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Electrochemical Decolorization of Reactive Dye from Synthetic Wastewater by Mono-Polar Aluminum Electrodes System

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Azo dyes are important groups of chromospheres having a particular structure in color-contaminated wastewater. In the present study, Reactive Red 198 (RR198) dye was chosen as a model of azo dyes group. Electrocoagulation technique as an effective and environmental-friendly process for wastewater treatment was applied. Hence; to determine the extent of decolorization process, the main different parameters such as pH (4-11), contact time (80 min), initial concentrations (25-400 mg/L), current density (1.9-23.1 mA/cm^2), distance between gaps (1-4 cm), and effect of supporting electrolytes were evaluated. Results show that optimum conditions were 20 min of operation time, 1 cm distance between electrodes, pH equal to 4 and optimum initial concentration of dye equal to 100 mg/L as well as NaCl was identified as the best electrolyte. Under these optimum conditions and also at both aeration and non-aeration operating conditions decolorization efficiency was more than 90%. The results also demonstrated that total organic carbon removal efficiency as (TOC), during 120 min of contact time was about 80.95%. XRF analyses show that a large portion of deposited sludge (58.282%) was aluminum oxide.

Keywords: Aluminum electrode; Electrochemical decolorization; Reactive Red 198, aqueous solutions

1. INTRODUCTION

Due to environmental concerns and other serious problems such as being toxic to aquatic life, and leading to carcinogenic and mutagenic effects on humans, today, complex structures of textile dyes, dyeing, printing, ink and color based industries are taken into serious consideration [1-3]. Based on chromospheres' characteristics of dyes, azo dyes are one of the main important groups of chemical compounds and compose the largest class (around 70%) [4]. Indeed, azo dyes form a very complex and biorecalcitrant class of synthetic compounds by binding to aromatic rings of azo group(s) [5-7].

For these reasons, the Reactive Red 198 (RR 198) was selected as a model of azo dyes group. There are many applied techniques for the treating of color-contaminated wastewater, such as: adsorption, oxidation (using chlorine, ozonation and AOP), and biological process (anaerobic–aerobic) [1, 8-10]. Recently, electrochemical technique (for example: electrocoagulation, microbial electrolysis cell, microbial fuel cell, and etc.) as an effective and environment-friendly process for wastewater treatment has been employed by many researchers [11-13]. This alternative ensures good quality effluent before its disposal into aquatic environment [14]. In addition, the EC process is a suitable potential way for the treatment of wastewater regarding the cost and the environment [15]. Contaminant removal with electrochemical methods offers several advantages, such as having no need of chemical requirements, not producing any sludge, occupying a small area in plants and simple operation [16]. In fact, the coagulant is generated by means of the dissolution of a sacrificial anode for the EC process. This process can be very effective for oil removal from synthetic oily wastes, textile dyes, suspended solids (as well as oil and greases), metal ions, and petroleum wastewaters [14, 17-23]. Expected chemical reactions, which occur near the electrodes and during the aqueous phase, are shown as the following [24]**:**

Near the anode surface:

In acidic pH $4OH^- - 4\bar{e} \rightarrow 2H_2O + O_{2(g)}$ (1)

In alkaline pH $2H_2O - 4\bar{e} \rightarrow O_{2(g)} + 4H^+$ (2)

$$Al_{(S)} - 3\bar{e} \rightarrow Al^{3+}_{(aq)} \quad (3)$$

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (4)$$

Near the cathode surface:

In acidic pH $2H_2O^+ + 2\bar{e} \rightarrow H_{2(g)} + 2H_2O$ (5)

In alkaline pH $2H_2O + 2\bar{e} \rightarrow H_{2(g)} + 2OH^-$ (6)

$$2H_2O + 2\bar{e} \rightarrow H_{2(g)} + 2OH^- \quad (7)$$

$$O_2 + 2H_2O + 4\bar{e} \rightarrow 4OH^- \quad (8)$$

$$Al_{(S)} + 4OH^- \rightarrow [Al(OH)_4]^- + 3\bar{e} \quad (9)$$

In the present research, decolorization of Reactive Red 198 by means of electrochemical method using the mono-polar arrangement of aluminum electrodes was evaluated. Finally, in order to evaluate the kinetic reaction dye decolorization, pseudo-first and second order model were used.

