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Removal of total organic carbon from peat solution by hybrid method – electrocoagulation combined with adsorption

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Abstract

Humic substances end up in water from the drainage basin causing eutrophication and the spread of algae. These natural organic substances have an influence on the physical, chemical and biological properties of the water system. Adsorption and electrocoagulation (EC) are commonly used purification methods in the water and wastewater treatment. Both methods are used by themselves for removing a wide range of impurities. In this research, the novelty was to study the effect of combined activated carbon (AC) adsorption and electrocoagulation method on the removal of organic substances as total organic carbon (TOC) from the peat solution. With the hybrid method, TOC content was efficiently removed (~95 %) by using first adsorption treatment followed by electrocoagulation with Al- or Fe -electrode. Instead, when using the adsorption and electrocoagulation separately, the removal of TOC was 79-89 %. Based on this study, the hybrid method could be efficiently used for removing organic substances from the water system.

Keywords: Humic acid removal, Electrocoagulation, Activated carbon, Adsorption, Water treatment

Highlights

- Efficient removal of humic substances, measured as TOC from an aqueous solution made from peat
- Activated carbon derived from lignocellulosic residue biomass was used as an adsorbent
- Most efficient method to remove organics was to use adsorption followed by electrocoagulation

1. Introduction

Humic substances are organic, high molecular weight, natural polymers and originate from the decomposition of organic substances. Organic substances come to the water from drainage basins and from water system itself. The toxic algae and microorganisms utilize inorganic and organic nutrients of humic substances in the water. Humic substances have an impact on the toxicity of heavy metals and organic pollutants forming complexes with many toxic substances. [1–4]

Humic substances occur in water as insoluble form, colloidal form and solid form. Humic substances are complex organic substances that vary from light brown (fulvic acids) to black (humins) in color. They consist of three groups of heterogeneous organic polymers: humic acids, fulvic acids and humin substances. Humic acids are alkali-soluble and fulvic acids are both alkali and acid soluble whereas humin substances are either alkali or acid soluble [5]. Humic acids are the most abundant fraction of humic substances in soil. Humic acids have various functional groups, such as carboxylic, alcoholic and phenolic groups and in a random way arranged aromatic rings [6]. These groups provide a number of potential binding sites for metal ions, for example, chlorinated organic compounds, which are toxic disinfection byproducts [7–9].

Electrocoagulation (EC) is an old but growing water and wastewater treatment method. Contaminants that can be removed by electrocoagulation are for example heavy metals [10,11], pharmaceuticals and antibiotics [12,13] and organic pollutants e.g. herbicides, phenols, textile dyes [14–17]. The electrocoagulation reactor is an electrochemical cell, which has two electrodes, an anode as a sacrificial metal, and cathode. Aluminum and

51 iron metals are typically used as anode metals. Electrocoagulation generates metal ions from a sacrificial
52 anode (Eq.1). The metal ions from the anode spontaneously hydrolyze in water forming various coagulant
53 species (Eq.2). These coagulant species agglomerate together forming larger particles by coagulation [18,19].
54 The purpose of coagulation is to destabilize particles by coagulant chemicals and enable them to become
55 attached to other particles. Aluminum and iron salts hydrolyze in the water forming insoluble precipitates, which
56 destabilize the charge of particles by adsorbing onto their surface. There are repulsive forces between the
57 particles because they have similar electric charge, usually negative. The hydrolyzed products have positive
58 electric charge.



64 Electrolytically formed gases, mainly hydrogen, are generated on the surface of the cathode (Eq.3). During
65 beneficial side reactions, gas bubbles are generated which promotes flotation. These agglomerated pollutants
66 form larger agglomerates, which rise upwards to be removed in the subsequent process. The electrochemical
67 reduction may take place on the cathode (Eq.4). [20,21]

68 Activated carbons (AC) are widely used in different industrial water purification processes as adsorbents
69 because of its high surface area and well-developed porous structure [22–28]. Adsorption has been considered
70 as one of the most economically viable techniques for water treatments and AC is the most widely used
71 adsorbent. Typically ACs have been prepared from carbonaceous materials e.g. coal. As an alternative eco-
72 friendly and low-cost raw material, AC can be prepared from residual or waste biomass materials [29–33]. For
73 the preparation of AC, thermal procedures including carbonization and activation are used. AC has been
74 proven as an effective adsorbent for the removal of a wide range of organic and inorganic pollutants dissolved
75 in aqueous media. During the adsorption, dissolved species diffuse into the pores of adsorbent. Because
76 adsorption takes place on the surface, a large surface area and a high number of pores are necessary for
77 adsorbent. With high porosity, adsorbents can have a pore volume of 0.1 to 0.8 mL g⁻¹ and a surface area
78 ranging from ~700 to 1500 m² g⁻¹. As a result, the adsorption capacity can be as high as 0.2 g of adsorbate
79 per gram of adsorbent, depending on the adsorbate concentration and type [21,34]. The size of the adsorbate
80 that can enter a pore is limited by the size of the pore. In the case of humic acids when adsorbate is a large
81 organic molecule, meso- and macroporous (pore diameter > 2 nm) structure of activated carbon is favored
82 [35]. Even though AC has a large market as an adsorbent in water treatment processes, the specific adsorption
83 mechanisms for solutes containing organic and inorganic material are still not clear [36].

