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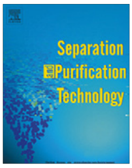

Effect of electrochemical cell structure on natural organic matter (NOM) removal from surface water through electrocoagulation (EC)

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ABSTRACT

This study analyzed the effect of electrocoagulation cell construction on NOM removal from Finnish surface water. Three types of cells were used in this research: one that only had aluminum electrodes, one that had aluminum anodes and inert cathodes, and one that had inert anodes and aluminum cathodes. Main water quality parameters such as TOC, apparent color, and concentrations of residual metals were measured from the samples. A statistical model was made from the results using partial least squares (PLSs) regression. According to the results, electrocoagulation was able to produce high quality water with low NOM concentration. Lowest measured TOC concentration was 4.02 mg/l (78% removal). The potential applications of water after the treatment could be potable water or industrial fresh water. Aluminum originating from the anodes or cathodes had similar NOM removal efficiency. According to TOC and ζ-Potential results, the mechanism of NOM removal was similar to chemical coagulation in different pHs. It seems that in low pH, double layer compression was the main destabilization mechanism whereas in higher pH, adsorption and bridging dominated.

1. Introduction

Electrocoagulation has been suggested to be a promising alternative to chemical coagulation for removing various pollutants from freshwaters and wastewaters [1–3]. Sacrificial metal anodes or cathodes produce metal ions or metal hydroxides into solution. Metal cations and hydroxides interact with pollutants by several mechanisms, including charge neutralization, precipitation, and enmeshment. Pollutants can be removed from water by electroflotation, which can occur simultaneously with electrocoagulation, or by sedimentation, or filtration. Electroflotation is caused by micrometer-sized bubbles (15–23 μm diameter), which are produced on the cathode surface [4]. Other mechanisms that may affect pollution removal are electromigration of ions towards electrodes and reduction of metals on the cathode surface. These reactions, as well as well-known advantages and disadvantages and applications of electrocoagulation, are presented in review articles [1–3,5,6].

It is well known that aluminum in the electrocoagulation process can be dissolved from aluminum anodes and cathode electrodes. Aluminum dissolves from anodes according to simple electrochemical reaction Eq. (1) and forms hydroxides in water Eq. (2). Meanwhile, aluminum cathodes dissolve due to high pH on the cathode surface Eq. (4), which is caused by OH^- that is produced by an electrochemical reaction Eq. (3). Aluminate also forms various hydroxides in water Eq. (2) depending on the water pH.

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^- \tag{1}$$

$$Al^{3+}(aq) + nH_2O \leftrightarrow Al(OH)_n^{3-n+} + nH^+(aq) \tag{2}$$

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

$$2Al(s) + 6H_2O + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g) \tag{4}$$

Electrocoagulation treatment of surface waters and removal of NOM from waters has been studied in several articles [7–16]. Jiang et al. applied a laboratory flow-through system, which they tested with model-colored water and lowland surface water [8]. Electrocoagulation performed better for DOC removal than chemical coagulation for the model-colored water, but for the lowland surface water both processes had similar performance. Yildiz et al. studied the effect of initial pH, supporting electrolyte, applied potential and initial humic substance concentration on NOM removal from synthetically prepared waters containing a high concentration of NOM [14,15]. According to their results, the optimum initial pH is 5 for electrocoagulation using aluminum plate electrodes. They concluded that Na_2SO_4 was the most favorable supporting

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electrolyte. However, it should be noted that applying supporting electrolyte takes away one advantage of electrocoagulation: lower salt concentration of produced water. The effect of temperature and initial pH of surface water on removing natural organic matter (NOM) was studied in our earlier research [11]. According to our results, temperature had a minor effect on removal of NOM in temperature range 275.15–295.15 K. The greatest NOM removal (80.4%) in the tested range of parameters, according to dissolved organic carbon results, was obtained when the initial pH was 4.3 and the maximum electric charge was applied (144 C/l).

Response surface method (RSM) is a statistical method that is used to study the relationship of the factors and responses. It has been used in several studies where factors affecting electrocoagulation efficiency have been studied and optimized. We have successfully used RMS in our previous studies [11,17]. RSM has also been used to optimize oil removal from oily wastewater [18], azo dye removal from simulated wastewater [19] and Cr(VI) from simulated wastewater [20] and real wastewater [21]. In this study RSM with partial least squares regression (PLS) was used to optimize the electrocoagulation treatment of surface water. Additional tests were done with optimized parameters to verify the empirical model.

It is possible that aluminum ions and hydroxides produced on the anodes and the cathodes have different properties if they react with pollutants on the electrode surface before they are stabilized in bulk water to similar hydroxides. The aim of this study was to investigate if aluminum dissolved from anodes and cathodes has different properties in NOM removal from surface water. This was conducted by using three different cell constructions: a cell with aluminum anodes and cathodes, a cell with aluminum anodes and inert cathodes, and a cell with inert anodes and aluminum cathodes.

2. Experimental

2.1. Electrochemical treatment

Water samples were collected from a Finnish river and stored in a cold room. The untreated samples had high NOM concentration according to photometric and DOC measurements. The physicochemical properties of the samples before and after EC treatment are presented in Table 1. Water pH was adjusted before treatment to the desired level using 0.1 M, 0.01 M and 0.001 M sulfuric acid solutions (analytical grade). Studies were made in acidic initial

Table 1

Factor and response values used in the model and initial water quality parameters.