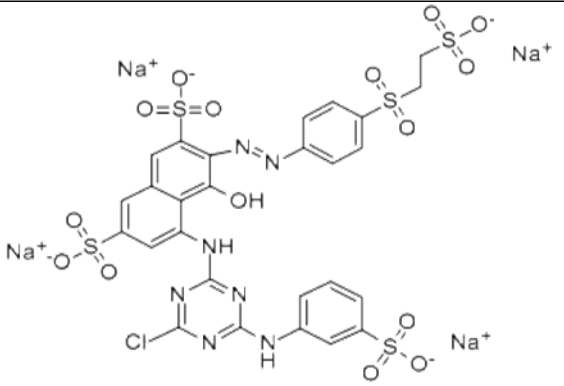
2. MATERIALS AND METHODS

2.1 Materials

Dye solutions were prepared by dissolving RR198 in distilled water.

The structure and characteristics of RR 198 such as CAS number, formula and molecular structure are presented in table1. All reagents in analytical grade including NaCl, KCl, KNO_3, NaOH, HCl, Na_2CO_3, H_2SO_4 were prepared by Merck and Sigma Company. Normal pH was adjusted to the desired value by using 1 M HCl and 1 M NaOH. The NaCl, KCl and KNO_3 solutions at 1g/L (0.1%) were prepared as supportive electrolytes.

Table 1. Reactive Red 198 characteristics

CAS Number	145017-98-7
Super list Name	Reactive Red 198
Formula	C27H22 Cl N7 O16 S5. 4 Na
Molecular Weight	968.21
Molecular Structure	

2.2 Analysis

In order to separate the formed flocs, all collected samples were filtered and their respective pH was measured using a pH meter (Eutech) and then registered as final pH.. The decolorization and removal rate of the RR 198 in the solution samples were analyzed by measuring the light absorbance of each sample at the wavelength of 518 nm using a UV/Vis T+80 spectrophotometer and TOC analyzer, respectively [25]. The XRF and also Scanning Electron Microscope (SEM) image were done by KYKY-EM3200 from a portion of electrocoagulation sludge. All experiments were duplicated and the average obtained result was recorded. Besides, all the experiments were performed at room temperature.

2.3 Reactor Set-up

Decolorization cell includes of a glass vessel as the laboratory reactor (250 ^{cc}), a DC Power Supply (TEK-8051, 30 V and 5 A double), and a peristaltic pump (Watson Marlow 101U/R) equipped with aeration tubes. During this study, we used from two electrodes in mono-polar state as Al/Al arrangement. Dimensions of Aluminum plates were equal to (65×20×2 mm)in all experiments. At the beginning of any run of electrocoagulation process, anode and cathode plates were cleaned using 0.1 M H_2SO_4 and then eliminate impurities by Rinse several times using distilled water. At the end of any run, all samples were filtered by means of Whatman filter and their absorbance was detected.

3. RESULTS AND DISCUSSION

3.1 Effect of pH

The pH as a significant parameter can be influenced by electro-coagulation process and have a principle role in the contaminant degradation mechanism during an oxidation process [4, 26]. Removal efficiency with 5% error bar at certain conditions under different pH values for the decolorization of Reactive Red 198 is shown in Fig 1. Removal efficiency and EC were determined at the end of 30 min under various pH values (4-11). With regard to the results, maximum removal was obtained about 92.34% at acidic pH (pH=4). Although at the acidic phase higher rates of decolorization were seen, the neutral pH was suitable. Due to alkaline pH, lower decolorization efficiency of about 54.63% was obtained. According to aluminum reactions on anode, the cationic (Al^{3+} and $Al(OH)_2^{+}$), monomeric units (such as $Al(OH)^{2+}$, $Al(OH)_2^{2+}$, $Al_2(OH)_2^{4+}$, and $Al(OH)_4^{-}$) and polymeric species(such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, Al_8-$(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al_{13}(OH)_{34}^{5+}$) at lower pH values (<6) are generated, and in this range there are two dominant mechanisms of precipitation and adsorption.