84 In this paper, the removal of organic substances has been studied by a hybrid method: electrocoagulation
85 combined with adsorption. This kind of experiment setup hasn't been studied before in removal of organic
86 molecules from waste waters. As an electrocoagulation material, iron and aluminum have been used and the
87 process was optimized for the reaction. As an adsorbent material activated carbon (forest-residue-based
88 spruce from Finland) has been used. The removal of total organic carbon has been studied with separate
89 adsorption or electrocoagulation methods and compared to the hybrid method. In the hybrid method, a
90 combination of adsorption and electrocoagulation has been tested in the order a) electrocoagulation followed
91 by adsorption and b) adsorption followed by electrocoagulation.

92

93 **2. Materials and methods**

94

95 **2.1 Raw materials**

96 Peat obtained from Northern Finland has been used in the preparation of an aqueous solution containing humic
97 material, activated carbon derived from residue fractions of lignocellulosic biomass; sawdust of spruce.
98

99 **2.2 Methods**

100 **2.2.1 Preparation of activated carbons**

101 The dried and sieved lignocellulosic biomass was carbonized and steam activated in a one-step process in a
102 rotating quartz reactor (Nabertherm GmbH RSRB 80). The thermal process was divided into two parts: the
103 first carbonization step, in which the temperature was raised to 800 °C, followed by the activation step. During
104 the activation, the temperature was kept at 800 °C for 120 min with a stream of steam, for the proper surface
105 activation. During the whole process, the reactor was flushed with an inert gas, N₂. Prepared AC was sieved
106 to particle size to 0.4-2.0 mm. By using Micromeritics ASAP 2020, the resulting AC was characterized by the
107 specific surface area and pore size distribution under isothermal conditions. Specific surface areas were
108 calculated from adsorption isotherms according to the BET method [37] and pore size distributions were
109 calculated using the BJH algorithm [38].

110 **2.2.2 Total carbon determination**

111 The content of carbon present in AC, given as total carbon (TC) percent, was measured using a solid phase
112 carbon analyzer (Skalar Primacs MCS). Dried samples were weighted in quartz crucibles, combusted at 1100
113 °C in an atmosphere of pure oxygen and the formed CO₂ was analyzed by an IR analyzer. Carbon content
114 values were obtained by reading the signal of IR analyzer from a calibration curve derived from known masses
115 of a standard substance, oxalic acid. The total mass of carbon was calculated as a percent of the mass initially
116 weighted and was measured after the carbonization and activation step. The content of organic carbon present
117 in each sample (± 5%), given as total carbon (TC) mg L⁻¹, was measured using a liquid phase carbon analyzer
118 (Skalar Primacs MCS). TC (Total carbon), TOC (Total organic carbon) and IC (Inorganic carbon) could be
119 determined with the method.
120

121 **2.2.3 Adsorptive properties**

122 The formed AC's adsorption properties were tested with the adsorption capacity of total organic carbon. A
123 solution containing a known amount of TOC was prepared, 50 mL of this solution was transferred into
124 Erlenmeyer flask with a defined amount of activated carbon and the solution was continuously agitated for 24
125 hours in order to achieve equilibrium between adsorption and desorption of the organic material. Portions of
126 each solution were filtered and, if needed, diluted, and the concentration of TC, TOC and IC was measured
127 with TOC analyzer. The adsorbed mass was calculated using Eq(5) and the percent removed was calculated
128 using Eq(6)
129

