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Effect of initial pH and supporting electrolyte on the treatment of water containing high concentration of humic substances by electrocoagulation

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Abstract

In this study, the effects of supporting electrolyte type and concentration were investigated on the batch removal of water with high concentration of natural organic matter (NOM) by the electrocoagulation method using plate electrodes. It was observed that the addition of supporting electrolyte has a twofold effect which can be summarized as follows: firstly increasing the ionic strength of the water causing compression of the double-layer and secondly raising the electrical conductivity of the water causing more current passing through the circuit under the same applied potential. It was observed that the concentration of 5 mM supporting electrolyte was optimum up to 100 mg/L of NOM, while concentration of 10 mM is more favorable for higher concentrations than 100 mg/L of NOM. In order to determine the most favorable supporting electrolyte type, NaCl, Na_2SO_4 and $NaNO_3$ were used as supporting electrolyte in the test runs. Under the conditions of initial pH of the solution equal to 5.0 and initial concentration of 100 mg/L NOM, charge loadings were within the range of 2.0934–3.7437 F/m^3 for Na_2SO_4 and NaCl, respectively. Additionally at the same initial conditions for a treatment period of 9 min specific energy consumptions and removal efficiencies were ranged between the 4.747 and 9.695 kWh/m^3, and between 96.84% and 99.64% for Na_2SO_4 and NaCl, respectively. Availability of the chloride (Cl^-) ions in the water can cause formation of disinfection by-products (DBPs) which are suspected carcinogenic compounds. It can be said that the most favorable supporting electrolyte type is Na_2SO_4 for this treatment technique.

Keywords: Electrocoagulation; Supporting electrolyte; Humic substances; Aluminum electrode; Drinking water

1. Introduction

Humic substances constitute major fraction of organic matter in natural waters [1]. Humic substances are structurally complex large macromolecules which occur in soil and natural waters as a consequence of the breakdown of plant and animal residues by microbial activity and a major portion approximately, 50%, of the earth's carbon is in the form of humic materials [2].

Humic substances have the typical properties of weak anionic polyelectrolytes [3], thus solutions of humic substances have low conductivity. They are heterogeneous in structure as well as in their chemical and biochemical reactivity [4]. Humic substances are close to non-biodegradable, therefore it is accepted that they cannot possibly undergo any further decomposition unless exposed to specific chemical agents, oxygen, radiation (sunlight) which they have not previously encountered.

Humic substances have molecular weights of several hundred or larger and carry weakly acidic functional groups such as carboxylic and phenolic groups [3], thus they can be aggregated by charge neutralization [2]. Presence of humic substances in potable waters does not have any known adverse effect. But interaction of humic substances with dissolved and particulate matter in the waters affects the quality of the water and the treatment leads to some problems which can be summarized as follows.

Humic substances cause formation of disinfection by-products (DBPs) such as chloroform, bromo-dichloromethane, etc., which are suspected carcinogenic compounds [4–9]. They manipulate the regrowth of the microorganisms in water distribution systems, causing color, taste and odor [6,8,9], probability of

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Nomenclature

C_0	initial concentration of humic substance (mg/L)
C_{SE}	supporting electrolyte concentration (mM)
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 symbol

ζ	zeta potential (mV)

presence of micro-pollutants and heavy metals associated with humic substances [6,8] and it has been known that the presence of humic substances can decrease the capacity of the adsorbent as the basis of target pollutant decreasing of the capacity sometimes occurs due to the competitive adsorption of humic substances on to adsorbents or formation of a complex with the target pollutant [1]. Due to the harmful effects noted above, humic substances should be removed from water.

2. Electrocoagulation

Recently, electrocoagulation is of great interest for water/wastewater treatment. Electrocoagulation is an electrochemical treatment process which use soluble and coagulating metal such as iron and aluminum [10]. When a dc voltage is applied the electrodes, the anodes start to dissolve electrochemically and produces Al^{3+} and Fe^{2+} ions which are good coagulants. When aluminum is used as electrode material, reactions occurring at the surface of the electrodes and in the bulk solution are shown in Eqs. (1)–(6) but reactions (2), (5) and (6) only occur in chloride containing waters.

At the anode:

$$Al \rightarrow Al^{3+} + 3e^- \quad (1)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (2)$$

at the cathode:

$$3H_2O + 3e^- \rightarrow \frac{3}{2}H_2(g) + 3OH^- \quad (3)$$

in the bulk solution:

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

$$Cl_2 + H_2O \rightarrow HOCl + H^+Cl^- \quad (5)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (6)$$

As seen in the reactions presented above, electrocoagulation is a process consisting of oxidation, flocculation and flotation [11]. Not only in electrocoagulation but also in any other electrochemical process the electrolysis voltage is one of the most important operation variables. And it strongly depends on the conductivity of water/wastewater, current density, inter-electrode distance and surface state of the electrodes [12]. Compared with traditional flocculation and coagulation, electrocoagulation has in theory, the advantage of removing the smallest colloidal particles: the smallest charged particles have a greater probability of being coagulated because of the electric field that sets them in motion. It has also the advantage of producing a relatively low amount of sludge [13]. In addition, it has been reported that the adsorption of the hydroxide on the mineral surface was 100 times more on "in situ" than on pre-precipitated hydroxides when metal hydroxides were used as coagulants [14]. Secondary pollution may be caused by chemical substance added at a high concentration when chemical coagulation is applied to treat wastewater. Excessively added coagulants can be avoided by electrocoagulation, due to the generation of the coagulants by electrooxidation of a sacrificial anode. The characteristics of electrocoagulation are simple equipment and easy operation, brief reactive retention period, decreased or negligible equipment for adding chemical and decreased amount of sludge [15]. Besides electrolytic processes in the electrocoagulation cell are easily controlled by electrical variables such as applied potential and current density, therefore require less maintenance [16].