At pH values below 6, precipitation is expected; and at higher pH values (> 6.5) the adsorption mechanism can be observed which occurred by amorphous aluminum hydroxide ($Al(OH)_3$) formation [19, 27]. However, generally the precipitation is a significant mechanism for higher decolorization efficiency at neutral and acidic pH. The loss of decolorization efficiency in alkaline pH (especially above 9) is considered to be due to the diminishment of flocks quantity, caused by consuming OH^- and amorphous spices for the formation of $Al(OH)_4^-$and buffering capacity [19]. Inan et al. (2004) stated the fall of efficiency at high pH values caused by the formation of hydrosol-complexes $[Al\ (OH)_n]^{-(n-3)}$ after the dissolution of $Al\ (OH)_3$ in water.

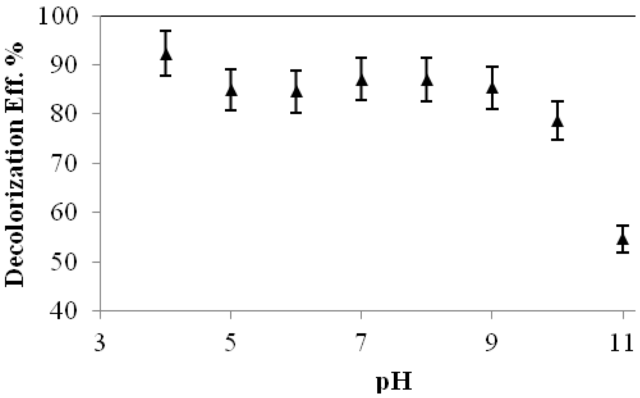


Figure 1. The effect of different pH on decolorization efficiency

3.2 Effect of contact time

The role of time can be expressed by means of Faraday’s law that has been shown in Eq. (10). With regard to this law, time has a significant effect on flock generation and oxidation of complex spices; hence, a better condition for dye removal is provided during electro-decolorization process.

$$A_W = CI \cdot T \cdot M \big/ n \cdot C \quad (10)$$

Where A_w is the amount of dissolved anode material (g); *CI* is the current intensity (A); *T* is the run time (s); *M* is the specific molecular weight (g/mol); *n* is the number of electrons involved; and *C* is Faraday’s constant (As/mol) [28]. To study the effect of contact time, an operating period of about 80 min was considered. Decolonization of Reactive Red 198 vs. removal efficiency at two conditions of aeration and non-aeration during operating process is illustrated in Fig. 2. According to the obtained results, maximum removal efficiency is observed from minute 20, and decolorization for both conditions rapidly occurred at a short time. Removal percentage of Reactive Red was not significant up to min 15. Similarly, some researchers reported that decolorizations of reactive dyes occurred at less than 20 min from the beginning [19, 29]. Somayajula et al. (2012) optimized the time of decolorization for Reactive Red 159 and reported the minimum time to be about 50 min, necessary for 100% decolorization [30]. In order to improve dye oxidation and solution mixing, simultaneous aeration and electrocoagulation were applied, but it was found that there was no significant difference between the two conditions; thus, it can be inferred that aeration is not necessary for decolorization during electrocoagulation. Furthermore, gases such as oxygen, hydrogen, and hydroxyl developed around electrodes, which can cause both agitation and oxidation.

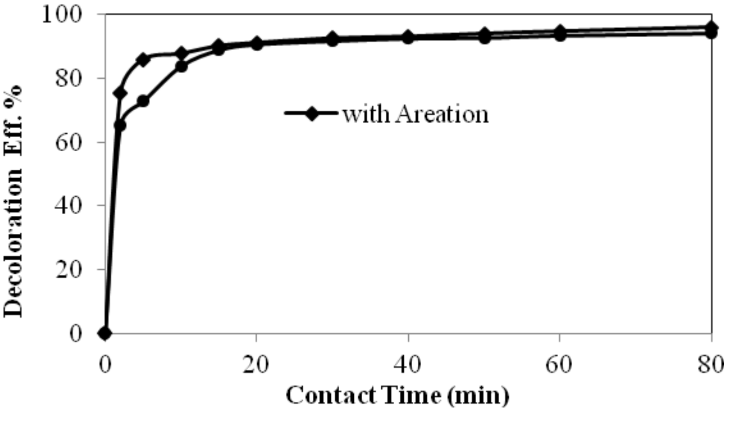


Figure 2. The effect of contact time on decolonization of Reactive Red 198 by electrocoagulation [conditions: Reactor volume 250 cc , Current density 11.5 mA/cm^2, pH 4, Distance 1 cm, 100 mg/L Conc. of RR 198, NaCl 1g/L].