$$130 \quad (ads) = (C_0 - C_t) \cdot \frac{V}{m} \quad (5)$$

$$132 \quad \% \text{ removed} = \frac{C_0 - C_t}{C_0} \quad (6)$$

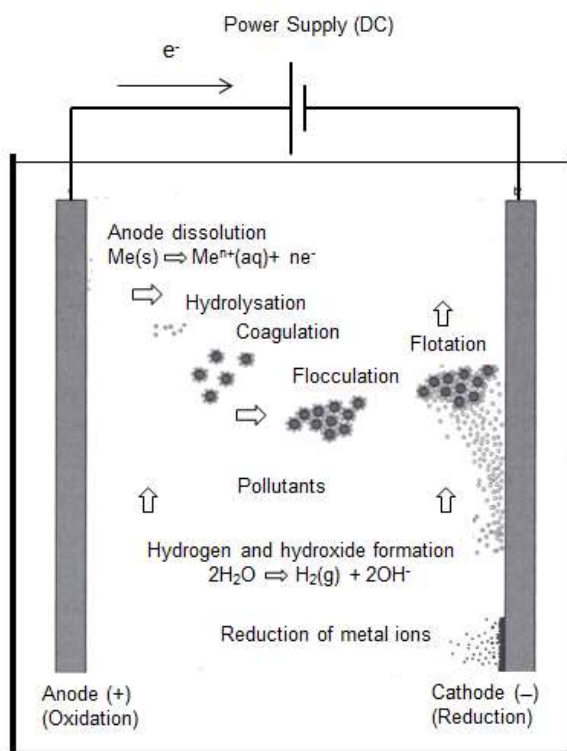
133
134 Where C_0 is initial concentration (mg L⁻¹), C_t is measured concentration after 24 h, V is the volume of the
135 solution used and m is a mass of the activated carbon used.
136

137 **2.2.4 Metal content**

138 Metal contents of samples were measured by inductively coupled optical emission spectrometry (ICP-OES)
139 using a Perkin Elmer Optima 5300 DV ICP-OES instrument. 0.10–0.12 g samples were added to 63 % nitric
140 acid and hydrogen peroxide, then digesting in a microwave oven (MARS, CEM Corporation) at 200 °C for 10
141 min. After digestion, the solution was diluted to 50 mL and measured by ICP-OES.
142
143
144

145 **2.3 Optimization of distance between anode and cathode**

146 Aluminum and iron metals were used as an anode and stainless steel (SS) was used as the cathode. Electrode
 147 plate dimensions were 50x50x10 mm. Electrodes were connected a laboratory electrical source (Tektronix DC
 148 Power Supply; 32V, 6A) and adjusted at 2 V and 1 A. The voltage was kept constant during the experiments.
 149 The distance between electrodes varies from 5 mm to 20 mm. During the coagulation experiments, the
 150 electrodes were completely immersed in the sample solution. Prior to experiments, both electrodes were
 151 cleaned with 1 M nitric acid, tap water and distilled water and finally, dried at 105 °C. Anode plates were
 152 weighted before and after EC experiments, which led to the discovery of the mass of dissolved anode metal.
 153 The number of metal cations dissolved during the electrocoagulation can be calculated according to Faraday's
 154 law. The experiments were carried out using 5 mm, 10 mm and 20 mm distance between anode and cathode.
 155 Figure 1 illustrates a schematic diagram of the electrocoagulation.

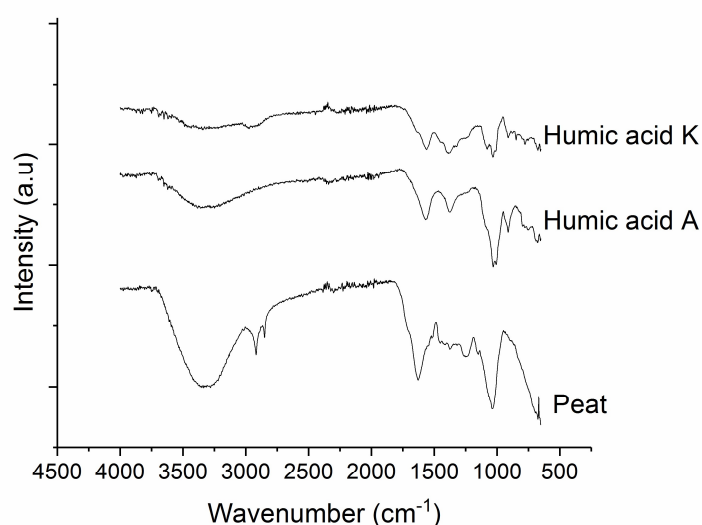


171 **Fig.1.** A schematic diagram of the electrocoagulation (adapted from [20]).

172 Suspension, 50 g L⁻¹ was prepared from air dry peat. The suspension was stirred for 24 hours, by which time
 173 humic substances dissolved from peat to water. The suspension was filtered through Whatman 4 (20 – 25 μm)
 174 filter paper. NaCl was added to the formed solution to ensure sufficient electrical conductivity (3.0 mS cm⁻¹).
 175 The initial pH value was 6.0 and initial temperature was 22 °C. Before experiments, the amount of TC (Total
 176 carbon), TOC (Total organic carbon) and IC (Inorganic carbon) content were measured. Almost all carbon
 177 occurred in the form of organic carbon (96.0 %), which are humic substances. Only 4.0 % occurred in the form
 178 of inorganic carbon. During electrocoagulation, the solution was stirred with magnetic stirrer. The speed of
 179 rotation of the magnetic stirrer was kept at 200 rpm. The voltage was kept as constant, 2V. Samples were
 180 taken at fixed-term intervals to measure the TC content of the solution. TC content was measured using a
 181 liquid phase carbon analyzer Skalar Primacs MCS.