Turbidity (NTU)	Apparent color (mg/l PtCo)	TOC (mg/l)	ζ-Potential (mV)	Residual Al (mg/l)	Residual Fe (mg/l)
Initial water quality parameters					
0.34	102.0	18.29	−15.2	0.3145	0.8838

Factors		Responses								
Electric charge (C/l)	Initial pH	Final pH	Turbidity (NTU)	Apparent color (mg/l PtCo)	TOC (mg/l)	ζ-Potential (mV)	Dissolved Al (mg/l)	Residual Al (mg/l)	Residual Fe (mg/l)	Residual Mn (mg/l)
Cell A+C: Aluminium anodes and aluminium cathodes										
48	3.0	3.50	1.24	61.8	15.19	−10.5	5.531	5.2770	0.2030	0.0842
96	3.0	3.80	1.01	51.4	14.35	−3.9	7.675	7.2800	0.1848	0.0863
144	3.0	4.36	1.52	18.4	7.06	7.6	15.490	8.4020	0.0754	0.0781
48	4.0	6.56	1.51	12.4	5.20	−26.4	5.613	0.0364	0.0068	0.0407
96	4.0	6.73	1.72	11.3	4.04	−29.2	12.840	0.0163	0.0000	0.0397
144	4.0	6.82	2.05	11.8	4.02	−27.4	19.650	0.0462	0.0015	0.0319
48	5.0	6.42	2.75	78.1	13.23	−22.6	5.703	2.7960	0.3990	0.0248
96	5.0	6.81	1.98	22.2	7.45	−24.0	12.590	0.5711	0.0324	0.0118
144	5.0	6.83	3.46	22.7	6.54	−17.0	18.420	0.7860	0.0047	0.0073
96	4.0	6.62	1.42	11.0	4.07	−29.9	12.090	0.0156	0.0000	0.0409
96	4.0	6.61	1.18	8.1	4.72	−27.7	11.790	0.0224	0.0017	0.0420
96	4.0	6.54	1.38	9.2	4.53	−26.6	11.200	0.0288	0.0046	0.0413
Cell A: Aluminium anodes and DSA cathodes										
48	3.0	3.53	1.08	73.0	16.70	−12.4	4.115	3.9600	0.2984	0.1694
96	3.0	3.97	0.80	59.2	14.78	−6.8	7.672	7.1710	0.2538	0.1650
144	3.0	4.39	0.76	24.2	8.99	−3.4	11.350	8.3230	0.1519	0.1390
48	4.0	6.98	1.19	18.0	7.77	−28.5	4.201	0.1319	0.0355	0.1190
96	4.0	7.02	1.24	9.3	5.45	−24.1	8.167	0.0240	0.0072	0.1086
144	4.0	7.13	1.00	8.5	5.38	−31.2	11.578	0.0310	0.0017	0.0874
48	5.0	7.18	2.70	96.2	15.69	−24.0	4.224	2.6940	0.5336	0.1169
96	5.0	7.68	3.96	57.2	11.01	−29.2	8.118	2.0170	0.2115	0.0805
144	5.0	7.76	3.22	33.7	8.81	−25.4	12.040	1.2270	0.0760	0.0515
96	4.0	6.65	1.53	10.8	6.10	−26.2	7.826	0.0535	0.0205	0.0874
96	4.0	6.94	1.29	9.0	5.45	−22.4	7.722	0.0395	0.0225	0.0822
96	4.0	6.75	1.29	9.1	5.36	−26.5	7.940	0.0358	0.0229	0.0884
Cell C: DSA anodes and aluminium cathodes										
48	3.0	3.27	1.17	71.6	16.53	−13.6	2.806	2.5370	0.3475	0.1465
96	3.0	4.09	1.17	28.5	9.96	−3.2	10.190	7.0370	0.1653	0.1427
144	3.0	4.43	0.88	11.0	5.37	11.7	17.764	6.2580	0.0652	0.1337
48	4.0	7.08	2.06	36.1	10.44	−32.6	3.590	0.2531	0.0912	0.1338
96	4.0	6.89	1.21	10.1	5.02	−27.6	7.744	0.0316	0.0046	0.1064
144	4.0	7.23	1.61	9.7	4.84	−31.7	11.160	0.0262	0.0157	0.0828
48	5.0	7.21	2.15	124.2	18.42	−23.2	3.633	3.2670	0.7600	0.0999
96	5.0	7.23	1.32	14.3	6.67	−21.6	9.627	0.0857	0.0111	0.0656
144	5.0	7.47	1.52	10.3	5.14	−23.6	16.258	0.0802	0.0114	0.0517
96	4.0	7.28	0.96	5.4	4.10	−29.0	10.070	0.0207	0.0003	0.0526
96	4.0	6.49	1.52	8.4	4.57	−23.7	6.672	0.0318	0.0025	0.0641
96	4.0	6.30	1.15	6.8	4.54	−21.2	6.670	0.0536	0.0102	0.0664

pH because our previous study shows that low initial pH enhances NOM removal [11]. Surface waters in Scandinavia are typically soft and therefore a low amount of acid is required for the pH adjustment.