3.3. Effect of initial concentrations of RR 198

In colored wastewaters, such as that of textile industry, the common concentration ranges between 50 and 250 mg/L [31]. However, to evaluate electrocoagulation method regarding RR 198 removal from colored wastewater, initial concentrations of 25, 50,100, 200 and 400 mg/L were used. As seen in Fig 3, the effect of different concentrations of RR 198 at the end of the operating time of 20 min is demonstrated. With regard to the decolorization efficiency, large portion of dye was removed under all concentrations. But maximum and minimum removal percentage was determined to be about 92.75% and 67.54% under 100 mg/L concentration at the optimum time, respectively. In similar cases, Song et al. (2010) observed that higher decolorization occurred under lower concentrations and this may be due to the faster reaction of electrochemical rather than diffusion itself. During anodic dissolution, a constant value of removal agents such as oxidative, perceptive, and adsorbent value were also provided. Therefore, with increasing of the initial concentration of dye (or pollutant), lower amounts of removal and also decolorization were observed.

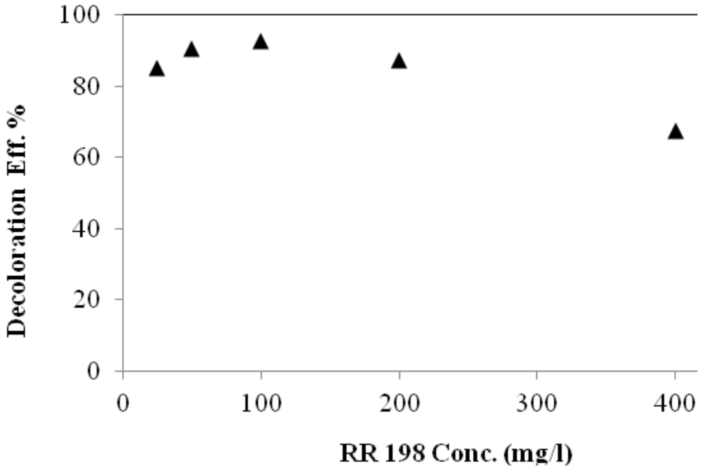


Figure 3. The effect of initial concentrations on decolonization of Reactive Red 198 by electrocoagulation [conditions: Reactor volume 250 cc, current density 11.5 mA/cm^2, pH =4, distance between gap= 1 cm, contact time= 20 min, NaCl= 1g/L].

3.4. Effect of current density and distances

During the EC process, the electrical current is one of the most important parameters affecting removal efficiency [32], and it has a considerable effect on electrocoagulation via the coagulant dosage rate [33]. To investigate the effect of current density, experiments were conducted under certain conditions with current density 1.9-23.1 mA/cm^2. The results of these experiments are presented in Fig. 4a. According to the plot, in Fig.4a with increasing of the electrical crossing flow between electrodes, decolorization rate increased through higher oxidation agents and more available coagulants. Based on Faraday’s law, direct increasing of current intensity precipitated more amounts of dissolved coagulants into the solution from the anode. Furthermore, higher current density generated high levels of oxidative bubble with decreased size [27], which provided more surface area between oxidant units and pollutants.

In order to achieve the influence of distance between electrodes gap, different distances (1-4 cm) were evaluated. Fig. 4b indicates the effect of linear distance between anode and cathode. Although, there is no significant difference with the increasing of distance, higher dye removal in lower distances was seen. Maximum decolorization efficiency of about 92% was found at the distance of 1 cm, and minimum decolorization was obtained of about 91% for both 3 and 4 cm. It is obvious that with the enlargement of space between electrodes, the electrical current decreased due to increasing the internal solution resistance; and also, less ions interaction with hydroxyl polymers was expected [34].