183 3. Results and discussion

184 The prepared solution from peat was compared with commercial humic acids (Fig 2.) with Perkin-Elmer
 185 Spectrum One FT-IR Spectrometer and the main peaks from spectrum at area 1030 cm⁻¹, 1370 cm⁻¹, 1550
 186 cm⁻¹ and 3300 cm⁻¹ were found from all samples.



187

188 **Fig.2.** IR-spectrum showing the curves of the peat used, of humic acid powder (Humic acid K) and of the
 189 industrial peat from Aldrich (Humic acid A).

190 Properties of the prepared activated carbon from spruce were analyzed with N₂-physisorption. The BET
 191 surface area of AC was 785 m² g⁻¹ with pore volume 0.46 cm³ g⁻¹ and composed mainly from mesopores (82
 192 %) according to BJH method (Table 1). The high amount of mesoporous structure is important when big
 193 particles like organic molecules are wanted to adsorb into the internal surface of AC. In this case, over 80% of
 194 the porous structure was mesopores, concluding that the prepared activated carbon was suitable for
 195 adsorption of organic molecules. The total carbon content of AC was analyzed with TC and was 92 % (Table
 196 2). The inorganic material in AC was studied with ash determination method [39] and content of ash was 2.6
 197 %, which is relatively low, compared to commercial ACs. Moreover, ICP-OES analyze showed the composition
 198 of metals in the AC (Table 2) and most prevalent metals in AC seemed to be calcium and potassium. According
 199 to these results, it was assumed that no interfering metals from AC material were present in the study or the
 200 amounts were really low.

201

202 **Table 1**

203 The surface area, pore volume, pore size and pore volume distribution of the prepared AC.

Sample	BET		BJH				
	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Total volume (cm ³ g ⁻¹)	Micro d<2nm (%)	Meso 2< d<50 (%)	Macro d>50 nm (%)
AC	785	0.46	2.36	0.28	17.9	82.1	0.0

204

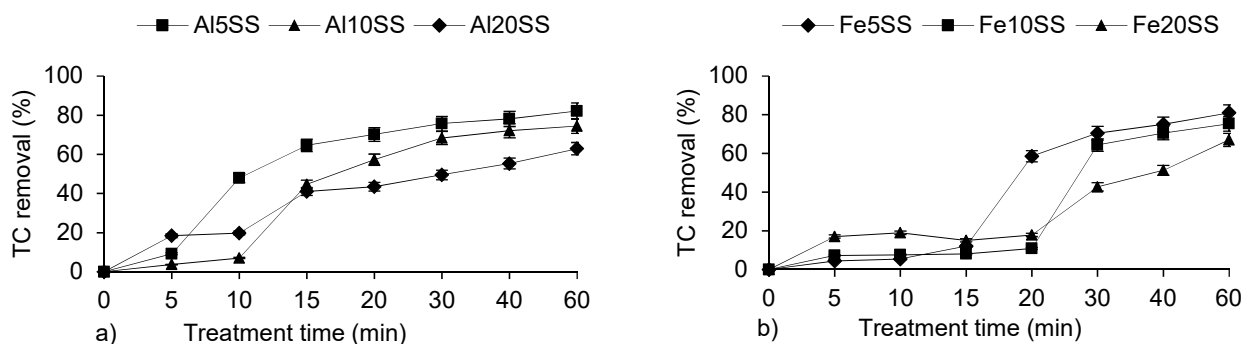
205 **Table 2**

206 Total carbon (TC), inorganic material (ash) content and metal content (ICP-OES) from AC-spruce.

Sample	TC (wt.%)	Ash (wt.%)	Ca (wt.%)	K (wt.%)	Mg (wt.%)	Na (wt.%)	Fe (wt.%)
AC	92	2.6	0.42	0.25	0.06	<0.01	<0.01

207

208 From optimization of electrodes, results showed that the best TC reduction (82.1 %) was achieved when the
 209 distance between the aluminum anode and stainless steel cathode was 5 mm. The worst TC reduction (62.9
 210 %) occurred when the distance between the aluminum anode and stainless steel cathode was 20 mm.
 211 Concerning both aluminum anode and an iron anode, the bigger the distance between electrodes the worse
 212 the TC reduction was (Fig. 3). It was found that the ranking order of electrocoagulation experiments was
 213 following: Al5SS > Fe5SS > Fe10SS > Al10SS > Fe20SS > Al20SS. The current density decreased when the
 214 distance between electrodes increased. All results are shown in Table 3.