In recent years, although there has been a lot of works on the wastewater treatment by electrochemical methods, there are so far no reports related to the treatment of water containing humic substances and supporting electrolytes and also no study that compare the supporting electrolyte types for the electrocoagulation process. Although other chemicals such as ferric sulfate and [17], sodium sulfate [12] have been used as supporting electrolyte. The most widely used supporting electrolyte is the NaCl in electrochemical studies [12,15,18,19]. As noted former availability of the chloride (Cl^-) ions in the water can cause formation of DBPs which are suspected carcinogenic compounds. Hence the question should be answered "Which chemical is the best potential supporting electrolyte for this pollutant?"

This study is primarily focused on some crucial questions which must find suitable answers before the process design step: which chemical is the best potential supporting electrolyte type and concentration for this type of water? Is there any need for the adjustment of initial pH of the wastewater before the electrocoagulation stage? For comparative purpose, the same experiments have been run in the same setup with all materials. Based on preliminary experimental results, the effects of initial pH, supporting type and concentration have been explored at potentiostatic mode.

3. Experimental details

3.1. Materials

In this study, humic substance obtained from Sigma–Aldrich Co. has been used as a model pollutant its properties are shown in Table 1.

Table 1
Properties of the used humic substances

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

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 as shown in Fig. 1 [20,21]. Recent studies have shown that carboxylic and phenolic groups in humic substances are most active and they complex and reduce metal ions at different pH values [22]. These groups in humic substance affect the charge of humic substances, due to the distinct behaviors at different pH values.

In preparing the synthetic water containing humic substance and dilutions of stock solutions distilled water. At the beginning of the runs, the initial pH was adjusted to the desired value using NaOH or HNO_3 and during the experiments pH of the waters only monitored.

3.2. Experimental setup and procedure

The experimental setup is shown in Fig. 2. The thermostated electrocoagulator was made of Plexiglas with the dimensions 50 mm × 55 mm × 80 mm. The anode and cathode, fully immersed in water, with dimensions of 40 mm × 50 mm, made of plate aluminum were connected to a digital dc power supply (Shenzen-Mastech HY 3005-3) in monopolar mode. Two digital multimeters (Brymen Bm 201) as ampermeter 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 water at a stirring speed of 100 rpm. During the experiments, temperature, conductivity and pH of the waters were measured by a multi-parameter (WTW Multiline P-4 F-Set-3). Treated water was collected after a desired period of time from the reactor and 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.

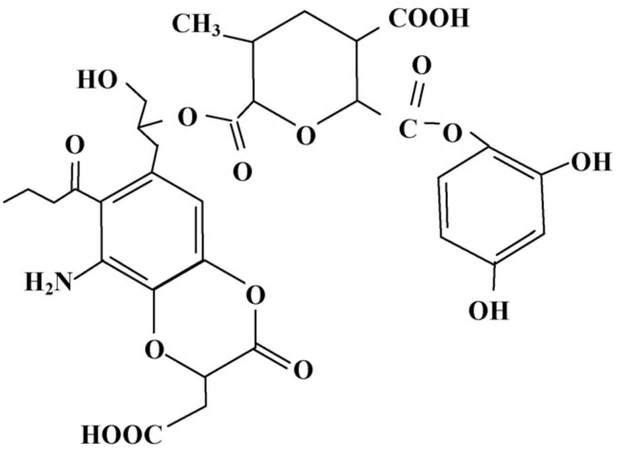
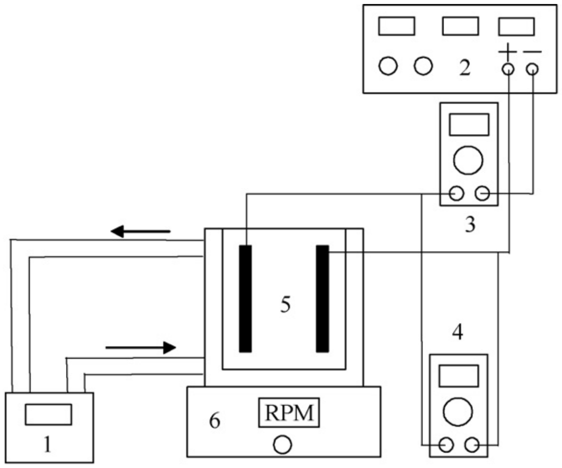


Fig. 1. Functional groups of humic substances.



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

Fig. 2. Schematic diagram of the experimental setup.

3.3. Analysis of humic substances

The humic substance was analyzed spectrophotometrically. A high precision, double-beam spectrophotometer (Shimadzu UV-160A) was used to measure the absorbance of humic substances at wavelengths between 200 and 800 nm and based on the observations from the Wang and Hisieh [23]. Three hundred and five nanometers is chosen as the suitable wavelength in this study to measure the concentration in water. The zeta potentials of the humic substance during each run were measured by using a micro-electrophoresis cell (Zeta-Meter 3.0+).

Space time yield (STY), is calculated as

$$\mathrm{STY}\ (\mathrm{kg/m^3\,h}) = \left(\frac{C_0 - C_e}{t}\right)$$

and charge loading (Q), is calculated as

$$Q\ (\mathrm{F/m^3}) = \left(\frac{It}{v}\right)$$

4. Results

4.1. Effect of initial pH on the removal efficiency

Based on preliminary experimental results, the effects of initial pH and supporting electrolyte concentration have been explored within the range of 5.0 and 9.1 and 5–15 mM, respec-