In this study, three EC cells were constructed. Cells A + C was made of 6 aluminum plates; 3 anodes and 3 cathodes. Cell A was made of aluminum anodes (3 plates) and inert cathodes (3 plates). Cell C was similar to Cell A, but inert plates were used as anodes and aluminum plates as cathodes. Inert electrode material used in this study was commercially available dimensionally stable anode (DSA) electrodes. These electrodes were made of titanium that was coated with a mixed metal oxide layer (iridium and ruthenium oxides). Aluminum alloy 1050 (99.5% Al) was used in the experiments. All electrode plates were 7 cm long and 5 cm wide. Distance between electrode plates was 1 cm. EC treatment was done in batch cells where electrodes were arranged into monopolar configuration. Water volume during the treatment was 500 ml.

GW Instek PSM-6003 was used as a power source throughout the experiments. The current used in this study was 0.100 A. Low current density 0.48 mA/cm^2 was selected on the basis of our previous studies [12]. Treatment time varied from 4 (48 C/l) to 12 min (144 C/l). Electrode plates were washed thoroughly with 4% HCl, tap water, and MilliQ-water after treatments.

Samples were magnetically stirred during the EC treatment at the speed of 300 rpm. After the treatment, samples were stirred with an overhead stirrer at the speed of 40 rpm for 10 min to facilitate flocculation. Settling time after flocculation was 30 min. Water samples were filtered through a glass fiber filter (GF/C Whatman, nominal pore size 1.2 μm) and stored in a cold room before further analysis.

2.2. Chemical analysis

Metal concentrations were determined using iCAP 6000 series ICP-OES (Thermo Electron) from samples in which 0.2 ml of 37% HNO_3 (analytical grade) was added to 10 ml of sample. Dissolved aluminum samples were taken right after electrochemical treatment before slow stirring stage. Residual metals were analyzed

Table 2
The fraction of the variation of the response explained by the model (R^2) and the fraction of the variation of the response predicted by the model according to cross validation (Q^2).

Term	Final pH	Turbidity	Apparent color	TOC	ζ-Potential	Dissolved Al	Residual Al	Residual Fe	Residual Mn
Cell A+C									
R^2	0.98	0.93	0.86	0.93	0.94	0.97	0.98	0.80	0.98
Q^2	0.85	0.53	0.52	0.62	0.70	0.70	0.82	0.57	0.80
Cell A									
R^2	0.99	0.97	0.98	0.96	0.94	1.00	0.98	0.93	0.94
Q^2	0.92	0.75	0.87	0.77	0.71	0.92	0.88	0.77	0.71
Cell C									
R^2	0.96	0.70	0.91	0.93	0.93	0.92	0.96	0.81	0.79
Q^2	0.84	0.12	0.40	0.46	0.58	0.41	0.74	0.43	0.32

Table 3
Coefficients of the model terms (X_1 is electric charge and X_2 is initial pH).

Response	Unit	Constant	X_1	X_2	X_1^2	X_2^2	$X_1{}^*X_2$
Cell A+C							
Final pH		−2.07E+01	−1.55E−02	1.26E+01	5.19E−05	−1.43E+00	2.66E−03
Turbidity[a]	NTU	4.86E−01	−1.05E−02	−1.14E−01	5.70E−05	3.30E−02	1.61E−04
App. Color[a]	PtCo mg/l	1.01E+01	−1.10E−02	−4.15E+00	3.27E−05	5.11E−01	2.50E−04
TOC[a]	mg/l	6.91E+00	−3.80E−03	−2.91E+00	1.03E−06	3.53E−01	2.47E−04
ζ-Potential[b]	mV	−1.09E+00	−3.71E−04	−4.71E−01	5.71E−06	5.53E−02	−1.01E−04
Dissolved Al	mg/l	−2.42E+01	3.62E−02	1.27E+01	3.29E−04	−1.50E+00	7.10E−03
Residual Al[a]	mg/l	3.18E+01	−2.92E−02	−1.56E+01	1.43E−04	1.89E+00	1.66E−04
Residual Fe[c]	mg/l	2.74E+01	−4.79E−02	−1.36E+01	2.22E−04	1.67E+00	−1.34E−03
Residual Mn[a]	mg/l	−1.63E+00	6.25E−03	4.29E−01	−3.54E−06	−8.09E−02	−1.98E−03
Cell A							
Final pH		−2.00E+01	6.94E−03	1.14E+01	2.28E−05	−1.18E+00	−1.45E−03
Turbidity[a]	NTU	1.64E+00	−1.30E−04	−1.03E+00	−2.69E−05	1.51E−01	1.19E−03
App. Color[a]	PtCo mg/l	1.25E+01	−6.42E−03	−5.51E+00	7.98E−06	6.92E−01	1.25E−04
TOC[a]	mg/l	6.23E+00	−4.29E−03	−2.55E+00	8.09E−06	3.14E−01	9.38E−05
ζ-Potential[b]	mV	−1.47E+00	1.42E−03	−3.16E−01	−2.50E−06	3.77E−02	−2.15E−04
Dissolved Al	mg/l	9.77E−01	6.52E−02	−1.79E−01	2.82E−06	1.20E−02	3.03E−03
Residual Al[a]	mg/l	2.86E+01	4.49E−03	−1.48E+01	3.69E−05	1.86E+00	−3.46E−03
Residual Fe[c]	mg/l	1.77E+01	1.84E−02	−9.96E+00	−8.00E−05	1.28E+00	−2.88E−03
Residual Mn[a]	mg/l	3.27E−01	2.58E−03	−5.41E−01	5.45E−06	6.57E−02	−1.41E−03
Cell C							
Final pH		−2.26E+01	9.60E−03	1.27E+01	7.57E−05	−1.32E+00	−4.67E−03
Turbidity[a]	NTU	−6.42E−01	−9.96E−03	5.50E−01	4.79E−05	−5.56E−02	−1.40E−04
App. Color[a]	PtCo mg/l	7.74E+00	−2.78E−02	−2.53E+00	1.29E−04	3.31E−01	−1.39E−03
TOC[a]	mg/l	4.70E+00	−1.44E−02	−1.52E+00	5.73E−05	1.92E−01	−3.43E−04
ζ-Potential[b]	mV	−1.24E+00	3.51E−03	−4.82E−01	−4.27E−06	6.19E−02	−5.77E−04
Dissolved Al	mg/l	3.06E+01	1.79E−01	−1.85E+01	−4.50E−05	2.43E+00	−1.22E−02
Residual Al[a]	mg/l	2.00E+01	6.41E−03	−1.01E+01	1.44E−04	1.31E+00	−1.04E−02
Residual Fe[c]	mg/l	1.43E+01	−5.51E−02	−6.53E+00	3.46E−04	8.52E−01	−5.70E−03
Residual Mn[a]	mg/l	5.18E−01	−4.79E−03	−5.11E−01	4.20E−05	6.02E−02	−1.28E−03

