Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes

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Abstract

The aim of this investigation is to evaluate the treatibility of synthetically prepared water with high concentration of humic substances by electrocoagulation in batch mode using iron cast electrodes. Effects of applied potential, initial humic substance concentration and supporting electrolyte type on humic substance removal efficiency were investigated. $NaNO_3$, Na_2SO_4 and $NaCl$ were used as supporting electrolyte. Among these supporting electrolytes, Na_2SO_4 and $NaCl$ have provided high removal efficiencies, whereas in the experiments using $NaNO_3$ as supporting electrolyte have been observed no flock formation. The highest removal rate is obtainable with $NaCl$ as supporting electrolyte. Removal efficiencies for initial humic substance concentration of $500\,mg\,L^{-1}$ with $NaCl$ and Na_2SO_4 equal to 97.95% for 35 min and 92.69% for 70 min, respectively. This behavior of the system has been derived from oxidation products, available in the bulk solution, of chloride ions. When $NaCl$ is used as supporting electrolyte, there is an advantage of providing the disinfection of water, but humic substances and chloride ions are available in the bulk solution with risk of formation undesirable organo-chlorine compounds, so the Na_2SO_4 is the most favorable supporting electrolyte.
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Keywords: Electrocoagulation; Humic substances; Iron cast electrodes

1. Introduction

Given the substantial content of aromatic and aliphatic residues present in humics and the relatively small content of ionisable carboxylic groups, the humics are easily aggregated and precipitated on charge neutralization. In the broadest terms the structures can be described as assemblies of covalently linked aromatic and aliphatic residues carrying carboxyl, phenolic and alkoxy groups although sulphate esters, alanine moieties, semiquinone, phosphate ester and hydroquinone groups have been proposed to exist in some humic isolates [1].

Humics are believed to be formed from plant and animal residues by microbial decay by the process of humification, which occurs in soils, sediments and natural waters. Given the long time span of the biodegradation of the organic precursors and the exposure of the products to water, oxygen and radiation (sunlight) in the environment, humics must be regarded as 'old molecules' which are at the end of the biodegradative and oxidative route [1] humic substances are close to being non-biodegradable and are the end-point of nature's biodegradation [2], thus it is believed that possibly cannot undergo much further breakdown unless exposed to specific chemical agents which they have not previously encountered [1].

Their presence has been a problem in the water industry and in environmental purification. These problems can be summarized as follows.

During the chlorination, natural organic matters (NOMs) cause formation of disinfection-by-products (DBPs). Trihalomethanes are the well known disinfection-by-products (chloroform, bromo-dichloromethane, chloro-dibromomethane, and bromoform) [3–8]. It has been suspected that some of the trihalomethanes (especially chloroform) are carcinogenic compounds [3–9]. They lead to color, taste and odor in waters [4,7,8]. NOMs stimulate the regrowth of the microorganisms in water distribution systems [4,7,8]. Availability of micro-pollutants and heavy metals associated with NOMs [4,7]. The contamination of humic substances has been known to induce a deterioration of adsorbents and a prevention of adsorption onto the adsorbents.

Nomenclature

C_e	final concentration of humic substance (mg L^{-1})
C_{SE}	supporting electrolyte concentration (mM)
C_0	initial concentration of humic substance (mg L^{-1})
I	current passing through the system (mA)
n	stirring speed (rpm)
pH_i	initial (influent) pH
Q	charge loading (F m^{-3})
STY	space–time–yield (kg m^{-3} h^{-1})
t	time (min)
v	cell volume (L)
V	applied potential (V)
W	energy consumption (kWh/m^3)

Greek letter

η	removal efficiency (%)

The humic substances often reduce the removal of the target substances through their adsorption onto adsorbents and/or a formation of a complex with the target substances [10].

Humic substances in water have several characteristics that influence on how they may be removed from water. First of all humic substances are large organic molecules that carry a negative charge. This gives them colloidal characteristics making them removable by coagulation and subsequent floc separation. The negative charge characteristic is also utilized when separating humic substances from water by ion exchange because of their large size. It is also possible to separate humic molecules from water by molecular sieving through membrane filters. They adsorb readily on activated carbon as well. Humic substances are close to being non-biodegradable and are the end-point of natural biodegradation. By treating them with a strong oxidizing agent, however, the long organic molecules may be broken into smaller biodegradable components, removable by biofiltration [2].

In removal of humic substances by sorption processes, various sorbents such as highly active granulated iron hydroxide [11], hydrotalcite, clay, zeolites, metal oxides and resins have been investigated as well as activated carbon [10]. Humic substances may be removed by macroporous anion exchangers because of the negative charge of the humic molecules at normal pH [2].