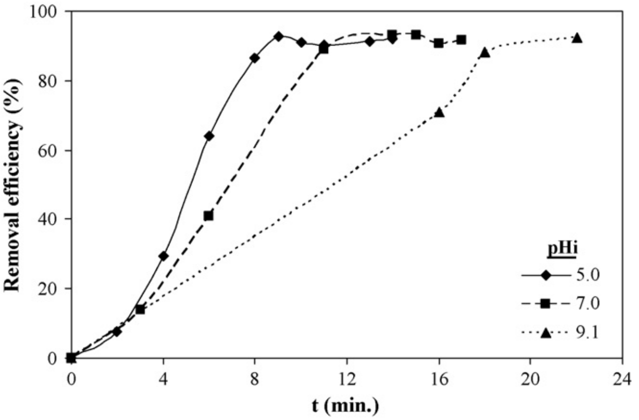


Fig. 3. Variation of removal efficiency as a function of time with humic substance concentration and initial pH of the water ($C_0 = 200$ mg/L, $V = 40$ V, $C_{SE} = 10$ mM Na_2SO_4, $n = 100$ rpm).

tively. It is well-known that the initial pH value of the solution plays an effective role on the system behavior [24,25]. Therefore, in order to determine the effect of type and concentration of supporting electrolyte on the removal efficiency, experiments were conducted primarily to find the most favorable initial pH value for removal of humic substance from waters by EC method and the obtained results are in Fig. 3.

When examining Fig. 3, it can be concluded that the highest removal rates are achievable when the initial pH equals to 5.0. As seen in Fig. 3, when pH_i is 5.0 the removal efficiency is about 92.7% for a treatment period of 9 min, as opposed to 92.3% for a treatment period of 22 for the initial pH of 9.1. This trend is also evident in data shown in Fig. 5 where the energy consumptions are 5.4 and 14.5 kWh/m^3 for pH 5.0 and pH 9.1 specimens, respectively.

On the other hand, initial concentration equals to 200 mg/L and at the original pH of the solution, removal rates are minimum (see Fig. 3, dotted line). This behavior of the system can be attributed to two factors. Firstly, when initial concentration of humic substance exceeds certain threshold value, humic substances form a gel layer on the surface of the anode and prevents delivery of enough coagulant (namely aluminum). In the earlier investigations of the authors, it was found that critical concentration at which the gel layer starts to form is about 120 mg/L [26]. Secondly, as a result of increasing pH, zeta potentials of the humic substances gradually increase (Fig. 4b), because of the deprotonation of some functional groups—such as COOH– [22,27]. At the same time, it has been known that the zeta potentials of $Al(OH)_3$ crystals decrease, as pH of the wastewater raises [21].

As shown in Fig. 4b, when the initial humic substance concentration is 200 mg/L, and supporting electrolyte is used, zeta potentials of the humic substance keep constant when varying the pH within the range of 5.0–9.0, due to the compression of the electrical double layer. It has been seen that zeta potentials increase as the pH raises (see Fig. 4b). It is important to understand that all metal cations hydrated in water and that such simple ions as Al^{3+}, Ca^{2+} and Na^+ do not actually exist. Instead, these ions exist as aqua-complexes such as $Al(H_2O)_6{}^{3+}$. Well-hydrated ions usually are not strongly adsorbed to the colloidal surface but remain in the diffuse part of the double layer. Due to this behavior of the ions, when the dominant mechanism is the double layer compression, probably it is not possible to cause a charge reversal colloid regardless of how much electrolyte is added [28].

When on an examining Fig. 4a, it can be seen that the supporting electrolyte has compressed the double layer, thus zeta potentials almost keep constant especially for 100 mg/L, although the pH of the water raises. It can be attributed to the supporting electrolyte has screened the increasing zeta potentials due to raising the pH of the medium. Because the humic substance concentration is relatively lower than the other initial concentrations. Whereas it can be seen that system has different behavior at an initial concentration 200 mg/L. while pH of the water is within 5.0–9.0, zeta potentials form a plateau, with an approximate value of −25 mV, derived from the compression of the double layer. Supporting electrolyte can compress the double layer, till pH increases up to 9.0, but after exceeding this threshold pH value, zeta potentials keep on raising because of increasing humic substance concentration. Similarly, at the initial humic substance concentration of 500 mg/L, it is only possible that the plateau noted above pH of the medium is in the range of 6.0–7.0. Plateau gets shorter, as initial concentration of humic substance increases. Thus, it can be concluded

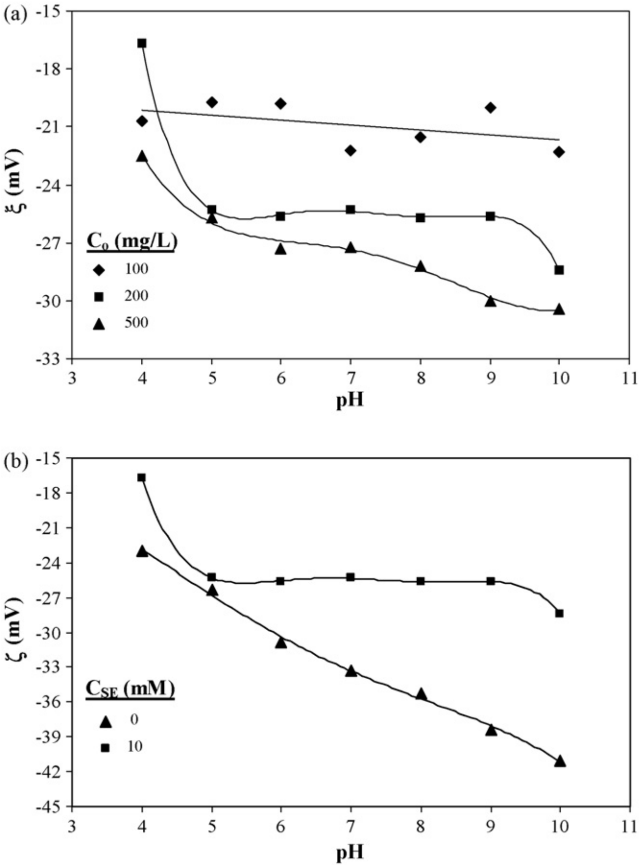


Fig. 4. Variation of the zeta potential of the Humic substance as a function of the water pH with initial humic substance concentration and supporting electrolyte concentration ($C_{SE} = 10$ mM, Na_2SO_4 (a), $C_0 = 200$ mg/L (b)).