[a] Logarithmic transformation Log 10(Y).
[b] Negative logarithmic transformation –Log 10(100 − Y).
[c] Logarithmic transformation Log 10(Y+0.001).

from samples that were taken after filtration. DOC was measured using TOC analyzer (Shimadzu) after filtering the samples through 0.45 μm pore size membrane.

Apparent color was analyzed with DR 2800 photometer (Hach), and turbidity with Model 2100P ISO turbidimeter (Hach). Conductivity was determined using a CON6 Conductivity Meter (Ecoscan), and pH with Multiline P3 (WTW). Absorbance of the samples at 254 nm wavelength was measured with a Lambda 45 UV/VIS spectrophotometer (Perkin-Elmer), while the zeta potential was determined using a Zetasizer Nano ZS (Malvern).

2.3. Design of experiments and response surface method (RSM)

Factors of the experiments were electric charge added per volume and initial pH. Due to the small number of factors, full factorial design was carried out for three electrochemical cell constructions. Responses included in the model were final pH, turbidity, apparent color, TOC, ζ-Potential, aluminum dissolved, residual aluminum, residual iron, and residual manganese. The experimental design contained 12 tests for each electrochemical cell construction, including the 3 repeating tests at the center point. Three additional tests were conducted using Cells A + C to verify the water quality at the predicted optimum region. The range and levels of the factors and measured values of responses are shown in Table 1.

The first method used in the modeling was partial least squares regression (PLS). PLS is a statistical method that finds the relationship between response variables (matrix Y) and the predictor of factor variables (matrix X). As with other statistical regression methods, such as multiple linear regression (MLR), an equation describing the relationship between the response variable and predictor variables (factors) is gained. The general form of the regression equation including single terms, square terms, and interaction terms is shown in Eq. (5), where Y is the response variable, b are the coefficients of the model, and X are the factor variables.

$$Y = b_0 + \underbrace{\sum_{i=1}^{k} b_i X_i}_{\text{single terms}} + \underbrace{\sum_{i=1}^{k} b_{ii} X_i^2}_{\text{square terms}} + \underbrace{\sum_{i}^{i<j} \sum_{j} b_{ij} X_i X_j}_{\text{interaction terms}} \tag{5}$$

The quality of the regression equation can be evaluated using analysis of variance (ANOVA). However, due to the high number of responses in this study only R^2 and Q^2 are presented for each response in Table 2. R^2 is the amount of variance explained by the model whereas Q^2 is an estimate of the model's predictive ability. Q^2 is calculated by cross-validation. Model terms are presented in Table 3.

3. Results and discussion

3.1. RSM model quality

According to R^2 values of the model responses (Table 2) all models explain the variance of final pH, apparent color, TOC, ζ-Potential, dissolved Al, and residual Al and Fe with high accuracy ($R^2 > 0.8$). Lower R^2 values were obtained for turbidity and residual Mn with Cell C. According to Q^2 values of the model responses, the predictive ability of the model made for Cell C is significantly lower than the predictive ability of the models made for Cells A + C and Cell A. This can be due to the mechanism of aluminum dissolving from the cathodes, which does not behave linearly at the initial stage of the electrocoagulation process.