215

216 **Fig.3.** Effect of electrode distances between a) aluminum anode and stainless steel cathode b) iron anode and
 217 stainless steel cathode on the removal of TC content from peat solution.

218 **Table 3**

219 The parameters of optimization of distance between anode and cathode.

Anode material	Distance anode/cathode (mm)	Voltage (V)	Current (A)	Current density (A m ⁻²)	TC removal efficiency (%)	Practical anode loss (mg)	Theoretical anode loss (mg)
Al	5	2	0.21	80	82.1	126	69.5
"	10	2	0.13	50	74.5	74.4	42.6
"	20	2	0.08	30	62.9	41.2	25.9
Fe	5	2	0.16	60	81.0	250	162
"	10	2	0.10	40	75.4	160	98.9
"	20	2	0.07	25	67.0	71.4	70.7

220

221 These optimizing studies showed that the distance between electrodes has to be 5 mm in the hybrid method.
 222 The hybrid method means that first electrocoagulation is carried out, after that adsorption, and vice versa. At
 223 the beginning of the experiments, the aluminum and iron contents were at the very low level and also after the
 224 experiments. It showed that all aluminum and iron from the sacrificed anodes were removed to the precipitation
 225 (Table 4).

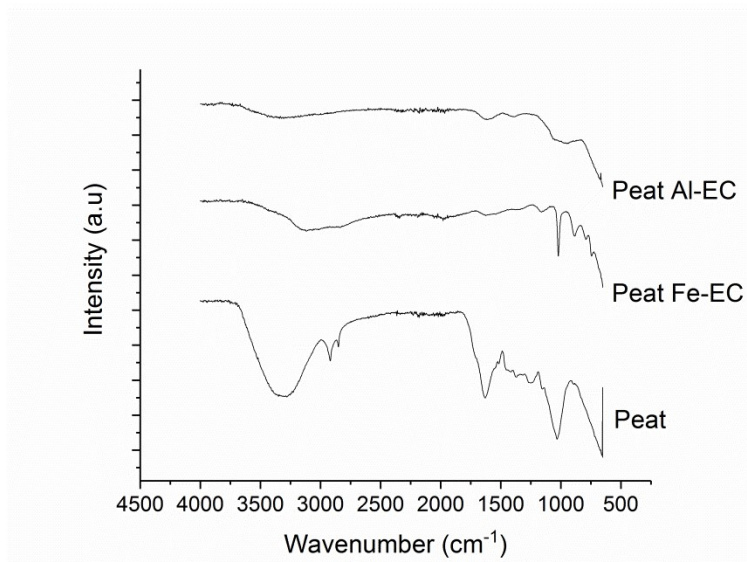
226 **Table 4**

227 The metal content in the peat solution (TC 500 mg L⁻¹) at the beginning and after the electrocoagulation
 228 experiment and metal residue in the precipitate after experiment.

Solution				Precipitate	
Al _{initial} (mg g ⁻¹)	Al _{final} (mg g ⁻¹)	Fe _{initial} (mg g ⁻¹)	Fe _{final} (mg g ⁻¹)	Al _{final} (%)	Fe _{final} (%)
<0.1	<0.1	1.8	0.2	136	168

229

230 Removal of TC after 60min EC was verified also with IR and results showed that humic substances were
 231 removed efficiently with an aluminum and iron electrode when the distance between electrodes was 5mm.
 232 From the spectrum (Fig. 4) changes with different peaks could be detected. Notable changes were at area
 233 1030 and 1370 cm^{-1} (C-O stretching), 1550 cm^{-1} (C=C stretching from aromatic rings), 2850 and 2900 cm^{-1} (C-
 234 H stretching) and 3300 cm^{-1} (OH stretching). Peaks around 1550 cm^{-1} , 1370 cm^{-1} might also indicate to N-
 235 structures. Some organic compounds were still showing presence after EC at the area 700-1100 cm^{-1} .



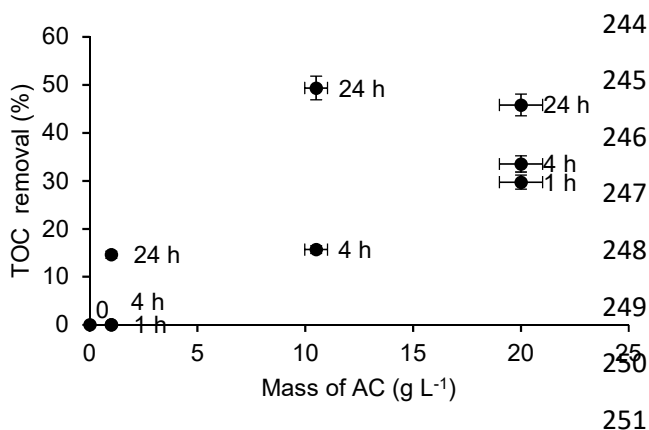
236

237 **Fig.4.** IR spectrums of peat before and after 60 min electrocoagulation with aluminum and iron electrode.