Electrocoagulation is a process consisting of creating metallic hydroxide flocks within the water by electrodissolution the soluble anodes, usually made of iron or aluminum [12]. The difference between electrocoagulation and chemical coagulation is mainly in the way of aluminum ions are delivered [13]. In electrocoagulation, coagulation and precipitation are not conducted by delivering chemicals—called coagulants—to the system, but via electrodes in the reactor [12]. Electrocoagulation is based on the fact that the stability of colloids, suspensions and emulsions is influenced by electric charges. Therefore, if additional electrical charges are supplied to the charged particles via appropriate electrodes, the surface charge of particles is neutralized

and several particles combine into larger and separable agglomerates [14].

Electrode assembly is the heart of the treatment facility. Therefore, the appropriate selection of its materials is very important. The most common electrode materials for electrocoagulation are aluminum and iron. They are cheap, readily available, and proven effective [15].

The mechanism of electrocoagulation is highly dependent on the chemistry of the aqueous medium, especially conductivity. In addition, other characteristics such as pH, particle size, and chemical constituent concentrations will also influence the electrocoagulation process.

Iron upon oxidation in an electrolytic system produces iron hydroxide, Fe(OH)$_2$ other Fe(OH)$_3$. Two mechanisms have been proposed for the production of Fe(OH)$_n$ and these can be summarized in reactions (1)–(7) [16].
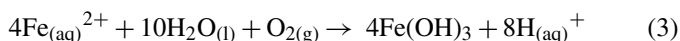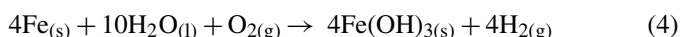
Cathode:

$$8H_{(aq)}^+ + 8e^- \rightarrow 4H_{2(g)} \tag{1}$$

Anode:

$$4Fe_{(s)} \rightarrow 4Fe_{(aq)}^{2+} + 8e^- \tag{2}$$

and with dissolved oxygen in the bulk solution:

$$4Fe_{(aq)}^{2+} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_3 + 8H_{(aq)}^+ \tag{3}$$

overall reaction:

$$4Fe_{(s)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \tag{4}$$

second mechanism:

Anode:

$$Fe_{(s)} \rightarrow Fe_{(aq)}^{2+} + 2e^- \tag{5}$$

Cathode:

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^- \tag{6}$$

overall reaction:

$$Fe_{(s)} + 2H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + H_{2(g)} \tag{7}$$
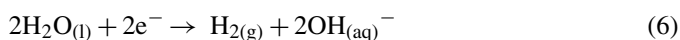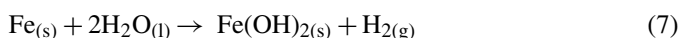
The Fe(OH)$_{n(s)}$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from water either by complexation or by electrostatic attraction, followed by coagulation. The H$_2$ produced as a result of the redox reaction may remove dissolved organics or any suspended materials by flotation. However, the Fe^{3+} ions may undergo hydration and depending on the pH of the solution Fe(OH)$^{2+}$ and Fe(OH)$_3$ species may be present under acidic conditions [16].

Aim of this investigation is to evaluate treatibility of synthetically prepared wastewaters with high concentration of humic substances by electrocoagulation and determining the effective parameters on the system. During the experiments, the system has been operated in batch mode and iron cast electrodes were used.

Table 1
Elemental composition of humic substance used

Element	%
C	39.3
H	4.43
N	0.68
Na	0.767
S	0.25
Fe	0.13
Ca	0.12
Mg	0.1091
P	0.0215
Li	0.0003

2. Materials and methods

2.1. Materials

In this study, the humic substance obtained from Sigma–Aldrich C_0 has been used as a model pollutant and elemental composition of humic substance have been presented in Table 1.

The most probable structures in humic substances are residues of phenolic structures in their core, and functional groups such as phenolic hydroxylgroups, carboxylgroups, and aminogroups [17,18].

In preparing the synthetic water containing humic substance and dilutions of stock solutions were used distilled water. The initial pH was adjusted to a desired value using NaOH or HNO_3.