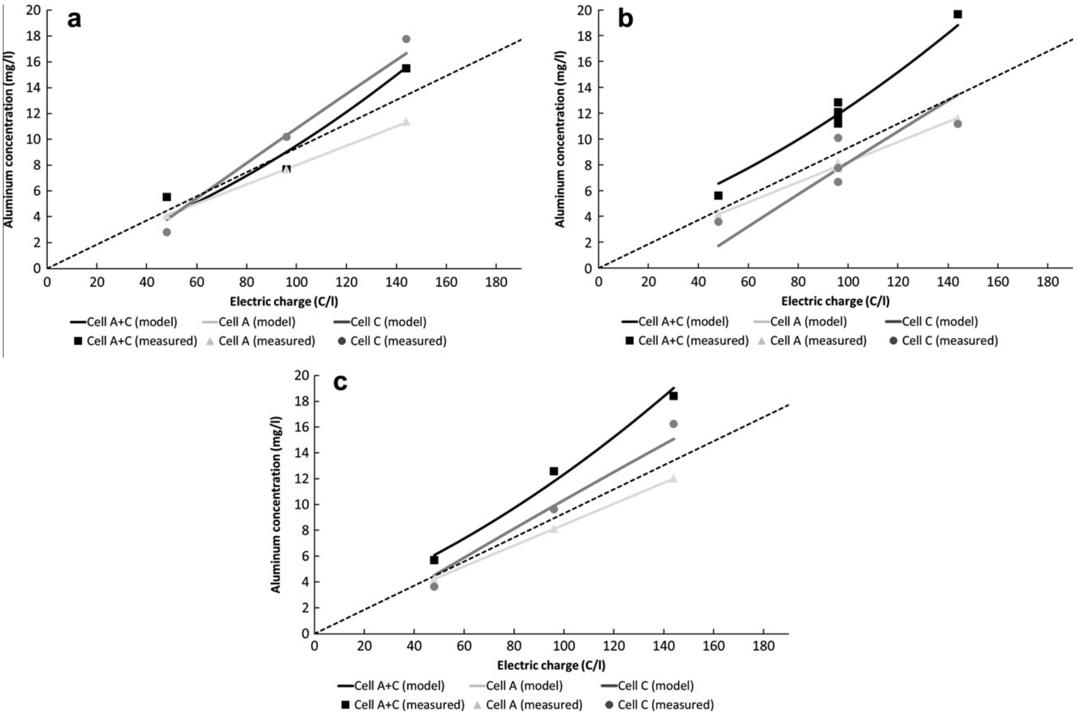

Fig. 1. Measured and predicted (statistical model) dissolving rates of the aluminum electrodes in different electrode constructions in (a) initial pH 3, (b) initial pH 4 and (c) initial pH 5.

3.2. Aluminum dissolved from the electrodes and metal residuals after treatment

Measured and predicted aluminum concentrations of the samples after EC treatment are shown in Fig. 1. The highest aluminum concentrations per electric charge were measured for Cells A + C when initial pH was 4 and 5. However, in initial pH 3 the highest dissolved aluminum concentrations with 96 C/l and 144 C/l were measured for Cell C. It is possible that at very low pH the chemical dissolution of aluminum from all electrode plates (Eq. (6)) occurs simultaneously with Eq. (1).

$$2\mathrm{Al(s)} + 6\mathrm{H}^+ \rightarrow 2\mathrm{Al}^{3+}\mathrm{(aq)} + 3\mathrm{H}_2 \tag{6}$$

There were small variations in the initial delay before the electric current was switched on, but the fact that the electrodes were immersed in the solution or on the metal surface state could explain the difference measured between the aluminum concentrations obtained with Cells A + C and Cell C in pH 3. According to Sasson et al. iron electrodes are significantly corroded without electricity at pH < 8 [22]. In this study, aluminum electrodes were used and dissolution rate of electrodes in the solution without electricity was not measured. However, it is well known that aluminum corrodes when pH is either acidic or alkaline [23]. Aluminum is naturally passive because continuous protecting alumina (Al_2O_3) layer is formed on the surface. This layer protects aluminum efficiently at the pH range 4–8. In higher and lower pH environment, alumina layer dissolves at considerable rate. The corrosion behavior of aluminum depends also on the other parameters of solution, such as the concentration of anions. Sulphate anions are passivating agents and therefore reduce the production of metal cations [24]. Chlorides, on the other hand, induce the breakdown of the passive layer and therefore cause pitting corrosion [23,25]. It is known that passivation and formation of deposits on electrodes increases the voltage of electrocoagulation system when current density is kept constant and hence reduces the power efficiency [1]. However, this was not observed in these short batch studies.

The dissolving of Cell A follows theoretical values calculated according to Faraday's law of electrolysis (Eq. (7)).

$$m = \frac{ItM_w}{zF} \tag{7}$$

where I is the current density, t is the operation time (s), M_w is molecular weight of the substance, F is Faraday's constant (96485 C/mol), z is the number of electrons involved in the reaction (3 for Al^{3+}) and m is the mass of the aluminum dissolved.