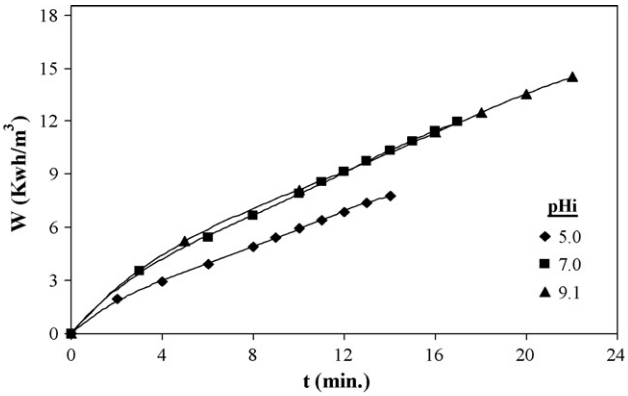


Fig. 5. Variation of energy consumption as a function of time with supporting electrolyte and initial pH of the water (C_0 = 200 mg/L, V = 40 V, C_{SE} = 10 mM Na_2SO_4, n = 100 rpm).

that the shortening of the plateau is caused by the increasing concentration of the humic substance.

Removal rates decrease due to these two factors. Similar system behavior has been clearly observed at higher initial humic substance concentrations. In the first 3 min, although removal rates are too close, for initial pH value (pH_i = 9.1) and the others, at the point of about 5 min removal rate has decreased the original pH. It can be concluded that the gel layer formed on the surface of the anode is effective from the point of about 5 min.

4.2. Effect of initial pH on the energy consumption

It has been shown that variation of energy consumption with initial pH of the water as a function of time in Fig. 5. When examining Fig. 5, it can be seen that energy consumptions have generally minimum values, when initial pH equals 5.0. This typical tendency in energy consumption curves will be explained in the latter section.

Fig. 6 illustrates the variation of removal efficiency with charge loading. Sharp increases of removal efficiencies are clearly observed initially. After charge loading beyond 3 F/m^3 the removal efficiencies approach plateaus at 85% (the point with arrow in Fig. 6). The charge loading term represents the specific energy consumption of the system thus; the optimum charge loading should be at the end of the sharp increase step. This approach provides cost-effectiveness for the system. In the light of these conclusions, later data and results are cited to evaluate corresponding to a removal efficiency of 85%.

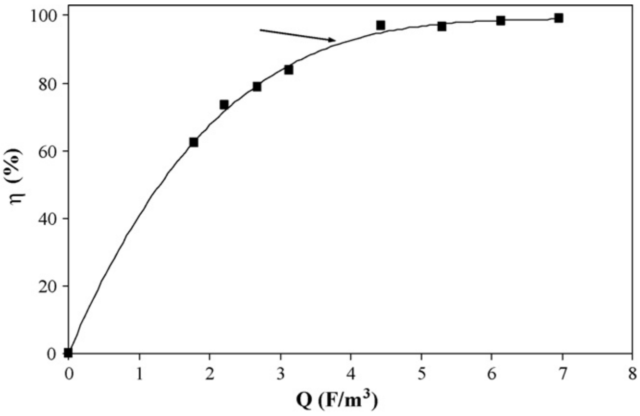


Fig. 6. Variation of removal efficiency with charge loading (C_0 = 100 mg/L, V = 40 V, C_{SE} = 10 mM Na_2SO_4, n = 100 rpm, pH_i = 5).

Table 2
Removal efficiencies and energy consumptions of the experiments without supporting electrolyte at the initial humic substance of C_0 = 200 mg/L

pH_i	t (min)	η (%)	W (kWh/m^3)
5	5	4.03	0.649
	10	6.76	0.960
	15	24.34	1.270
	20	24.95	1.580
	25	52.76	1.889
	30	90.74	2.192
	35	97.49	2.493
	45	99.30	3.089
	61	98.21	4.023
	70	98.53	4.539
7	10	15.13	0.987
	20	17.50	1.472
	55	81.20	3.181
	60	89.83	3.418
	70	92.67	3.880
Org.[a]	10	35.20	0.728
	20	53.26	1.032
	30	63.91	1.299
	40	75.87	1.564
	50	80.06	1.814
	60	82.95	2.090
	70	87.15	2.359
	80	88.26	2.622
	90	91.88	2.887
	100	94.13	3.145

[a] "Org." represents the original pH of the water and it equals to 9.1 for 200 mg/L humic substance concentration.

Results obtained from the runs conducted without supporting electrolyte have been presented in Table 2. Because the results especially for energy consumptions are rather high for the experiments performed with supporting electrolyte (see Fig. 5).

Fig. 7 summarizes the variations of energy consumptions corresponding to a removal efficiency of 85% with applied potential. It can be clearly concluded that of all applied potentials investigated energy consumptions have minimum values when initial pH of the water equals 5.0. When examining Fig. 7a and b, it can be seen that energy consumption values increase with raised applied potentials for initial pH values are 8.5 and 9.1. This can be attributed to increases in the current passing through the circuit with raised applied potentials. A certain fraction of the total current is spent for the side reactions, which are not desirable to occur, such as IR potential drop, formation of H_2 and Cl_2 gases, etc. Thus, in higher applied potentials, more current should be passed than that of the lower potentials for obtaining desired removal efficiencies.

In Fig. 7b, when examining the energy consumption curve for the initial pH of 9.1, it has been seen that energy expenditure has increased especially with applied potentials above 30 V.