238

239 From optimization of adsorption with activated carbon, results showed (Fig 5.) that the most effective TOC
 240 removal was achieved when the amount of AC was 10 g L^{-1} and the adsorption time was 24 hours. Therefore,
 241 the 24 h adsorption test was chosen to be used in adsorption tests with AC loading 10 g L^{-1} . In this study, no
 242 further kinetic studies were performed.

243



252 **Fig.5.** Total organic carbon removal by adsorption using AC 1, 10 or 20 g L^{-1} and adsorption time 1, 4 or 24
 253 hours.

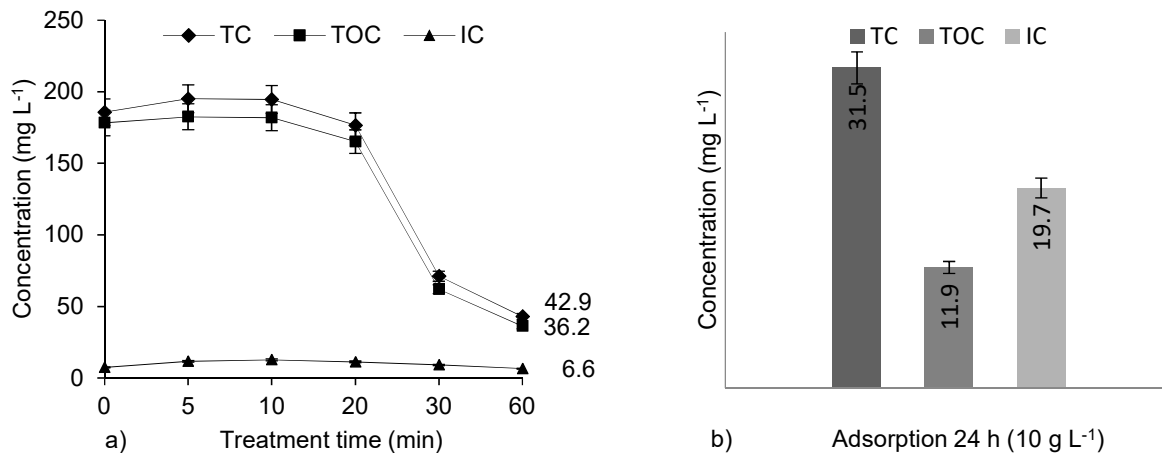
254

255 3.1 Comparing electrocoagulation/adsorption and adsorption/electrocoagulation experiments

256 As previously discussed, the optimal distance between electrodes was chosen for 5 mm. With the use of the
 257 aluminum electrode as anode reduced the concentration of TC from 185.6 mg L^{-1} to 42.9 mg L^{-1} and TOC from

258 178.2 mg L⁻¹ to 36.2 mg L⁻¹ after 60 min electrocoagulation experiment (Fig. 6a). After electrocoagulation
 259 experiment, a 24 h adsorption was carried out with the use of AC 10 g L⁻¹ as adsorbent (Fig. 6b). The adsorption
 260 enhanced the concentration of TOC to 11.9 mg L⁻¹, giving the total reduction of TOC 93.3 %. Instead, IC value
 261 was increasing after 24-hour adsorption, most likely from the increase of carbon dioxide in solution.