2.2. Experimental setup and procedure

The experimental setup is shown in Fig. 1. The thermostated electrocoagulator was made of plexiglas with the active dimensions 50 mm × 55 mm × 80 mm. The anode and cathode, fully immersed in water, with dimensions of 40 mm × 50 mm, made of iron cast were connected to a digital DC power supply (Shenzen-Mastech HY 3005-3) in monopolar mode. Gap

1. Water Circulator
2. Digital D.C. Power Supply
3. Digital Ampermeter
4. Digital Voltmeter
5. Electrochemical Reactor
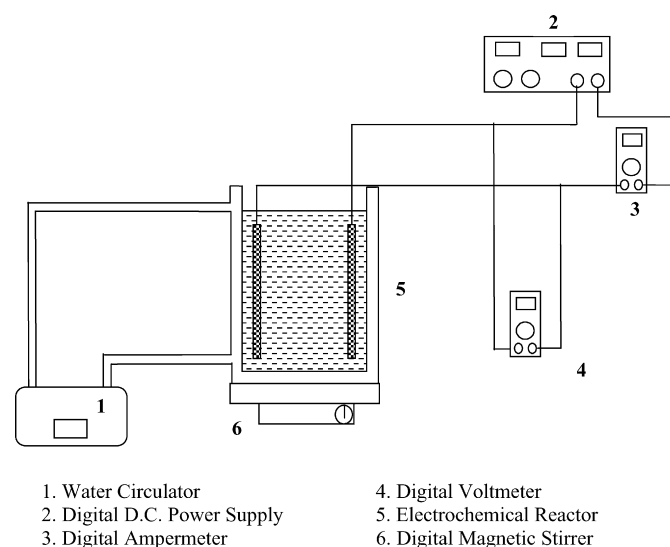6. Digital Magnetic Stirrer

Fig. 1. Schematic diagram of the experimental setup.

between the electrodes was 50 mm. Two digital multimeters (Brymen Bm 201) as amperemeter and voltmeter were used to measure the current passing through the circuit and the applied potential, respectively. A magnetic stirrer (Heidolph MR 3003) was used to stir the wastewater stirring speed of 100 rpm. During the experiments, conductivity and pH of the wastewaters were measured by a multi-parameter (WTW Multiline P-4 F-Set-3). Treated wastewater was collected over a desired period of time from the reactor and collected samples were filtered by a filter paper with equal specifications to Whatman no. 40 before the analysis. Reactor was operated in batch and potentiostatic mode.

2.3. Analysis of humic substances

Humic substance measurements have been carried out based on chemical oxygen demand (COD) according to Standard Methods for Examination of Water and Wastewater [19].

The removal efficiency of humic substance is calculated as follows:

$$\eta\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{8}$$

3. Results and discussion

3.1. Effect of applied potential on system parameters

Applied potential is varied by 30 and 50 V for initial pH of 9 and by 40 V for an initial pH value of 5 and obtained data is presented in Fig. 2a. Removal rate has increased, as applied potential raised for equal initial pH values. This trend is in accordance with literature findings [14,20–23]. The increase in the removal rate has been derived from raising of the anode dissolving rate. Current passing through the circuit has raised due to the increased applied potential (see Fig. 2a, solid and dashed lines).

In these experiments, initial pH values of the water have been adjusted to 9 because optimum pH of the solutions between 9 and 12 [24], as expected according to the nature of the reaction of ferrous and hydroxide ions, but this optimum pH value is significantly high. As known, increasing the pH causes raising the charge zeta potential of the humic substance molecule [18,25] due to the deprotonation of some functional groups in humic substance. For example, an initial humic substance of 200 mg L^{-1}, with a zeta potential equaling to −23 mV for initial pH of 4 it equals to −41.1 mV for initial pH of 10.

System has been adversely affected by this behavior of charge distribution of the humic substance molecule. Removal efficiency increases rapidly up to 60% and then it remains almost constant for an applied potential of 40 V and initial pH of 5, whereas average current passing through the circuit values are 13.98 mA for 40 V and 19.76 mA for 50 V, respectively. Although amount of Fe(II) delivered to the bulk solution is a function of the current, removal rate at 50 V is lower than that of 40 V. Due to increasing the negative charge at high pH values requiring more Fe(II), the humic substance binding capacity
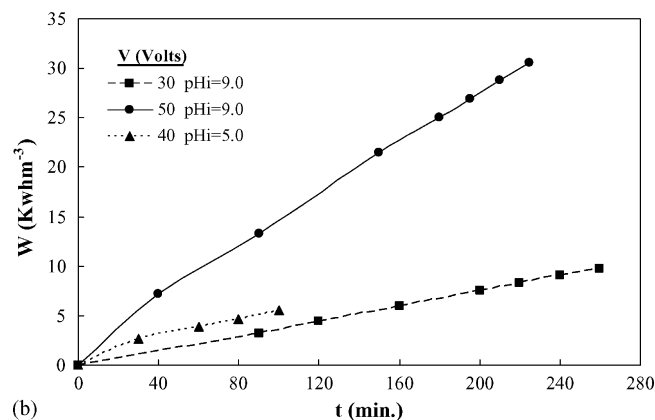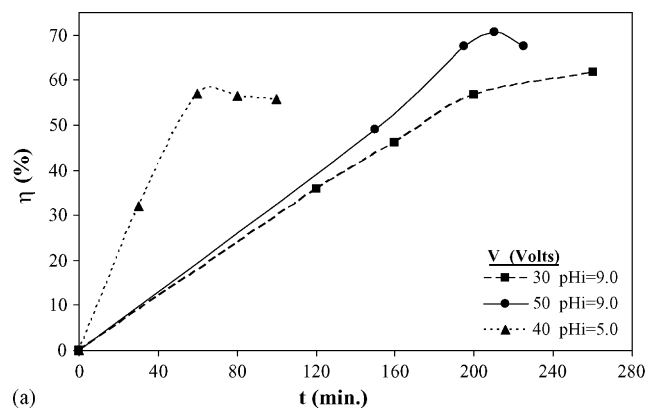
Fig. 2. (a) Variation of removal efficiency as a function of time with applied potential and (b) variation of energy consumption as a function of time with applied potential ($C_0 = 100$ mg L^{-1}, $n = 100$ rpm).

