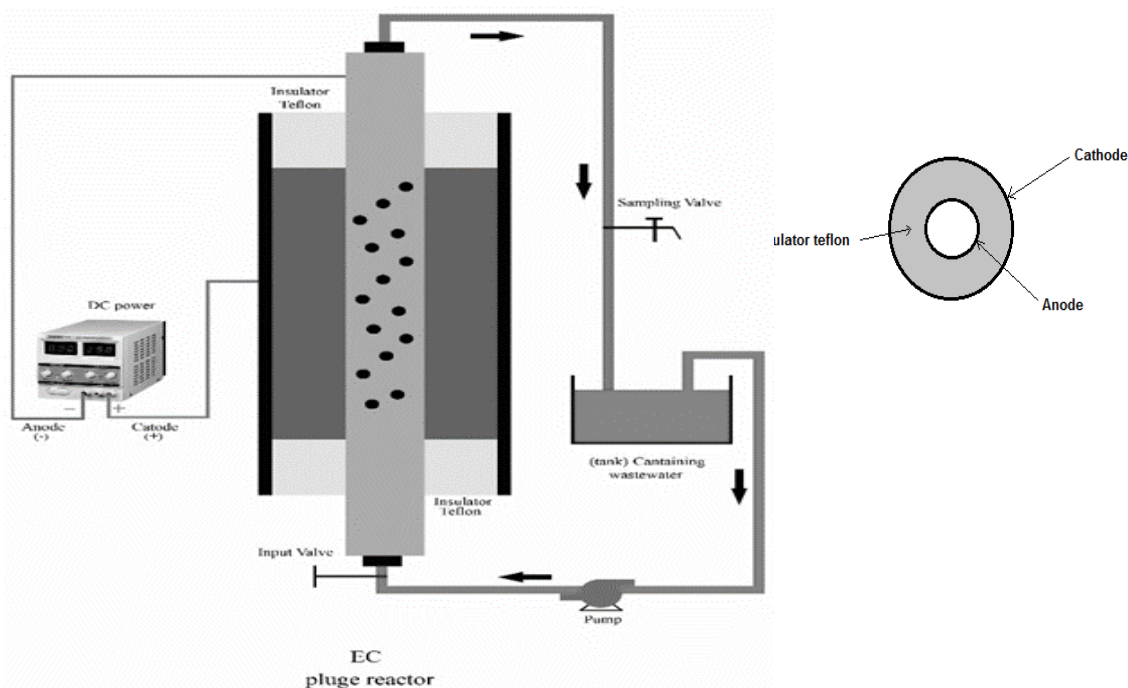


Fig. 1: Experimental setup and cross section of the reactor.

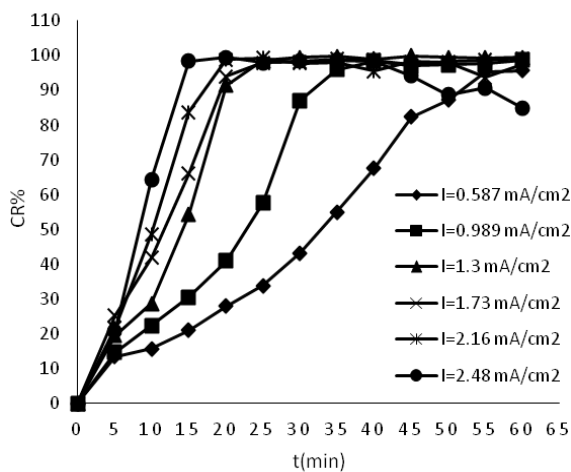


Fig. 2: Effect of electrolysis time on the dye removal efficiency at different current density:
 [AR1]: 30 mg L⁻¹, [NaCl]: 0.05 g L⁻¹, pH: 6,
 Flow rate: 2 L min⁻¹

As the results in Table-2 indicate, and according to the estimated charge used in the process of electrolysis, the optimal value for the current density was identified as 1.3 mA cm⁻² with an electrolysis time of 25 min. Fig. 3 shows that if the current density increases to more than 1.3 mA cm⁻² the stable removal efficiency of 98% is obtained.