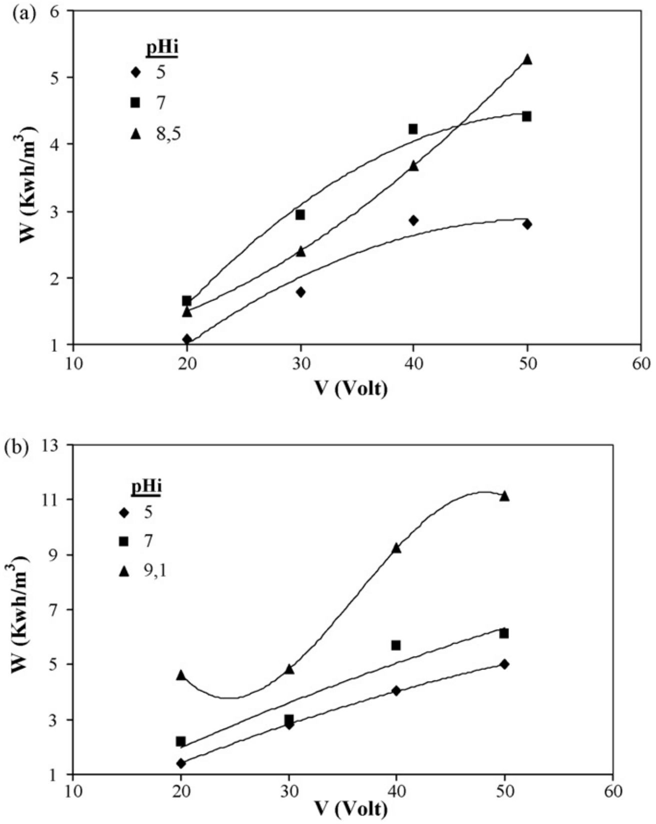


Fig. 7. Variation of energy consumption as a function of applied potential with initial pH of the water ($C_0 = 100$ mg/L (a), $C_0 = 200$ mg/L (b), $C_{SE} = 10$ mM Na_2SO_4, $n = 100$ rpm, energy consumptions have been calculated according to removal efficiencies of 85%).

At an initial concentration of 100 mg/L of humic substance, conductivity of the water and current passing through the circuit at a treatment period of removal efficiency corresponding to 85% equal to 2165 μs/cm and 232.2 mA respectively for 50 V whereas for 200 mg/L humic substance, conductivity and current values are 2310 μs/cm and 195.9 mA. According to conductivity values of water presented above, it is expected that when the initial concentration equals to 200 mg/L more current should pass the circuit. But that does not happen. It can be explained that the current passing through the circuit is not only related to the conductivity of the water but at the same time also to the surface state of the electrodes [12]. Because the gel layer formed on the surface of the anode constitutes additional resistance (although the conductivity of the water with 200 mg/L initial humic substance is higher than that of the 100 mg/L). Lower current passes through the circuit.

When Figs. 3, 5 and 7 are considered, it can be said that the optimum initial pH is 5.0 for this treatment system.

Effect of supporting electrolyte on space time yield (STY) and charge loading has been investigated and the obtained results are presented in Fig. 8. STY values have decreased, as initial pH raises within the investigated range. STY has maxima, for all investigated initial concentrations when initial pH value equals to 5.0. In addition, it can be said that STY has been raised with increasing concentration because at relatively high initial concentrations, it is possible that more pollutant can be removed. Besides charge loading also increases with initial pH values. In view of providing more cost effectiveness, system should be operated at conditions of minimum charge loadings [26].

4.3. *Effect of supporting electrolyte concentration on the removal efficiency*

Effect of supporting electrolyte concentration on removal efficiency has been investigated at initial humic substance concentrations of 100 and 200 mg/L, using Na_2SO_4 concentrations of 5, 10 and 15 mM as supporting electrolyte.

As seen in Fig. 9a and b supporting electrolyte concentration does not have any clear effect on removal rate or efficiency.

4.4. *Effect of supporting electrolyte concentration on energy consumption*

Effect of supporting electrolyte concentration on energy consumption has been investigated at the same conditions of removal efficiency and results are presented in Fig. 10. Energy expenditure increases as supporting electrolyte concentration raises. One of the important factors for the electrochemical processes which consist of heterogeneous ion transfer reactions is the conductivity of the water to be treated. Because the current passing through the circuit is a function of the conductivity under a certain applied potential. Conductivity of the water increases as the supporting electrolyte concentration raises thus, current passing through the circuit increases in potentiostatic mode [18,29].

Effect of supporting electrolyte concentration on STY and charge loading was investigated at initial concentration of humic substance concentrations of 100 and 200 mg/L and the obtained results were presented on the basis of removal efficiency which equals to 85% in Fig. 11. STY increases, as supporting electrolyte concentration – in other words conductivity – raises. It can be said that raising conductivity causes achieving higher current passing through the circuit and consequently the removal rate increases. Thus the reaction time required for the desired removal efficiency is getting shorter. Additionally charge loadings at higher humic substance concen-

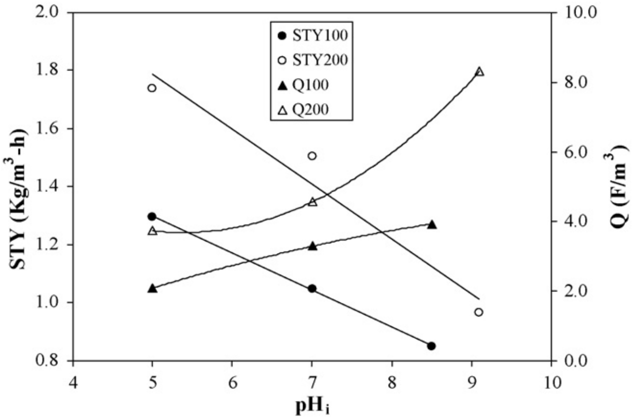


Fig. 8. Variation of space time yield and charge loading with initial pH of the water ($V = 50$ V, $C_{SE} = 10$ mM Na_2SO_4, $n = 100$ rpm).