Fig. 3. (a) Variation of STY as a function of applied potential and (b) variation of charge loading as a function of applied potential ($C_0 = 100$ mg L^{-1}, $n = 100$ rpm, pH$_i$ = 9 for 50 V, pH$_i$ = 5 for 40 V).

is the dominant factor responsible for decreasing removal efficiency.

Effect of applied potential on energy consumption has been investigated in the same conditions as in Fig. 2a and depicted in Fig. 2b.

It can be said that energy consumption rises with increasing applied potential as would be expected in any other electrolytic process. When evaluating Fig. 2b, it can be seen that the system has consumed higher energy while initial pH equals to 9 (solid and dashed lines) than that of initial pH of 5. The energy consumption almost equals to 20 kWh/m^3, when initial pH of the solution is 9 and treatment period of 140 min under this conditions, removal efficiency equals to about 55%, whereas energy consumption is about 4 kWh/m^3 for initial pH of 5 and system has reached the same removal efficiency as initial pH of 9 within 60 min.

Investigating the effect of applied potential on the space–time–yield (STY), experiments were performed at initial humic substance of 100 mg L^{-1} and applied potential of 50 V for initial pH of 9 and applied potential of 40 V for initial pH of 5. The obtained STY values for both applied potential have been presented corresponding to a removal efficiency of about 57% (Fig. 3a).

As seen in Fig. 3a, increased applied potential also can not provide as high STY values as initial pH of 5 for initial pH of 9.
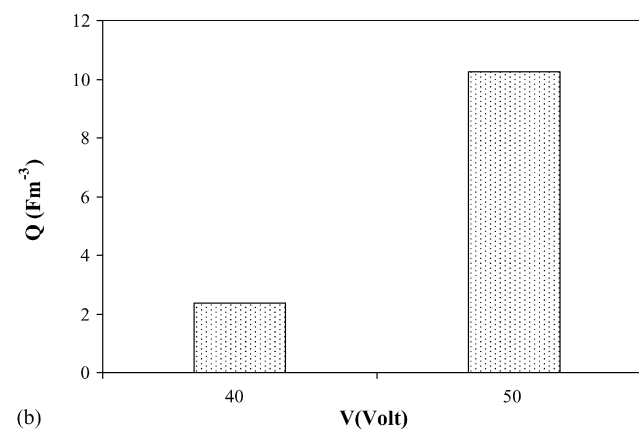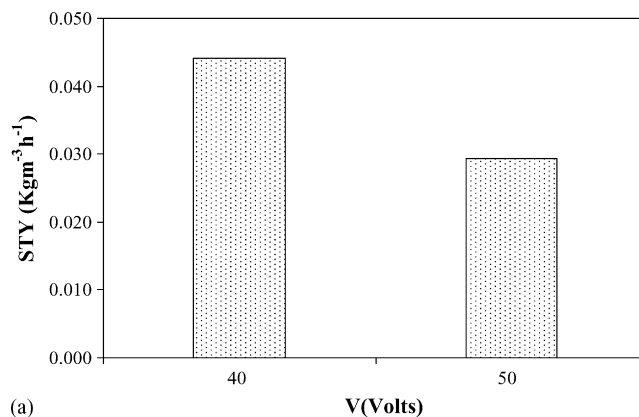
Performance and removal capacity of an electrochemical reactor are determined by energy consumption and STY, respectively. Energy consumption is characterized by charge loading. All of the electrochemical systems should be operated within the range of keeping the space time yield values maximum, while charge loadings are minimum [26].

