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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

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

$$M(s) \rightarrow M^{n+}(aq) + ne^{-} \quad (1)$$

$$M^{m+}(aq) + nH_2O \rightarrow M(OH)_n^{m-n} + nH^{+}(aq) \quad (2)$$

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

$$M^{n+}(aq) + ne^{-} \rightarrow M^{o}(s) \quad (4)$$

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

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

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

## 2. Materials and methods

### 2.1 Raw materials

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

## 2.2 Methods

### 2.2.1 Preparation of activated carbons

The dried and sieved lignocellulosic biomass was carbonized and steam activated in a one-step process in a rotating quartz reactor (Nabertherm GmbH RSRB 80). The thermal process was divided into two parts: the first carbonization step, in which the temperature was raised to 800 °C, followed by the activation step. During the activation, the temperature was kept at 800 °C for 120 min with a stream of steam, for the proper surface activation. During the whole process, the reactor was flushed with an inert gas, $N_2$. Prepared AC was sieved to particle size to 0.4-2.0 mm. By using Micromeritics ASAP 2020, the resulting AC was characterized by the specific surface area and pore size distribution under isothermal conditions. Specific surface areas were calculated from adsorption isotherms according to the BET method [37] and pore size distributions were calculated using the BJH algorithm [38].

### 2.2.2 Total carbon determination

The content of carbon present in AC, given as total carbon (TC) percent, was measured using a solid phase carbon analyzer (Skalar Primacs MCS). Dried samples were weighted in quartz crucibles, combusted at 1100 °C in an atmosphere of pure oxygen and the formed $CO_2$ was analyzed by an IR analyzer. Carbon content values were obtained by reading the signal of IR analyzer from a calibration curve derived from known masses of a standard substance, oxalic acid. The total mass of carbon was calculated as a percent of the mass initially weighted and was measured after the carbonization and activation step. The content of organic carbon present in each sample (± 5%), given as total carbon (TC) mg $L^{-1}$, was measured using a liquid phase carbon analyzer (Skalar Primacs MCS). TC (Total carbon), TOC (Total organic carbon) and IC (Inorganic carbon) could be determined with the method.

### 2.2.3 Adsorptive properties

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

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

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

Where $C_0$ is initial concentration (mg $L^{-1}$), $C_t$ is measured concentration after 24 h, $V$ is the volume of the solution used and $m$ is a mass of the activated carbon used.