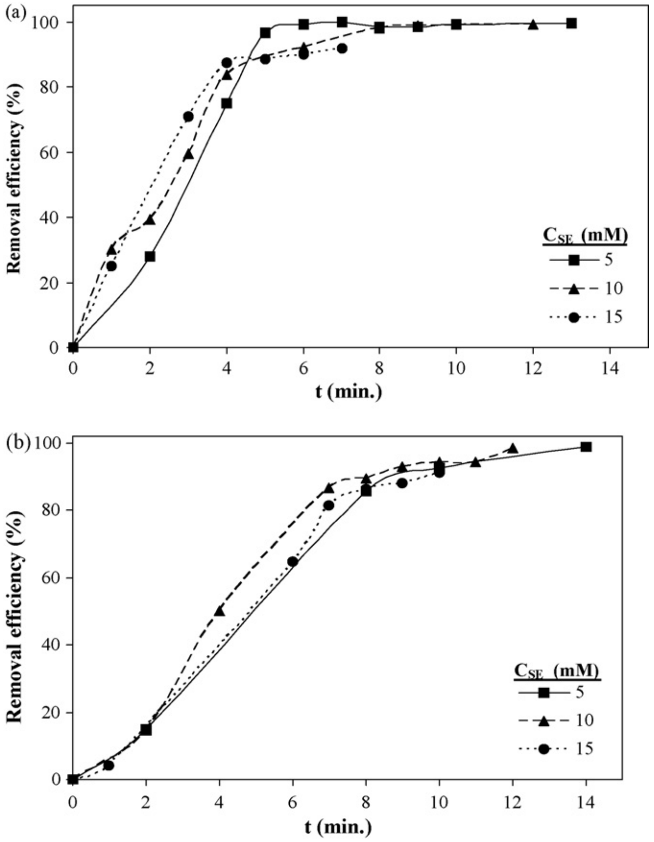


Fig. 9. Variation of removal efficiency as a function of time with supporting electrolyte concentration ($C_0 = 100$ mg/L (a), $C_0 = 200$ mg/L (b), $V = 50$ V, $n = 100$ rpm, $pH_i = 5$, supporting electrolyte Na_2SO_4).

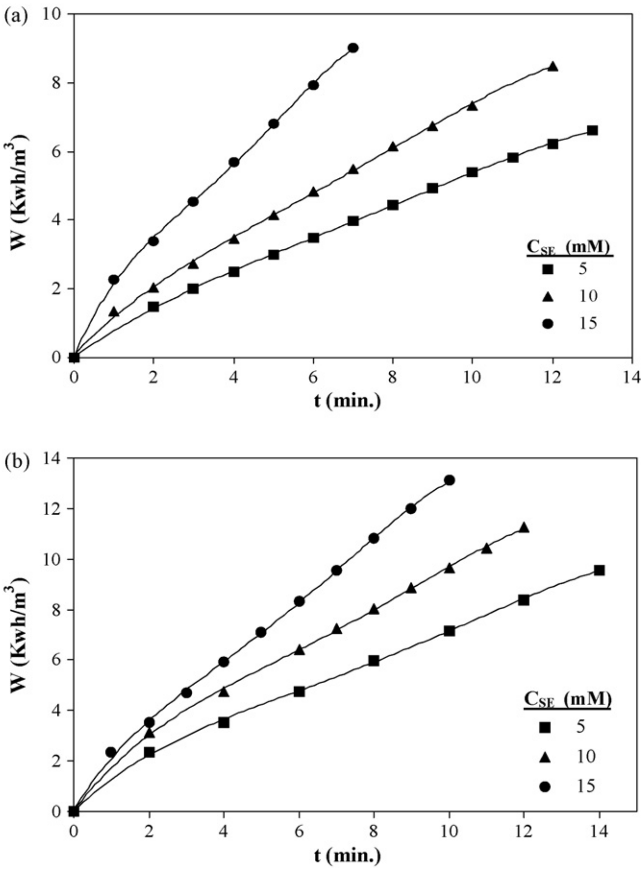


Fig. 10. Variation of energy consumption as a function of time with supporting electrolyte concentration ($C_0 = 100$ mg/L (a), $C_0 = 200$ mg/L (b), $V = 50$ V, $n = 100$ rpm, $pH_i = 5$, supporting electrolyte Na_2SO_4).

trations have sharply increased when the supporting electrolyte concentration exceeds 10 mM while at lower humic substance concentrations (100 mg/L) are nearly constant.

It can be said that determining the optimum supporting electrolyte concentration should be taken into consideration. Within the investigated range, 5 mM is the most favorable supporting electrolyte concentration, when initial humic substance concentration is up to 100 mg/L while with concentrations exceeding 100 mg/L, 10 mM is more favorable.

4.5. Effect of supporting electrolyte type on removal efficiency

The effect of supporting electrolyte type on removal efficiency was investigated at initial humic substance concentrations of 100 and 200 mg/L using Na_2SO_4, $NaNO_3$ and NaCl as supporting electrolyte at an applied potential of 40 V. Supporting electrolyte type does not have any considerable effect on removal efficiency, when initial humic substance concentration equals 100 mg/L (Fig. 12a). Whereas supporting electrolyte type has an important effect on it. At higher initial humic substance concentrations, it can be clearly seen that higher removal rates are only achievable with NaCl as supporting electrolyte. When chloride ions are available in the water, the reactions (2), (5) and (6) occur either on the electrode surfaces or in the bulk solution. As a result of these reactions, chlorine gas and hypochlorite ions which are a strong oxidizing agent form in the bulk solution.