Table-2: The calculated amount of used charge during the electrolysis process.

Current density (mA cm ⁻²)	Time of electrolysis (min)	Used charge (C cm ⁻²)
0.587	60	2.11
0.989	35	2.07
1.3	25	1.95
1.73	25	2.59
2.16	20	2.59
2.48	15	2.23

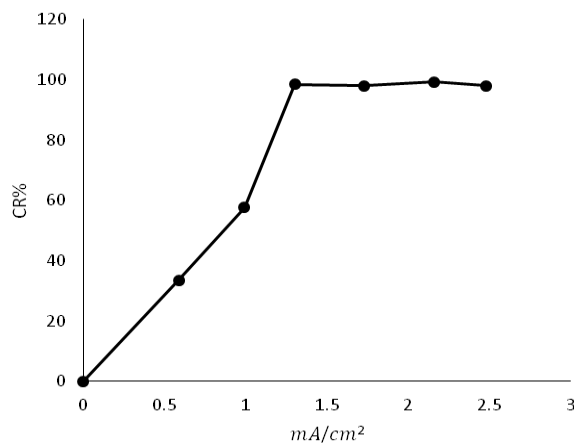


Fig. 3: Effect of current density on the dye removal efficiency: [AR1]: 30 mg L⁻¹, [NaCl]: 0.05 g L⁻¹, Electrolysis time: 25 min, pH: 6, Flow rate: 2 L min⁻¹

Effect of pH on the dye removal efficiency

As we know, pH plays a significant role in the efficiency of electrocoagulation process. Therefore, sodium hydroxide or hydrochloric acid were used to adjust the pH to a desirable rate. As Fig. 4 indicates, at a pH of 2 and 12, poor color removal was experienced, but when the pH varied between 4 and 10, the percentage of color removal was between 90.7 and 96.2%. The maximum efficiency of color removal was observed at pH of 6. In acidic pH, iron hydroxide is dissolved in the solution and in highly alkaline pH values, the produced iron hydroxides are converted into $\text{Fe}(\text{OH})_4^-$ which is more soluble than ferric hydroxide. Thus, it can be maintained that as the hydroxide clots decrease in both very acidic and alkaline media, dye removal efficiency decreases too [12, 13].

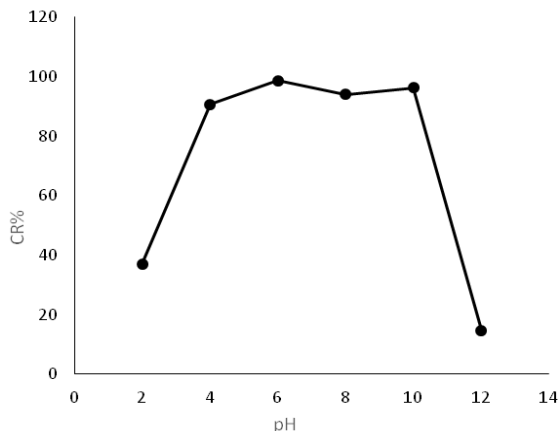


Fig. 4: Effect of pH on the dye removal efficiency: [AR1]: 30 mg L^{-1} , [NaCl]: 0.05 g L^{-1} . Current density: 1.3 mA cm^{-2} , Electrolysis time: 25 min, pH: 6, Flow rate: 2 L min^{-1} .

Effect of electrolyte concentration on the dye removal efficiency

It is necessary to mention that solution conductivity is highly important in electrochemical process because the ions in the solution transmit electric current among the electrodes. As Fig. 5 shows, as the electrolyte dosage increases, dye removal efficiency increases slowly as well [14].