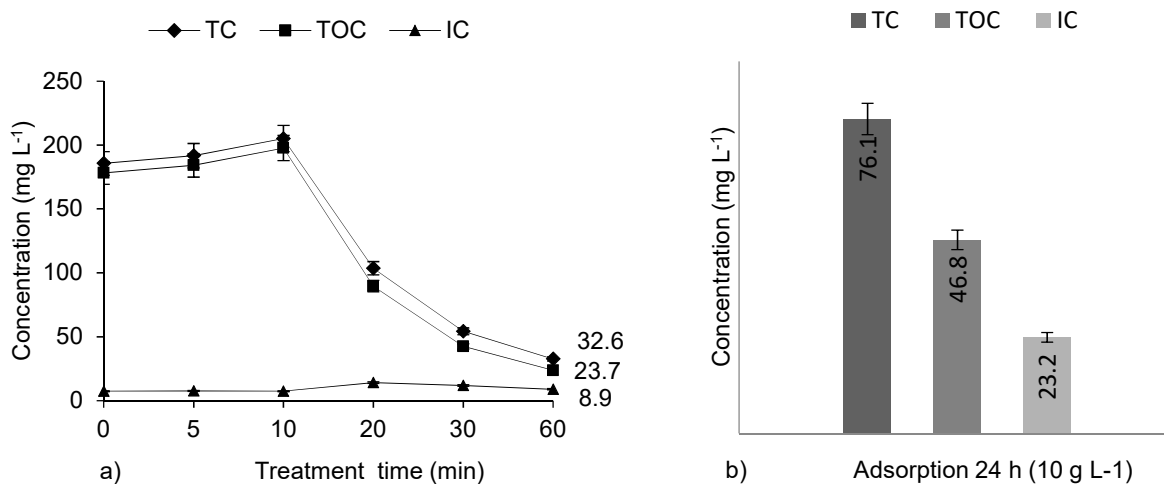
262



263 **Fig.6.** Total carbon (TC), total organic carbon (TOC), inorganic carbon (IC) concentration after (a) 60 min
 264 electrocoagulation experiment with aluminum electrode followed by (b) 24-hour adsorption experiment with
 265 AC load of 10 g L⁻¹.

266

267 With the use of the iron electrode as anode reduced the concentration of TC from 185.6 mg L⁻¹ to 32.6 mg L⁻¹
 268 and TOC from 178.2 mg L⁻¹ to 23.7 mg L⁻¹ after 60 min electrocoagulation experiment (Fig. 7a). After
 269 electrocoagulation experiment, a 24 h adsorption was carried out with the use of AC 10 g L⁻¹ as adsorbent
 270 (Fig. 7b). In this case, the adsorption increased the concentration of TOC to 46.8 mg L⁻¹ and IC from 8.9 to
 271 23.2 mg L⁻¹. This could be due carbon leaching from the adsorbent.



272 **Fig.7.** Total carbon (TC), total organic carbon (TOC), inorganic carbon (IC) concentration after (a) 60 min
 273 electrocoagulation experiment with iron electrode followed by (b) 24-hour adsorption experiment with AC load
 274 of 10 g L⁻¹.

275

276 Since almost all humic acids are present in solution as organic carbon, the TOC value was used when the total
 277 removal of carbon was studied. With the use of the iron electrode, the total organic carbon removal was more
 278 efficient than with aluminum electrode and the results are presented in Table 5. Moreover, a better result in
 279 the removal of TOC was achieved with a combination of Al-electrocoagulation followed by adsorption giving
 280 the total TOC removal 93.3 %. Instead, with the combination of Fe-electrocoagulation followed by adsorption
 281 TOC removal was 73.7 %.

282

283 **Table 5**

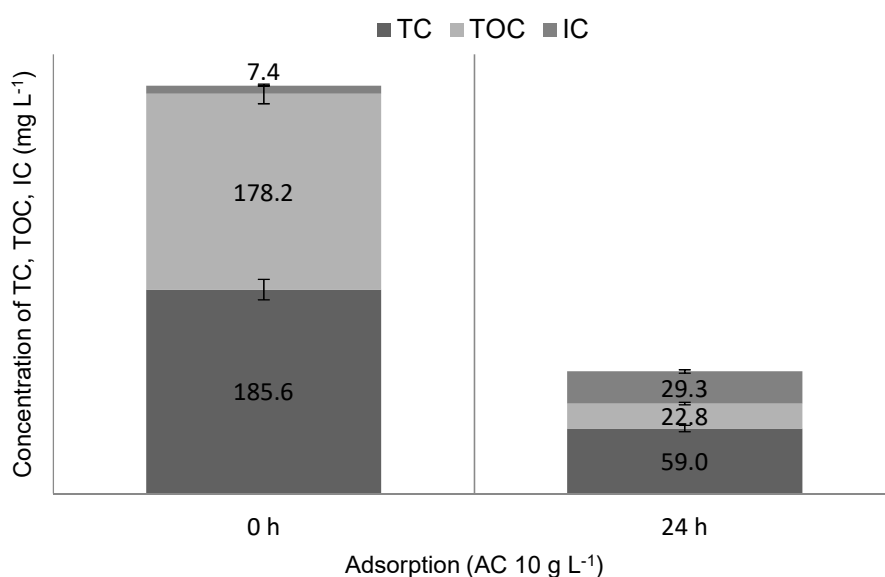
284 Total organic carbon (TOC) removal percent from peat solution by electrocoagulation (Al or Fe) followed by
 285 24-hour equilibrium adsorption with 10g L⁻¹ of AC.