4.6. Effect of supporting electrolyte type on energy consumption

Effect of supporting electrolyte type on energy consumption has been investigated at the same conditions as removal effi-

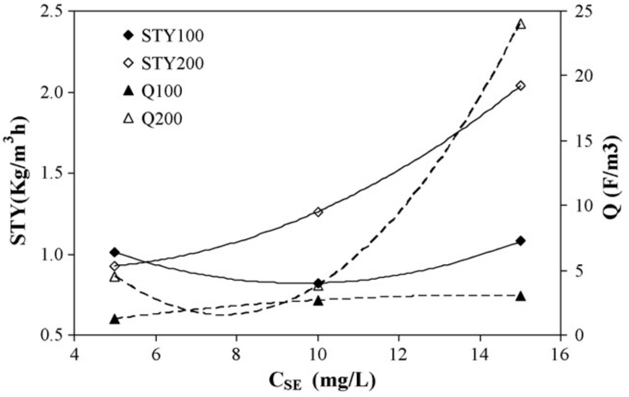


Fig. 11. Variation of space time yield and charge loading as a function of supporting electrolyte concentration with initial humic substance concentration ($V = 50$ V, $C_{SE} = 10$ mM Na_2SO_4, $n = 100$ rpm, $pH_i = 5$).

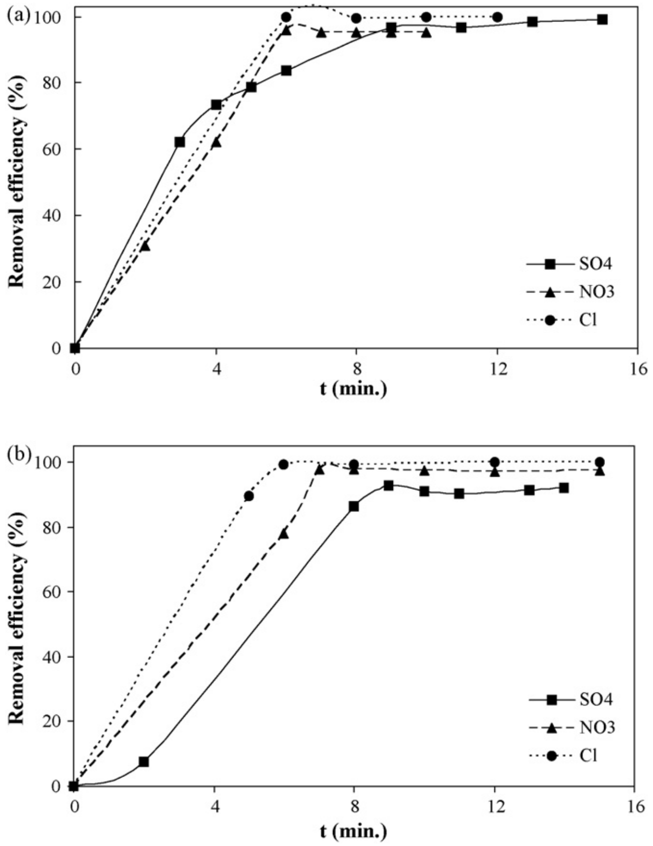


Fig. 12. Variation of removal efficiency as a function of time with supporting electrolyte type ($C_0 = 100$ mg/L (a), $C_0 = 200$ mg/L (b), $C_{SE} = 10$ mM, $V = 40$ V, $n = 100$ rpm, $pH_i = 5$).

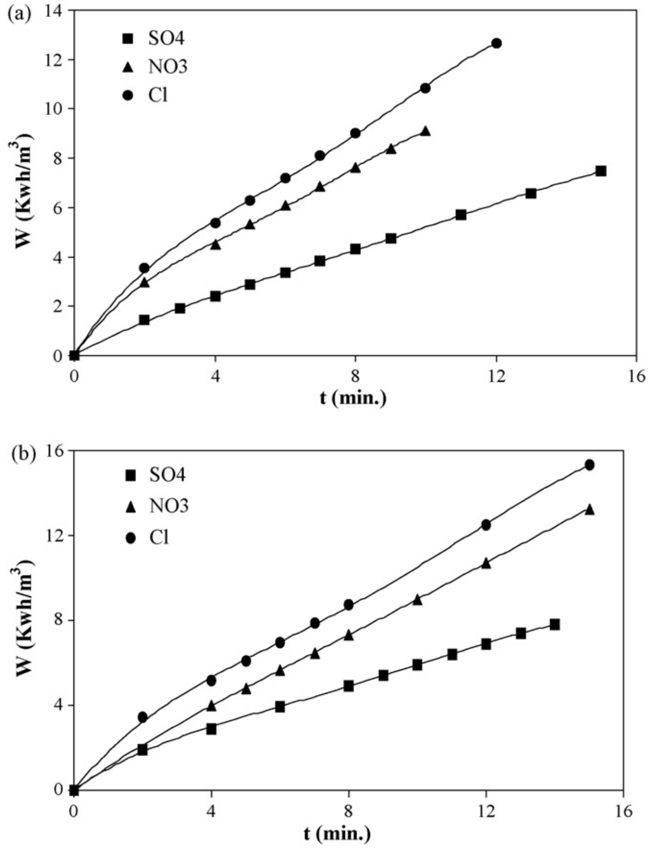


Fig. 13. Variation of energy consumption as a function of time with supporting electrolyte type ($C_0 = 100$ mg/L (a), $C_0 = 200$ mg/L (b), $C_{SE} = 10$ mM, $V = 40$ V, $n = 100$ rpm, $pH_i = 5$).

ciency and results are presented in Figs. 13 and 14. It can be seen that NaCl has the highest energy expenditure among the investigated supporting electrolytes. Additionally, as shown earlier, availability of chloride ions in water causes forming of the hypochlorite and this ion stimulates the formation potential of Disinfection by-products (DBPs) by combining with the humic substance present in the wastewater [4–9,30]. Thus, Na_2SO_4 and $NaNO_3$ should be taken into consideration determining the favorable supporting electrolyte type. Especially at high humic substance concentrations, NaCl has about equal removal efficiencies with other supporting electrolytes, whereas it provides higher removal rates.