When the initial pH was 3, aluminum concentrations dissolved from Cells A + C and Cell C were close to theoretical values (Fig. 1a). With the higher initial pH, theoretical values were different to measured values for Cells A + C and Cell C (Fig. 1b and c). Faraday's law only considers direct electrolysis reactions occurring at the electrodes, e.g. dissolving of aluminum from anodes. The dissolution reaction rate is nearly constant in all cases in the range of variables studied, except in pH 3 with Cells A + C. With initial pH 3 and 4, linear fits of Cell C and Cells A + C results cross the *X*-axis at 0–10 C/l range, whereas linear fits of Cell A cross the *X*-axis almost at the 0 C/l (origin). This indicates that there is a short lag period before aluminum dissolving at the cathodes initiates in low pH. Aluminum cathodes dissolve chemically due to local high pH environment at the electrode surface that is formed when hydroxyl-ions form according to Eq. (3). Hence in low pH environment at the initial stage, hydroxyl ions are consumed by acidic water close the electrode surface which may cause this lag period in acidic solution. It is interesting that the aluminum concentration obtained with Cells A + C is not the sum of concentrations of Cell A and Cell C. It is unclear what mechanism inhibits the dissolving reactions of Cells A + C.

Our results support the conclusion made by Mouedhen et al. [26]. According to their results, no secondary reactions such as oxygen evolution took place at the aluminum anodes. Our results verify that the proportion of side-reaction on the aluminum anodes is low or negligible. Moudhen et al. concluded that chemical dissolution of cathodes contributed significantly to the total amount of aluminum dissolved into solution. Solution pH increased during the treatment. However, in very low pH environment (initial pH 2) the alkalinity produced during by cathodic reaction was not sufficient to increase the pH of the solution. Solution pH 9 was stable during treatment. When the initial pH was very low (pH < 3), less aluminum was produced on the cathode surface. Current density also had a significant influence on the aluminum produced on the cathode surface. The highest current efficiencies were measured with the lowest current densities. Aluminum dissolved from the anode was practically equal to theoretical values and insensitive to current density (in the range tested).

Residual metals can cause problems, such as deposition and process chemical decomposition, in processes where water is consumed. Concentration of residual metals (Al, Fe and Mn) was high in EC treated samples when the final pH of water was low. These metals are highly soluble in acidic and alkaline pH. Neutral amorphous metal hydroxides, such as $Al(OH)_3$ and $Fe(OH)_3$ are poorly soluble species [27]. Minimum solubility for $Al(OH)_3$ and $Fe(OH)_3$ is in neutral to slightly alkaline pH region. In addition to monomeric hydrolysis products, also polynuclear species, e.g. Al_{13} [$AlO_4Al_{12}(OH)_{24}^{7+}$] are formed in water. The formation of the hydrolysis products of Al(III) and Fe(III) are gone through in detail in [27]. Insoluble hydroxides can be removed by sedimentation or filtration. The residual manganese concentration was low in

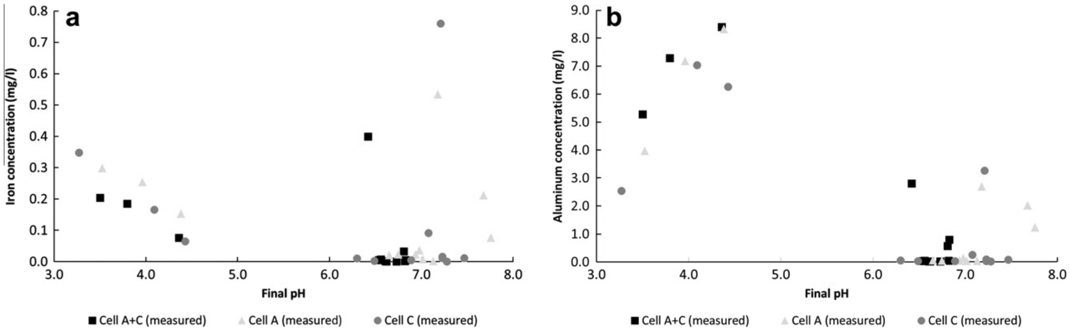

Fig. 2. Measured concentration of residual metals (a) iron and (b) aluminum in the samples after electrocoagulation.

untreated water and was still reduced due to treatment. The lowest manganese concentrations were measured from samples treated with Cells A + C. The lowest residual aluminum and iron concentrations were measured from samples that had high final pH and were treated longer (Fig. 2). High pH and aluminum concentration promote the formation of larger flocs in water, as was visually observed, and therefore more metals were removed from the solution.

According to our results optimum organic matter removal can be obtained simultaneously with minimum residual metal concentrations when acidified surface water is treated with electrocoagulation. This could be a significant benefit of electrocoagulation in surface water treatment compared to chemical coagulation. According to Chow et al. minimum residual aluminum concentration following alum treatment was obtained between pH 6 and 7 whereas optimum DOC removal was obtained at pH 5 [28]. They concluded that optimum DOC removal and minimum residual aluminum concentration cannot be obtained in same pH when alum is used. In electrocoagulation treatment initial pH can be acidic and in these conditions optimum DOC removal occurs. Neutral final pH, on the other hand, is optimum for metal removal because they form insoluble precipitates in these conditions.