The effect of the carrier electrolyte on removal efficiency and specific energy consumption is displayed in Fig. 6. When electrolyte concentration increased, there was a decrease in energy consumption (about 80%). The obtained results indicated that with an increase in electrolyte concentration, the ohmic resistance of the solution

decreases leading to lower current density needed for reaching optimal applied voltage and lower energy consumption. According to the rate of specific energy consumption shown in Fig. 6, the optimal value for electrolyte concentration with logical removal efficiency of 98% and relatively low level of specific energy consumption, about 0.08 g L^{-1} was determined.

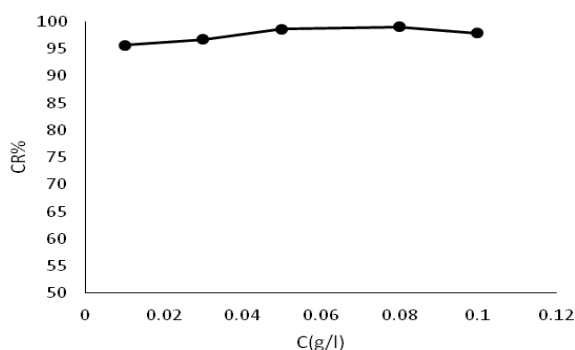


Fig. 5: Effect of electrolyte dosage on the dye removal efficiency: [AR1]: 30 mg L^{-1} , Current density: 1.3 mA cm^{-2} , Electrolysis time: 25 min, pH: 6, Flow rate: 2 L min^{-1}

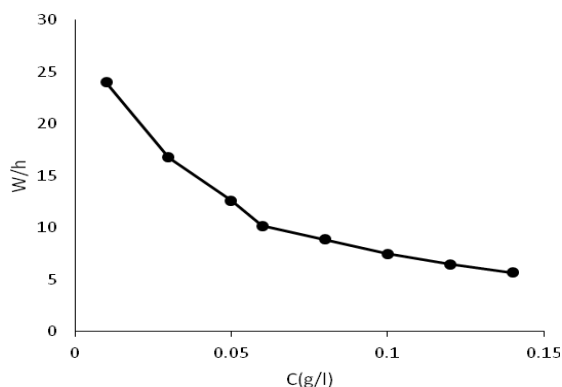


Fig. 6: Effect of electrolyte dosage on the specific energy: [AR1]: 30 mg L^{-1} , Current density: 1.3 mA cm^{-2} , Electrolysis time: 25 min, pH: 6, Flow rate: 2 L min^{-1} .

Effect of the type of electrolyte on the dye removal efficiency

In real dye baths, different types of salt are used as dye auxiliaries. For instance, dye diffusion increases by using NaCl and facilitates its adsorption into the fiber. Meanwhile, some types of salts such as Na_2CO_3 increases the pH of dye bath; it also facilitates dye fixation by forming covalent bonds [15]. NaCl, Na_2SO_4 , NaBr and KCl were used as a carrier electrolyte having a concentration of 0.08 g L^{-1}

¹. In optimal conditions of pH=6 and current density of 1.3 mA cm^{-2} some runs were performed. As the results in Fig. 7 shows, when NaCl is used as an electrolyte, removal rate is high (99%). When KCl is used, lower rates of 95% are observed. It is generally known that, the formed passivation layer on iron electrode may be destroyed by Cl^- anions, which can increase the anodic dissolution rate of the metal; this will, in turn, lead to greater production of ferric hydroxide.