### 2.2.4 Metal content

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

## 2.3 Optimization of distance between anode and cathode

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

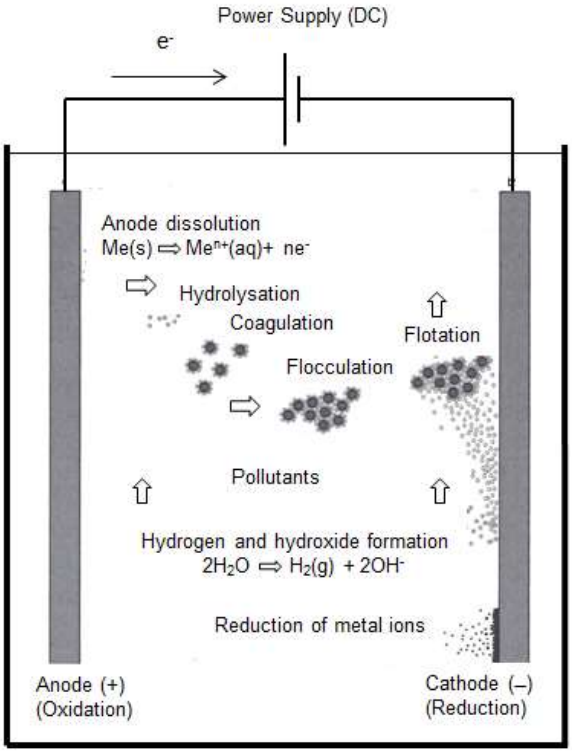



**Fig.1.** A schematic diagram of the electrocoagulation (adapted from [20]).

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

## 3. Results and discussion

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

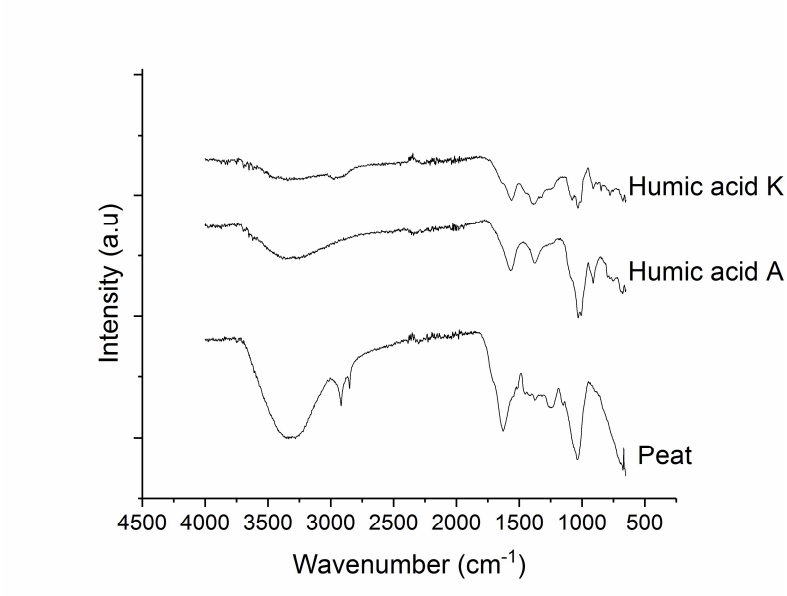



**Fig.2**. IR-spectrum showing the curves of the peat used, of humic acid powder (Humic acid K) and of the industrial peat from Aldrich (Humic acid A).

Properties of the prepared activated carbon from spruce were analyzed with $N_2$-physisorption. The BET surface area of AC was 785 $m^2$ $g^{-1}$ with pore volume 0.46 $cm^3$ $g^{-1}$ and composed mainly from mesopores (82 %) according to BJH method (Table 1). The high amount of mesoporous structure is important when big particles like organic molecules are wanted to adsorb into the internal surface of AC. In this case, over 80% of the porous structure was mesopores, concluding that the prepared activated carbon was suitable for adsorption of organic molecules. The total carbon content of AC was analyzed with TC and was 92 % (Table 2). The inorganic material in AC was studied with ash determination method [39] and content of ash was 2.6 %, which is relatively low, compared to commercial ACs. Moreover, ICP-OES analyze showed the composition of metals in the AC (Table 2) and most prevalent metals in AC seemed to be calcium and potassium. According to these results, it was assumed that no interfering metals from AC material were present in the study or the amounts were really low.

**Table 1**

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

| | **BET** | | | **BJH** | | | |
|---|---|---|---|---|---|---|---|
| Sample | 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 |

**Table 2**

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 |

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

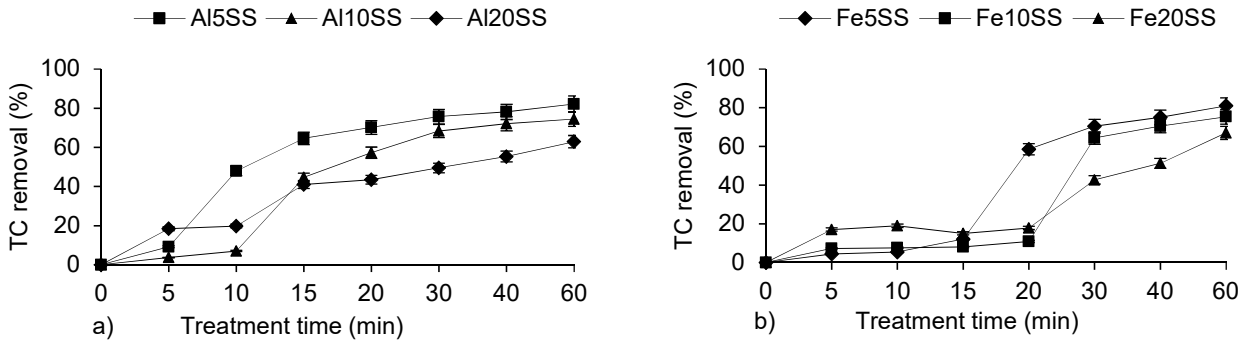



**Fig.3**. Effect of electrode distances between a) aluminum anode and stainless steel cathode b) iron anode and stainless steel cathode on the removal of TC content from peat solution.