Fig. 14 illustrates the variations of energy expenditures corresponding to removal efficiencies of 85% with applies potentials. It can be concluded that the lowest energy is with $NaNO_3$ in view of removal efficiency. It can be said that the most favorable supporting electrolyte is Na_2SO_4.

4.7. *Effect of supporting electrolyte on STY and charge loading*

Effect of supporting electrolyte type on STY and charge loading was investigated between 100 and 500 mg/L of initial humic substance concentration and 40 V of applied potential. As shown in Fig. 15a, STY values have changed with initial humic substance concentration and supporting electrolyte type $NaNO_3$ and NaCl have higher STY values in relatively higher initial humic substance concentrations. But all of the electrochemical systems should be operated within the range of having the STY values maximum, while charge loadings are minimum. Therefore determining the most favorable supporting electrolyte type charge loading values also should be taken into consideration. Fig. 15b depicts the charge loadings the same conditions as STY.

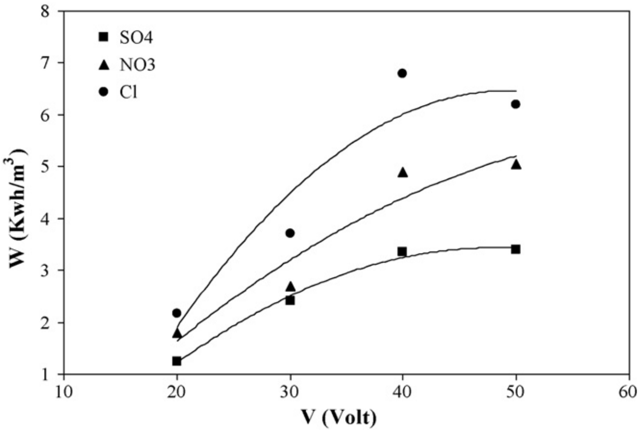


Fig. 14. Variation of energy consumption as a function of applied potential with supporting electrolyte type ($C_0 = 100$ mg/L, $C_{SE} = 10$ mM, $n = 100$ rpm, $pH_i = 5$, energy consumptions have been calculated according to removal efficiencies of 85%).

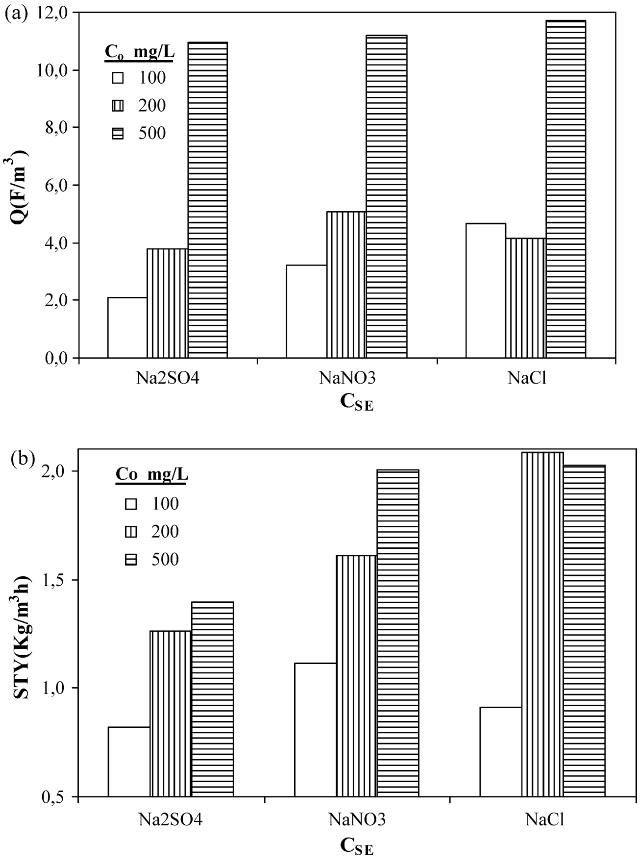


Fig. 15. Variation of space time yield and charge loading as a function of supporting electrolyte type with initial humic substance concentration ($V = 40$ V, $C_{SE} = 10$ mM, $n = 100$ rpm).

It can be seen that Na_2SO_4 has lower energy consumption values than the others. It can be concluded that Na_2SO_4 is the most favorable supporting electrolyte for this system. Its STY is lower than that of the others. Because $NaNO_3$ used as supporting electrolyte even equals to 5 mM, NO_3 ion concentration exceeds the European drinking water standards.

5. Conclusions

In this present work, effect of supporting electrolyte and concentration on the electrocoagulation of humic substance has been investigated Na_2SO_4, NaCl and $NaNO_3$ were used as supporting electrolyte and effects of these supporting electrolytes on the system performance have been evaluated based on removal efficiency and energy consumption. It can be concluded that NaCl should not be used as supporting electrolyte in electrocoagulation of humic substances although it provides similar results with Na_2SO_4.

1. Determining optimum supporting electrolyte concentration, humic substance concentration should be taken into account. It was observed that the concentration of 5 mM supporting electrolyte was optimum up to 100 mg/L of humic substance, while concentration of 10 mM is more favorable for higher concentrations than 100 mg/L of humic substance.
2. Especially for higher humic substance concentrations, optimum initial pH is 5.0 for electrocoagulation technique using aluminum plate electrodes.
3. During the experiments conducted for determining the most favorable supporting electrolyte, when observed removal efficiencies and specific energy consumptions are evaluated, it can be concluded that Na_2SO_4 the most favorable electrolyte type.
4. Electrocoagulation is an efficient process to remove humic substances from waters especially in the condition of using favorable supporting electrolyte type and concentration.

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