Effect of applied potential on charge loading has been investigated in the same conditions as in Fig. 3a and presented in Fig. 3b.

It can be seen from Fig. 3b that charge loading has considerably decreased when initial pH of the water equals to 5. It can be concluded that iron electrodes have provided better results for initial pH of 5, when Fig. 3a and b are evaluated.

3.2. Effect of initial humic substance concentration on system parameters

Initial humic substance concentration is varied at 100 and 200 mg L^{-1}, for an initial pH of 5 and applied potential of 40 V and obtained data is depicted in Fig. 4a.

Removal efficiency falls from about 57–34% when humic substance initial concentration is increased from 100 to 200 mg L^{-1}, so the decrease in removal efficiency with increasing initial humic substance concentration may be attributed to requiring more coagulant when increasing levels of pollutant.
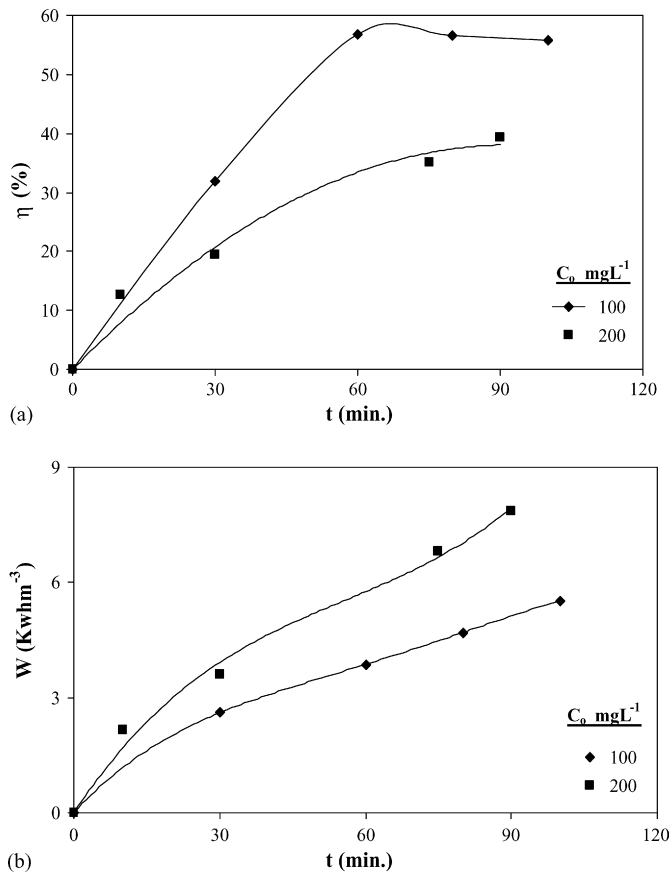
Fig. 4. (a) Variation of removal efficiency as a function of time with initial humic substance concentration and (b) variation of energy consumption as a function of time with initial humic substance concentration ($V = 40$ V, $n = 100$ rpm, pH$_i$ = 5.0).
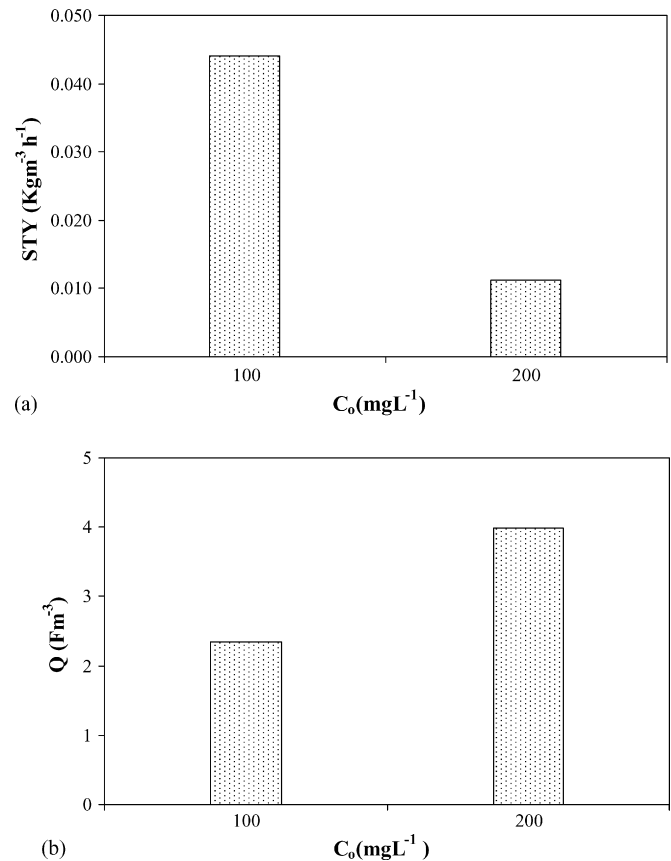

Fig. 5. (a) Variation of STY with initial humic substance concentration and (b) variation of charge loading with initial humic substance concentration ($V = 40$ V, $t = 60$ min, $n = 100$ rpm, pH$_i$ = 5.0).