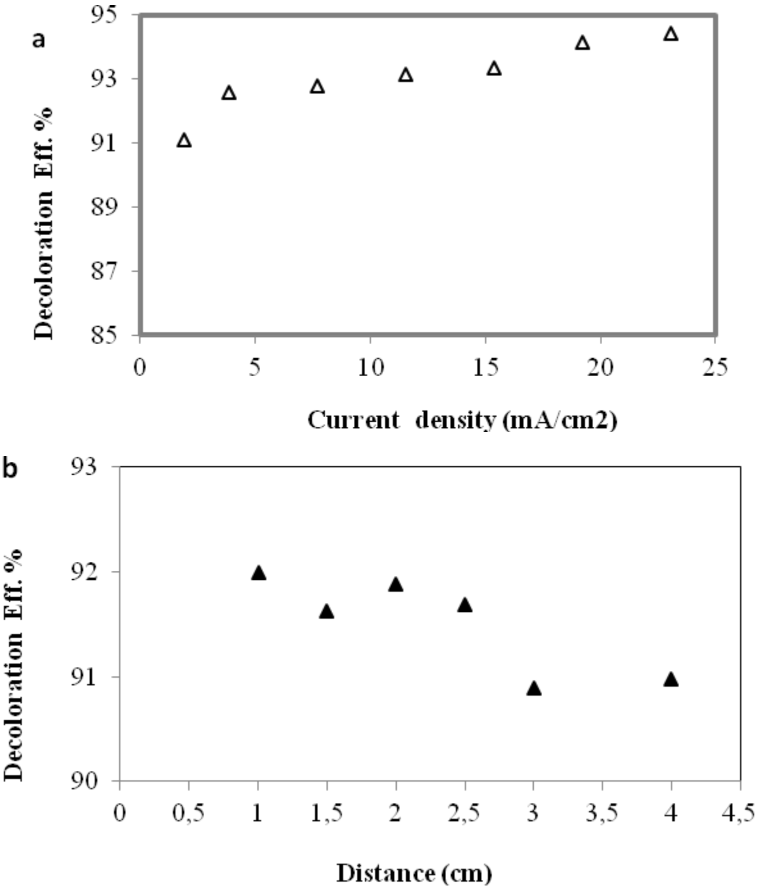


Figure 4. The effect of current density(a) and distances between electrodes (b) during decolorization of Reactive Red 198 by electrocoagulation [conditions: Reactor volume 250 cc , pH= 4, RR 198 concentration=100 mg/L, C NaCl 1g/L, contact time= 20 min].

3.5. Effect of supporting electrolytes

As seen in Fig. 5, the influence of added salts for higher decolorization and needed voltage was investigated. Selective salts included potassium chloride, sodium chloride, potassium nitrate, andsodium carbonate. Voltage variation was performed by keeping current density about 11.5 mA/cm^2. Among the salts, sodium and potassium chloride were more desirable with respect to both responses decolorization efficiency and voltage. Generally, in presence of sodium chloride, solution conductivity and its current density were enhanced and the necessary voltage for reaching a certain current density decreased; which can led to a reduction in electrical energy consumed [35]. In other words, chlorinated salts like potassium and sodium are hydrolyzed and led to produce highly oxidative agents such as hypochlorite, chlorine, hypochlorite ions, and hypochlorous acid(Eq. 11-13) from chloride ions at the anode surface [8, 36].

$$2Cl^{-} \rightarrow 2Cl_2 + 2\bar{e} \qquad (11)$$

$$Cl_2 + H_2O \rightarrow HClO + HCl \qquad (12)$$

$$6HClO + 3H_2O \rightarrow 2ClO_3^{-} + 4Cl^{-} + 12H^{+} + \frac{3}{2}O_2 + 6e^{-} \qquad (13)$$