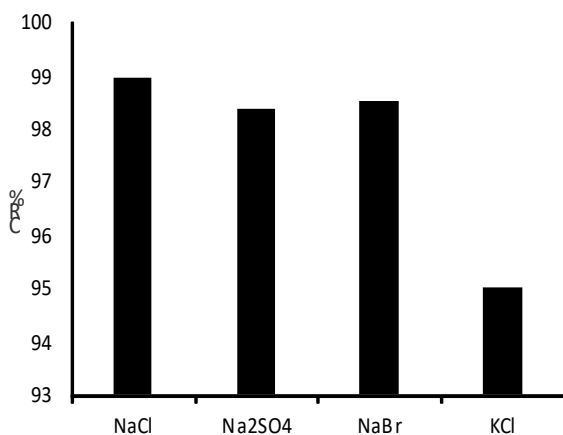


Fig. 7: Effect of electrolyte type on the dye removal efficiency: [AR1]: 30 mg L^{-1} , Current density: 1.3 mA cm^{-2} , Electrolysis time: 25 min, pH: 6, Flow rate: 2 L min^{-1} .

NaCl with higher color removal percentage (99%) is the best electrolyte because it is cheap and according to Table-3, the solution has high conductivity (190.7 ms cm^{-2}); thus, it needs low voltage for electrocoagulation (14.7 V), so it is economical in industrial scale. Chlorine and hypochlorite are the products from anodic discharge when chlorides are present in the solution. So, added NaCl not only increases the conductivity but also contributes strong oxidizing agents. Therefore, NaCl is selected as the electrolyte in this investigation.

Table-3: Conductivity of solution and applied voltage in EC process with different electrolytes.

Voltage (V)	Cond. (ms cm^{-2})	Electrolyte
14.7	190.7	NaCl
17.2	163.6	Na ₂ SO ₄
22.1	123	NaBr
15.8	170.9	KCl

Effect of initial dye concentration on dye removal efficiency

Today treatable wastewater from textile industry varies in its concentration. Therefore, it is necessary to examine the effect of the initial

concentration of dye on electrocoagulation process. As a result, different concentrations of dye (in a range of $10\text{-}60 \text{ mg L}^{-1}$) were studied in a stable current density. As Fig. 8 shows, with an increase in the initial concentration of dye, removal efficiency decreases. More precisely, with an increase of initial dye concentration of 10 to 60 mg L^{-1} , the percentage of removal decreased from 98% to 88%. Conversely, there was a decrease in removal efficiency by increasing the initial pollutant concentration in a stable current density. One of the most important pathways of dye removal by electrocoagulation method is adsorption of dye molecules on metallic hydroxide flocs. According to Faraday's law, a constant amount of iron ions released to the solution at the same current density and time for all dye concentration. Thus same amount of flocs would be produced in the solution. The adsorption capacity of flocs is limited and specific amount of flocs able to adsorb specific amount of dye molecules. So with increasing of dye concentration, amount of produced flocs insufficient to adsorb all dye molecules, therefore the dye removal efficiency decreases [16].

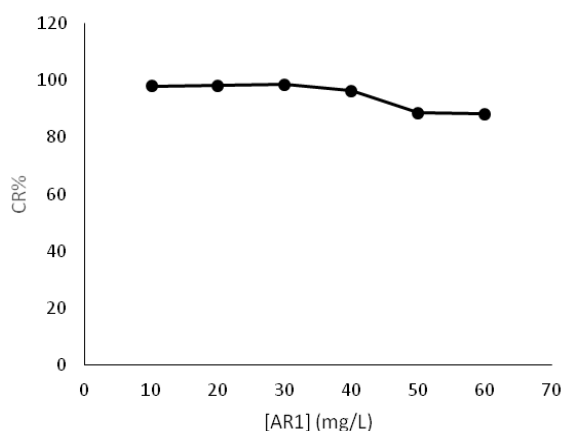


Fig. 8: Effect of the initial dye concentration on the dye removal efficiency: Current density: 1.3 mA cm^{-2} , Electrolysis time: 25 min, pH: 6, [NaCl]: 0.08 g L^{-1} , Flow rate: 2 L min^{-1}