Using supporting electrolyte is getting mandatory above the 100 mg L^{-1} because in order to remove more pollutant from the water more coagulant should be delivered to the medium. It is possible to achieve that the delivering the enough amount of coagulant to the water in reasonable reaction time by using supporting electrolyte. This effect of the supporting electrolyte can be seen in Fig. 6a.

Effect of initial humic substance concentration on energy consumption was investigated in the same conditions as noted above. Specific energy consumption has raised as initial humic substance concentration increased (see Fig. 4b) because changing electrical conductivity—especially raising—causes passing more current through the circuit under constant applied potential. For example, as humic substance concentration was increased from 100 to 200 mg L^{-1}, the average conductivity and current passing through the circuit were increased from 70 μs/cm to 13.7 mA and 125 μs/cm to 25.1 mA, respectively.

Effect of initial humic substance concentration on space–time–yield (STY) has been investigated at initial humic substance concentration of 100 and 200 mg L^{-1} and applied potential of 40 V. Obtained data is presented corresponding to a treatment period of 60 min. Examining on Fig. 5a, STY decreases with increasing humic substance concentration. Removal efficiency equals to 34% for 200 mg L^{-1} and

57% for 100 mg L^{-1} of initial humic substance concentration, respectively (see Fig. 4a). Thus, STY falls from 0.044 to 0.012 k gm^{-3} h^{-1}.

Effect of initial humic substance concentration on charge loading has been presented in Fig. 5b. It can be concluded that charge loading increases with increasing pollutant concentration. This behavior of the system was explained in the Section 3.2 (see explanation of Fig. 4b).

3.3. Effect of supporting electrolyte type on system parameters

Ten millimeter of Na$_2$SO$_4$, NaNO$_3$ and NaCl were used as supporting electrolyte in the experiments conducted to see the effect of supporting electrolyte type on the removal efficiency. All the experiments were performed at an initial concentration of 500 mg L^{-1}, applied potential of 40 V and initial pH of 5.

Any flock formation was not seen, when NaNO$_3$ was used as supporting electrolyte. Data obtained from Na$_2$SO$_4$ and NaCl were depicted in Fig. 6a.

It can be said that removal rate is higher for NaCl than that for Na$_2$SO$_4$ (see Fig. 6a). It has been thought that NaCl has provided higher rates due to formation of hypochlorite, corresponding to reactions (9)–(11) noted below. The equilibrium constant for reaction (10) is approximately 4×10^{-4} which means that pH
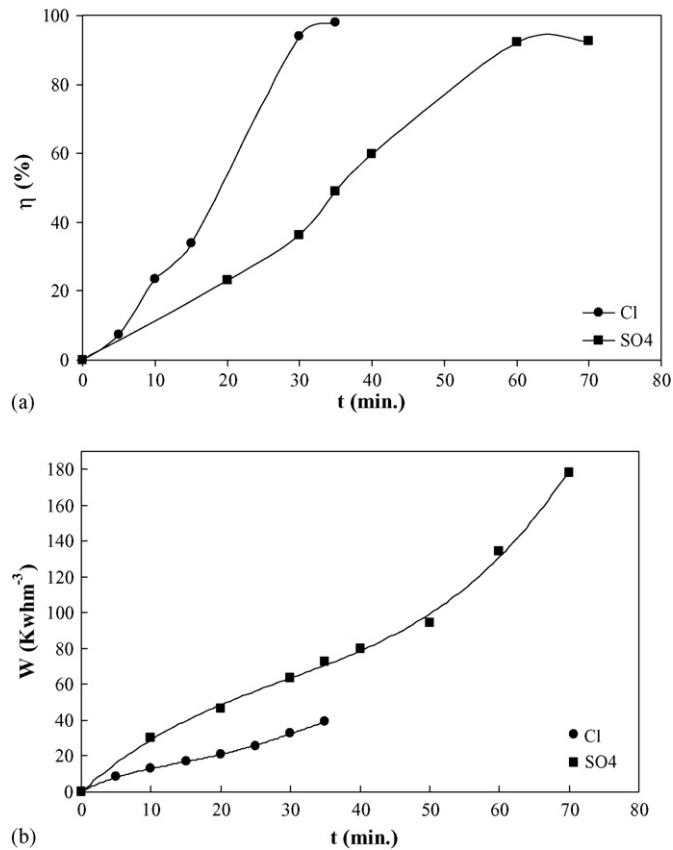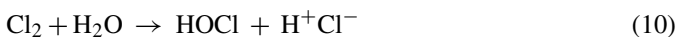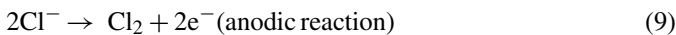
Fig. 6. (a) Variation of removal efficiency as a function of time with supporting electrolyte type and (b) variation of energy consumption as a function of time with supporting electrolyte type ($C_0 = 500$ mg L^{-1}, $V = 40$ V, $C_{SE} = 10$ mM, $n = 100$ rpm, pH$_i = 5.0$).