TOC removal by Al-EC (%)	TOC removal by adsorption after Al-EC (%)	TOC removal by Fe-EC (%)	TOC removal by adsorption after Fe-EC (%)
79.7	93.3	86.7	73.7

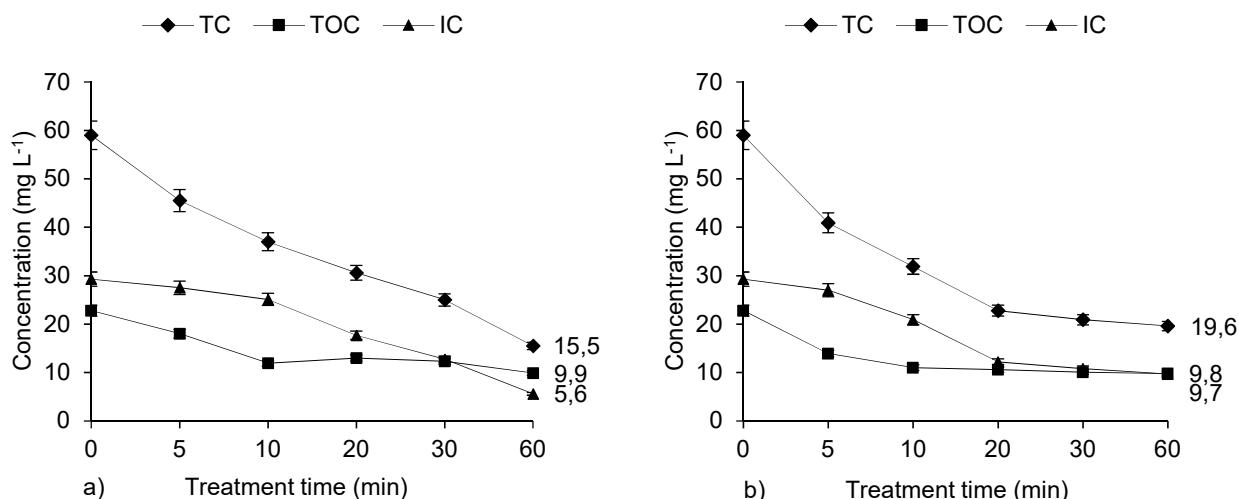
286

287 After 24 h equilibrium adsorption, (Fig. 8) with the use of 10 g L⁻¹ activated carbon, the concentration of TOC
 288 was reduced from 178.2 to 22.8 mg L⁻¹ by giving the 89.9 % TOC reduction. Also, in this case, the concentration
 289 of IC was increased from 7.4 to 29.3 mg L⁻¹. When continuing the reduction by electrocoagulation, the
 290 concentration of TOC decreased to around 9.9 mg L⁻¹ with both aluminum and iron electrode (Fig. 9).
 291 Moreover, with the use of the aluminum electrode, the IC content was reduced to minimum 5.6 mg L⁻¹. With
 292 adsorption followed by electrocoagulation, the total reduction of TOC was almost the same for both electrodes,
 293 ~94.5 % (Table 6).

294



306 **Fig.8.** The concentration of total carbon (TC), total organic carbon (TOC) and inorganic carbon (IC) after 24-
 307 hour adsorption with activated carbon 10 g L⁻¹.



308
 309 **Fig.9.** a) Electrocoagulation experiment with the aluminum electrode and b) electrocoagulation experiment
 310 with iron electrode performed after 24 h adsorption with AC 10 g L⁻¹.

311

312 **Table 6**

313 Total organic carbon (TOC) removal from peat solution by 24-hour equilibrium adsorption with 10g L⁻¹ of AC
 314 followed by electrocoagulation with Al- or Fe- electrode.

TOC removal by adsorption (%)	TOC removal by Al-EC after adsorption (%)	TOC removal by Fe-EC after adsorption (%)
89.9	94.4	94.5

315

316

317

318 4. Conclusions

319 In this study, the removal of total organic carbon from aqueous peat solution was performed by using
 320 electrocoagulation with aluminum or iron electrode combined with adsorption by activated carbon prepared
 321 from lignocellulosic residual biomass. With the optimized hybrid method, the total organic carbon (TOC)
 322 content was removed efficiently, about 95 % from peat solution by using first adsorption treatment followed by
 323 electrocoagulation. Moreover, the TOC removal was the same for both Al- (94.4 %) and Fe (94.5 %) electrodes
 324 after adsorption. Instead, when using the adsorption or electrocoagulation method one at the time the removal
 325 was between 79-89 %. As a conclusion the removal of total organic carbon from peat solution by the hybrid
 326 method: activated carbon adsorption combined with Al/Fe- electrocoagulation approved a good method for
 327 removing organic matter from aqueous solution.

328

329

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332

333

334

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336

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