Effect of the flow rate of solution on the dye removal efficiency

The flow rate levels of 1.7 , 2 , 2.1 , 2.2 , and 2.4 L min^{-1} were respectively used for conducting experiments to analyze the effect of flow rate on the efficiency of dye removal while keeping the other parameters at a constant value. Fig. 9 indicates removal efficiency as a function of flow rate. The fig shows that the removal efficiency decreased from 98.73% at 1.7 L min^{-1} to 68.53% at 2.4 L min^{-1} . It was highly expected to observe a decrease in removal

efficiency with an increase in flow rate because with slower flow rate, higher residence time was observed. This higher residence time indicates that it takes longer for the solution containing untreated wastewater to leave the reactor. The low flow rate facilitated proper mixture of the coagulant produced through electrochemical oxidation of the anodic material and the pollutants residing in the polluted water. All this improved coagulation rate [17].

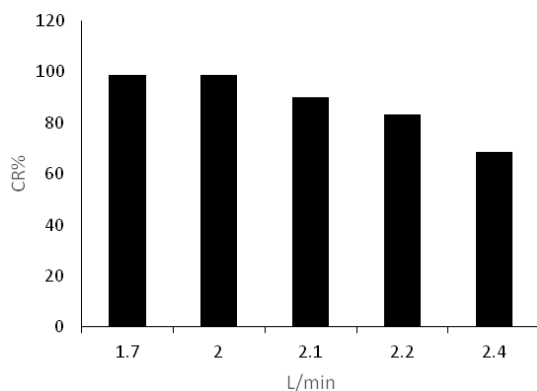


Fig. 9: Effect of flow rate of solution on the dye removal efficiency: [AR1]: 30 mg L⁻¹, Current density: 1.3 mA cm⁻², Electrolysis time: 25 min, pH: 6, [NaCl]: 0.08 g L⁻¹.

SEM and BET analysis of sludge

Fig.10 shows SEM images of produced sludge in the electrocoagulation process in the reactor. The figure indicates that the size of the constituent particles of sludge as a cluster is about 0.5 μm. By BET analysis results, specific surface area, total pore volume, and mean pore diameter of the sludge as 56.4 m² g⁻¹, 0.27 cm³ g⁻¹, and 19.23 nm were determined, respectively.

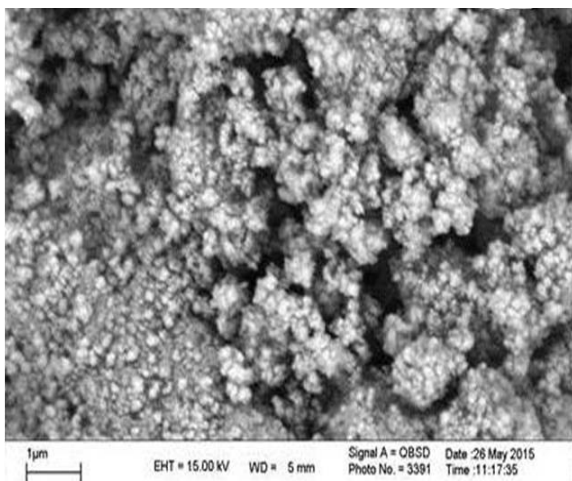


Fig. 10: SEM image of produced sludge of EC.

Conclusion

The findings in this study pointed to the fact that a reliable technique for removing dye from wastewater is electrocoagulation process. Dye removal rate by electrocoagulation method using a recirculating tubular reactor in a solution containing Acid red 1 was a function of current density, pH, electrolyte and dye concentration, flow rate in recycling the solution, and the time needed for electrolysis. The results indicated that increasing current density to 1.3 mA cm⁻² enhanced dye removal up to 98%. Moreover, with an increase in electrolyte concentration, electrical conductivity of the solution increases, and the voltage for accessing a certain electric current density decreases; in this way, less electric energy is also consumed. It was also found that with an increase in initial dye concentration, dye removal efficiency decreases as well, and pH = 6 is the optimal pH level to work with. With an increase in the rate of the flow rate through the reactor, dye removal efficiency decreases.

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