3.3. Organic matter removal during treatment

Apparent color and TOC was measured from the samples after the treatment. Color was removed from the water with high efficiency, and the lowest measured color value, 5.4 mg/l PtCo, was obtained with Cell C. According to the results and model, color removal was slightly higher with Cell C than Cell A or Cells A + C. However, all cell constructions were able to remove more than 90% of the color with optimum parameters. Jiang et al. achieved comparable efficiency in their article [8]. According to WHO guidelines for drinking water, drinking water should ideally have no visible color [29]. Levels of color below 15 as true color units (TCO) are acceptable to consumers. However, WHO does not give health-based guideline for color in drinking water.

TOC removal with different cell constructions can be compared when TOC concentration of the samples is presented as a function of aluminum concentration dissolved from the electrodes (Fig. 3). With pH 3, there was no significant effect if the aluminum originated from either the anodes or the cathodes. TOC concentration depended linearly on the aluminum concentration added to the solution. In low pH (typically at pH < 6), the mechanisms of NOM removal are mainly charge neutralization and compression of double layer because hydroxides are not stable in this environment [3,30]. It is interesting that TOC removal did not show any stabilization at low concentrations, and it is possible that even lower TOC concentrations could be achieved with longer treatment times. Models show some errors for this pH, especially with Cell C, which predicts stabilization of TOC concentration at approximately 6 mg/l.

Also, with pH 4 electrode construction did not have a significant effect on the TOC removal per aluminum added. With pH 4, TOC removal was not linear as a function of aluminum, but rather asymptotic, and TOC removal stabilized at approximately 4 mg/l concentration with the cell constructions tested. It seems that aluminum concentrations higher than 8 mg/l were not effective. Final pH was near neutral, and therefore metal hydroxides are the predominant form of aluminum in the solution. Hydroxides form flocs, and sweep coagulation and bridging are the predominant mechanisms of the NOM removal. In adsorption, mechanism charged

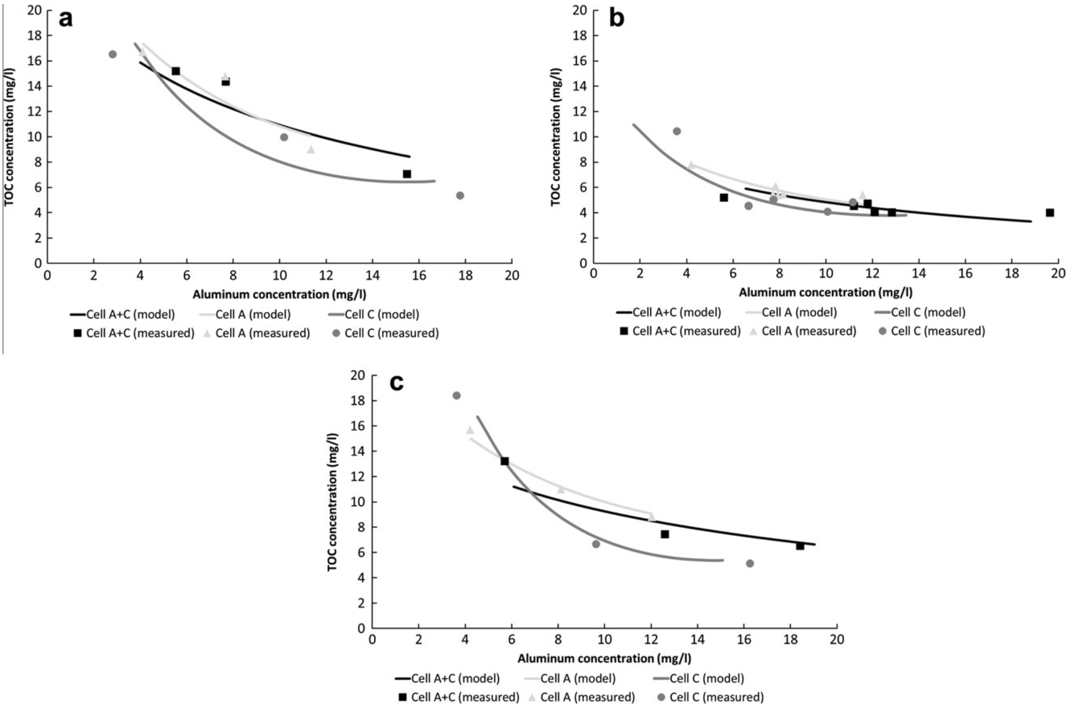

Fig. 3. Measured and predicted (statistical model) TOC concentrations of electrocoagulation treated samples as a function of aluminum concentration dissolved from the electrodes in (a) initial pH 3, (b) initial pH 4, and (c) initial pH 5.

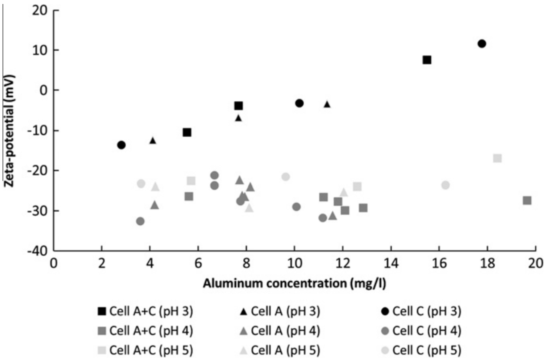

Fig. 4. Measured ζ-Potentials of the samples after electrocoagulation and filtration.

coagulant species are adsorbed onto the particle surface and the effective surface charge is reduced. Bridging mechanism occurs when polynuclear metal hydroxides form bridges between particles, and thus promote the destabilization of NOM. It is likely that residual TOC (4 mg/l) is composed mainly of hydrophilic substances, such as fulvic acids, which are not easily removed in neutral pH [30].