of the medium higher than 6, there is very little free elemental chlorine present in solution at equilibrium. Additionally, hypochlorous acid is a weak acid, it dissociates according to reaction (11) [27]. It can be concluded that reaction (10) is nearly completed because pH of the water sharply increases up to 10.3 in the first 5 min:

$$2Cl^- \rightarrow Cl_2 + 2e^- \text{ (anodic reaction)} \qquad (9)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+Cl^- \qquad (10)$$

$$HOCl \rightarrow H^+ + OCl^- \qquad (11)$$

Distribution of both hypochlorite and hypochlorous acid is affected by the pH. When pH of the water equals to about 5, while ratio of hypochlorous acid available in the medium is about 100%, equilibrium changes to hypochlorite as pH increases and hypochlorous acid has been completely transformed into hypochlorite approximately at a pH of 9.5 [28]. Both hypochlorous acid and hypochlorite ions obtained from reactions (10) and (11) are highly oxidizing agents. Additionally, available free chlorine (Cl$_2$, HOCl, OCl$^-$) oxidizes Fe(II) to Fe(III) corresponding to reaction (12). Thus this change in distribution of the coagulant has increased the overall removal efficiency.

$$2Fe^{2+} + Cl_2 + 6H_2O \rightarrow 2Fe(OH)_3 + 2Cl^- + 6H^+ \qquad (12)$$

It can be seen that removal rate increases when Na$_2$SO$_4$ is added. It may be attributed to the fact that more coagulant is delivered to medium due to the higher current values. Na$_2$SO$_4$ available in the water average current passing through the circuit equals to 713.8 mA and average charge loading is 55.94 Fm^{-3} for the treatment period of 35 min whereas these parameters are 323 mA and 32.8 Fm^{-3}, respectively, for NaCl under the same treatment period. Coagulant delivered to medium is a function of the charge loading, so it may be concluded that more coagulant is delivered to the medium when Na$_2$SO$_4$ used as supporting electrolyte.

For the investigation of the effect of supporting electrolyte type on the energy consumption, experiments were performed at initial humic substance concentration of 500 mg L^{-1} applied potential of 40 V and initial pH values adjusted to 5. A 10 mM of Na$_2$SO$_4$ and NaCl are used as supporting electrolyte and obtained results are shown in Fig. 6b.

As seen in Fig. 6b, the system has consumed lower energy when NaCl is used as supporting electrolyte. Na$_2$SO$_4$ has provided a higher electrical conductivity than NaCl. For example 10 mM of Na$_2$SO$_4$ and NaCl result in approximately electrical conductivity of 3180 and 1746 µs/cm, respectively. Therefore higher current is passing through the circuit when Na$_2$SO$_4$ is used as supporting electrolyte, so energy consumption of the system increases.
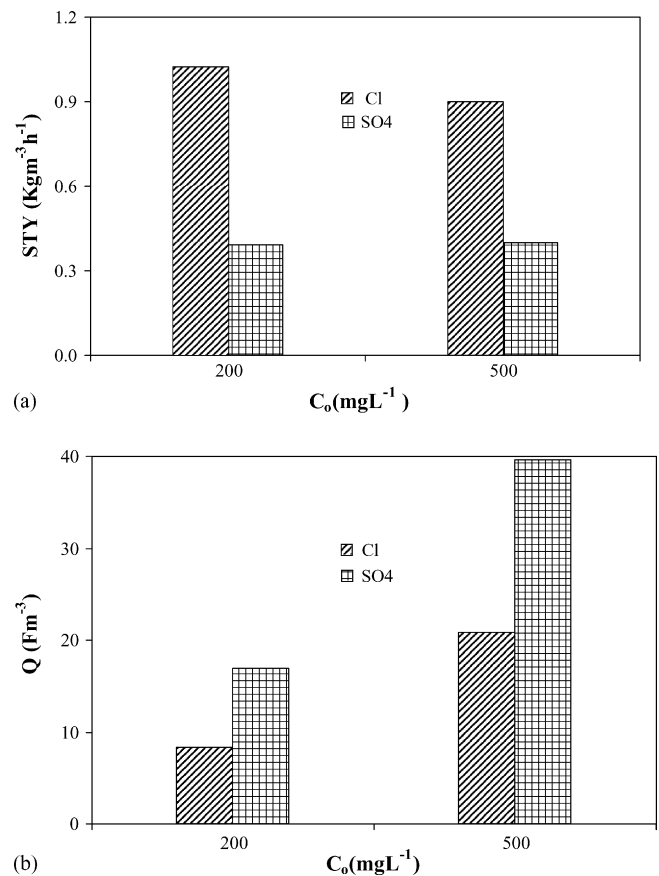