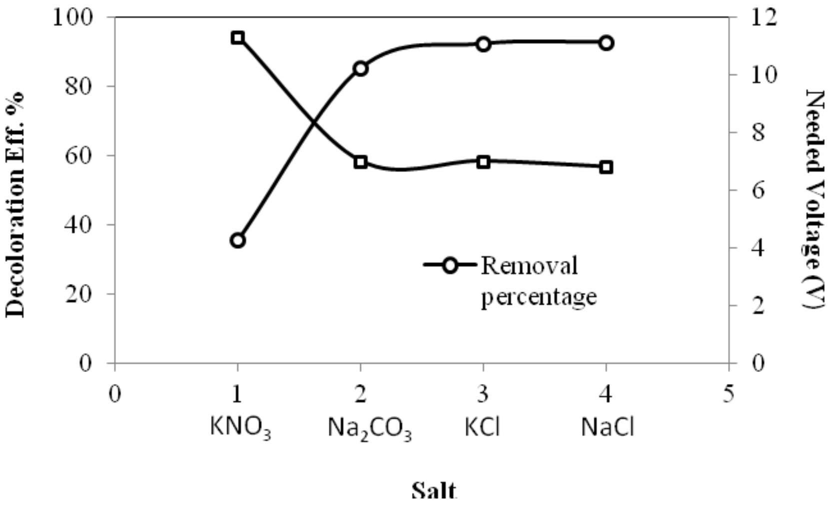


Figure 5. The effect of supporting electrolytes during decolorization of Reactive Red 198 by electrocoagulation [conditions: Reactor volume 250 cc, pH= 4, RR 198 100 mg/L, Distance between gap= 1 cm, Current density 11.5 mA/cm^2, time 20 min].

3.6 Total organic carbon

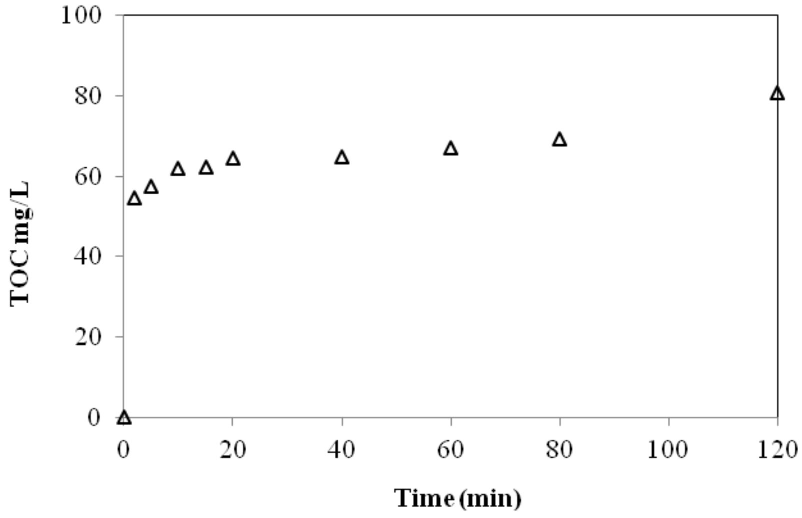


Figure 6. Removal percent of RR 198 by TOC analysis

During the electro-decolorization, TOC was measured. Fig.6 shows the variation of TOC analysis for 100 mg/L RR 198. Initial TOC was approximately assessed to be 23.1 mg/L, but it was determined to be about 4.4 mg/L, at the end of the process. With regard to the plot, the degree of decolorization of RR 198 was observed. After 2 minutes of reaction, TOC suddenly reduced to around 55%. Maximum removal was estimated to be about 80.95% at the end of 120 min. Based on TOC results, electrocoagulation process removes the organic contents and dye effectively. Reduction of TOC can occur due to the destruction of azo (–N≡N–) bond on RR 198 structure by the oxidizing agents [25, 37].