With pH 5, there was more variation in the results of the different cells. Slightly better TOC removal per aluminum added was measured from the samples that were treated with Cell C. However, the efficiency of EC treatment was lower with this pH in all cell constructions when compared to pH 4, and more aluminum was required for the same TOC removal. It also seems that the TOC level stabilizes to a slightly higher TOC level (5 mg/l) than with pH 4 (4 mg/l). It possible that the mechanism of NOM removal changed even further from charge neutralization and double layer compression to adsorption and bridging mechanisms, which were unable to remove hydrophilic colloids from the water.

ζ-Potential of the filtered samples was measured (Fig. 4). These results support the previously mentioned findings. With pH 3, the aluminum has a higher charge (Al^{3+}) due to lack of hydrolysis. This affects NOM destabilization through double layer repression. ζ-Potential in initial pH 3 increased linearly with increasing aluminum concentration. With this pH, small precipitates are formed that are not easily removed with sedimentation, flotation, or filtration. According to ζ-Potential results, it seems that with this pH no specific NOM fraction was enriched to filtered samples. When aluminum concentration was over 12 mg/l ζ-Potential was over 0 mV, which may cause restabilization of colloids. ζ-Potentials of the samples with initial pH 4 and 5 were similar after filtration. In these pH's aluminum exists predominantly as hydroxides and easily settleable or filterable flocs are formed. It seems that highly charged, and probably hydrophilic, NOM fraction was enriched into the samples during the treatment. According to ζ-Potential results, the same NOM fractions were removed whether aluminum was dissolved from the anodes or the cathodes. However, this should be verified with research where composition of the remaining NOM fraction is studied.

Three additional tests were done with optimum parameters of Cell C (Table 4). The initial pH in these tests was 4.1 and the electric charge per volume was 115 C/l. Results were similar to results at the center point of the mode, which was expected because the factor values were close to each other. The model predicts a TOC value of 4.04 mg/l, which is slightly lower than the measured value. The predicted final pH was 7.1, which is slightly higher than the measured value. The predicted aluminum concentration dissolved from the electrodes was 9.97 mg/l, whereas the measured aluminum concentration was 7.90–9.52 mg/l. Turbidity, color, and residual metal concentrations were close to predicted values. According to the results of these verification tests, the model predicts water quality parameters with high accuracy.

4. Conclusions

This study analyzed the effect of electrocoagulation cell construction on NOM removal. Three types of cells were studied: one that only had aluminum electrodes, one that had aluminum anodes and inert cathodes, and one that had inert anodes and aluminum cathodes. Besides the TOC concentration of the water, the other main parameters measured were final pH, turbidity, color, and concentration of residual metals of the water produced. A model was made from the results of each cell construction using PLS regression. The model quality was high for the most of the responses. The following conclusions can be made from the results:

- Aluminum dissolved from the Cells A + Chat was constructed from aluminum anodes and inert cathodes followed theoretical values calculated according to Faraday's law.
- Aluminum dissolved from the cathodes did not follow electric charge per volume linearly. Low initial pH (pH 3) decreased the dissolving reaction rate, probably because the hydroxyl ions produced were consumed by the acidic water.
- Low residual metals concentrations (Al, Fe, Mn) were measured from the samples when the final pH was high and treatment time was long and hence aluminum concentration was high.
- The efficiency of aluminum in TOC removal was similar in all cell constructions in the pH range tested. According to these results, the efficiency of electrocoagulation cannot be enhanced significantly by using either aluminum anodes or cathodes or both. High TOC removal was measured with all constructions tested.
- When the initial pH was 3, the TOC concentration of the treated samples depended linearly on aluminum added to the solution. In pH 4 and 5, the TOC removal per added aluminum followed asymptotic regression. This is probably due to the transition of the destabilization mechanism of colloids from double layer compression to adsorption and bridging. This conclusion was supported by the ζ-Potential results.

The results of this research indicate that reactions between NOM and aluminum occur in the bulk water and not on the electrode surface. It seems that destabilization mechanisms of NOM are similar compared to chemical coagulation. According to our results, optimum organic matter can be obtained simultaneously

Table 4
Measured water quality parameters of the samples from the additional repeating tests. Initial pH was 4.1 and electric charge per volume was 115 C/l.

Responses							
Final pH	Turbidity (NTU)	Apparent color (mg/l PtCo)	TOC (mg/l)	Dissolved Al (mg/l)	Residual Al (mg/l)	Residual Fe (mg/l)	Residual Mn (mg/l)
5.95	0.92	6.1	4.61	7.904	0.0518	0.0018	0.0187
6.39	1.22	7.3	4.48	9.520	0.0235	0.0024	0.0210
6.29	1.09	6.6	4.29	8.357	0.0184	0.0015	0.0228

with minimum residual metal concentrations when surface water is treated with electrocoagulation. The potential applications of water after the treatment could be potable water or industrial fresh water.

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