Fig. 7. (a) Variation of STY as a function of initial humic substance concentration with supporting electrolyte type and (b) variation of charge loading as a function of initial humic substance concentration with supporting electrolyte type ($V = 40$ V, $C_{SE} = 10$ mM, $n = 100$ rpm, pH$_i = 5.0$).

Investigating the effect of supporting electrolyte type on the STY, experiments were conducted at initial humic substance concentrations of 200 and 500 mg L^{-1}, applied potential of 40 V and initial pH values adjusted to 5, 10 mM of Na$_2$SO$_4$ and NaCl are used as supporting electrolyte.

Obtained data from initial humic substance concentration of 200 and 500 mg L^{-1} are evaluated corresponding to desired treatment periods ($t = 10$ min for 200 mg L^{-1} and $t = 30$ min for 500 mg L^{-1}) and presented in Fig. 7a. Therefore each initial concentration should be evaluated separately while the effect of supporting electrolyte on STY is examined. As seen in Fig. 7a, NaCl gives higher STY values for both initial humic substance concentrations.

Investigating the effect of supporting electrolyte type on the charge loading, experiments were performed at initial humic substance concentrations of 200 and 500 mg L^{-1}, applied potential of 40 V and initial pH values adjusted to 5, 10 mM of Na$_2$SO$_4$ and NaCl are used as supporting electrolyte.

Obtained data from initial humic substance concentration of 200 and 500 mg L^{-1} are evaluated corresponding to desired treatment periods ($t = 10$ min for 200 mg L^{-1} and $t = 25$ min for 500 mg L^{-1}) and presented in Fig. 7b. Therefore each initial concentration should be evaluated separately while effect of supporting electrolyte on charge loading is examined.

It can be concluded from Fig. 7b that charge loading values for both initial humic substance concentration have lower levels for NaCl. It can be said that NaCl is more favorable than Na$_2$SO$_4$ as supporting electrolyte when Fig. 7a and b are evaluated together, but there is a risk of formation of hazardous by-products. Therefore Na$_2$SO$_4$ should be preferred to NaCl as supporting electrolyte.

4. Conclusions

In this investigation, the treatibility of waters containing high concentration of NOMs using iron cast electrodes has been explored based on removal efficiency by electrocoagulation method. Effects of initial humic substance concentration, applied potential and supporting electrolyte type on the electrocoagulation have been investigated. It can be concluded that electrocoagulation is an effective method for the treatment of waters containing NOMs.

1. In the removal of NOM by electrocoagulation using iron cast electrodes, as NOM is a weak anionic polyelectrolyte a supporting electrolyte should be used.
2. In this investigation, Na$_2$SO$_4$, NaCl and NaNO$_3$ were examined as supporting electrolyte and in the experiments with NaNO$_3$ were observed no flock formation. Comparing other supporting electrolyte types, NaCl is more advantageous than Na$_2$SO$_4$ based on space–time–yield (STY) and charge loading, but it should be kept in mind that risk of formation of organo-chloride by-products increases for NaCl. Thus it can be said that the most favorable supporting electrolyte type is Na$_2$SO$_4$.
3. Initial pH is a highly effective parameter on system performance the effect of initial pH on the system performance

can be considered two-fold. First one is the effect of pH on the reaction between the Fe and hydroxyl ions. As noted earlier, optimum pH range is 9–12 for that reaction. Additionally oxidation reactions of Fe(II) ions by chlorine gas or other oxidants are also strictly related to pH (see reactions (10)–(12)). Latter, pH effects the charge distribution of humic substance molecule. Optimum pH of reaction between the Fe and hydroxyl ions is significantly high. Increasing the pH leads to raise the zeta potential of the humic substance molecule. Hence, increasing the negative charge at high pH values cause more Fe(II) consumption.

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