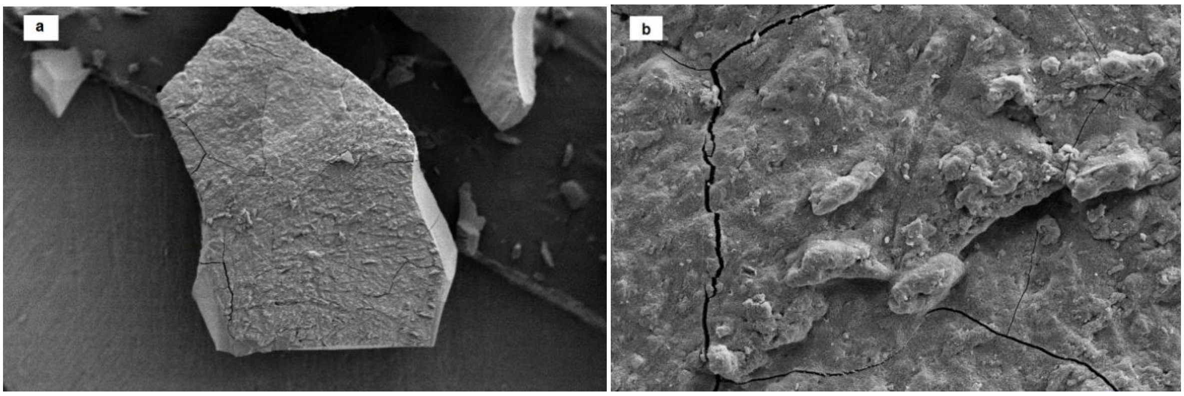
3.8. XRF and SEM analysis

To determine sludge constituents, we used XRF analysis. The results of XRF analysis are presented in table 2. In this table L.O.I indicate the loss on ignition and shows the volatile portion of producedsludge after the ignition of the sample, and it is also a commonly used method for determining the organic and carbonate content of sediments [38]. As can be seen in table 2, the L.O.I is equal to 36.73%. This portion of sludge can be representative of(RR 198) that is adsorbed on formed flocs and precipitated in sludge and also can be related to the degradation of its byproducts. A large portion of sludge (58.285%) includes aluminum oxide (Al_2O_3). Furthermore, iron oxide and zinc were detected. The presence of sulfophenyl groups can be confirmed by the decomposition of RR 198 during electrocoagulation process. High levels of chlorine can also be derived by adding chlorinated salts.

Table 2. Electrocoagulation sludge analysis using XRF

Constituents	L.O.I.	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	Fe_2O_3	Zn
(%)	36.73	0.67	0.13	58.28	0.44	2.07	1.47	0.19	0.01

Fig. 7 illustrates the Scanning Electron Microscope (SEM) of the portion of sludge produced in decolorization process. These figures range between 1 μm and 1 mm magnification, and also provide pore diameter between 50 nm and 500 nm. Due to these pore sizes, it is expected that a suitable space for the adsorption of dyes and their degradation products provided. With regard to the SEM image and sediment morphology, high levels of porosity and larger surfaces formed by nanopore and micropore spaces of amorphous structure were detected.



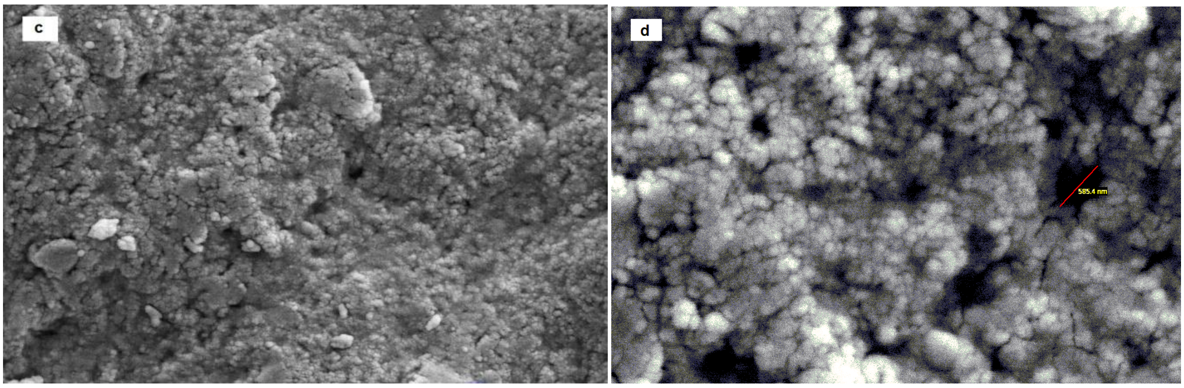


Figure 7. SEM images of the generated sludge during electrocoagulation process, 1mm (a) 100 µm (b) 10 µm (c) 1 µm (d).

4. CONCLUSIONS

Decolorization of Reactive Red (RR) 198 using electrocoagulation method by aluminum electrodes was investigated in batch mode. Main parameters such as pH, contact time, initial concentration, current density, electrode gaps, and effect of supporting electrolytes were evaluated. Optimum conditions for these parameters are: 20 min, 1 cm of distance, NaCl electrolyte, pH= 4, and initial concentration of 100 mg/L. Under these conditions the decolorization efficiency was more than 90% both with aeration and without aeration. During 120 min, TOC removal was around 80.95%. XRF analysis also showed that aluminum oxide formed 58.28% of the deposited sludge.

CONFLICT OF INTEREST

The authors certify that there is no conflict of interest with any financial organization regarding the material discussed in the manuscript.

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