**Table 3**

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 |

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

**Table 4**

The metal content in the peat solution (TC 500 mg $L^{-1}$) at the beginning and after the electrocoagulation 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 |

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

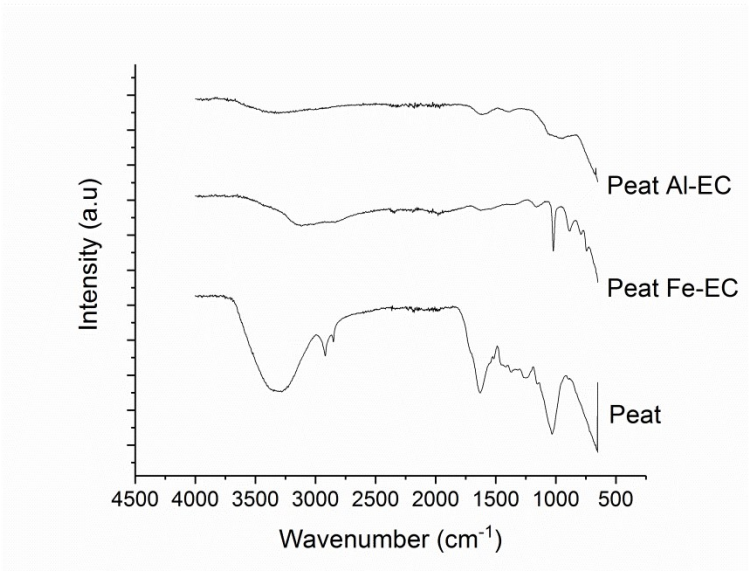



**Fig.4**. IR spectrums of peat before and after 60 min electrocoagulation with aluminum and iron electrode.

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

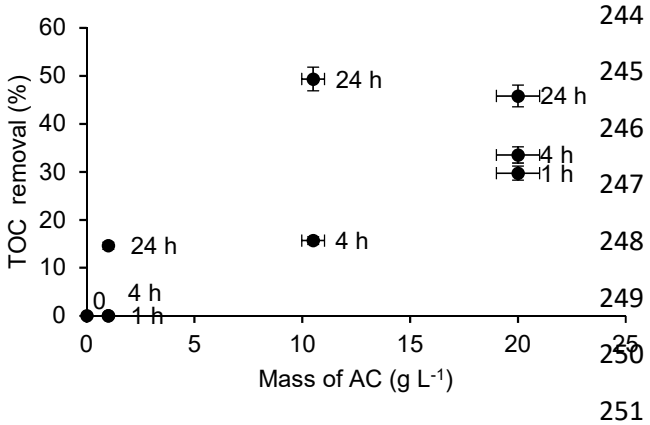



**Fig.5.** Total organic carbon removal by adsorption using AC 1, 10 or 20 g $L^{-1}$ and adsorption time 1, 4 or 24 hours.

### 3.1 Comparing electrocoagulation/adsorption and adsorption/electrocoagulation experiments

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

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

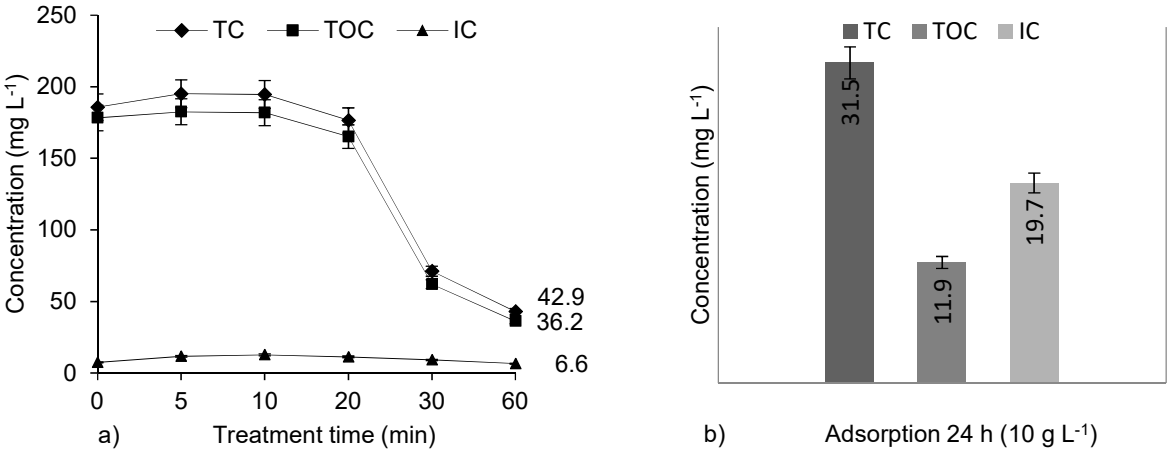



**Fig.6**. Total carbon (TC), total organic carbon (TOC), inorganic carbon (IC) concentration after (a) 60 min electrocoagulation experiment with aluminum electrode followed by (b) 24-hour adsorption experiment with AC load of 10 g $L^{-1}$.

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

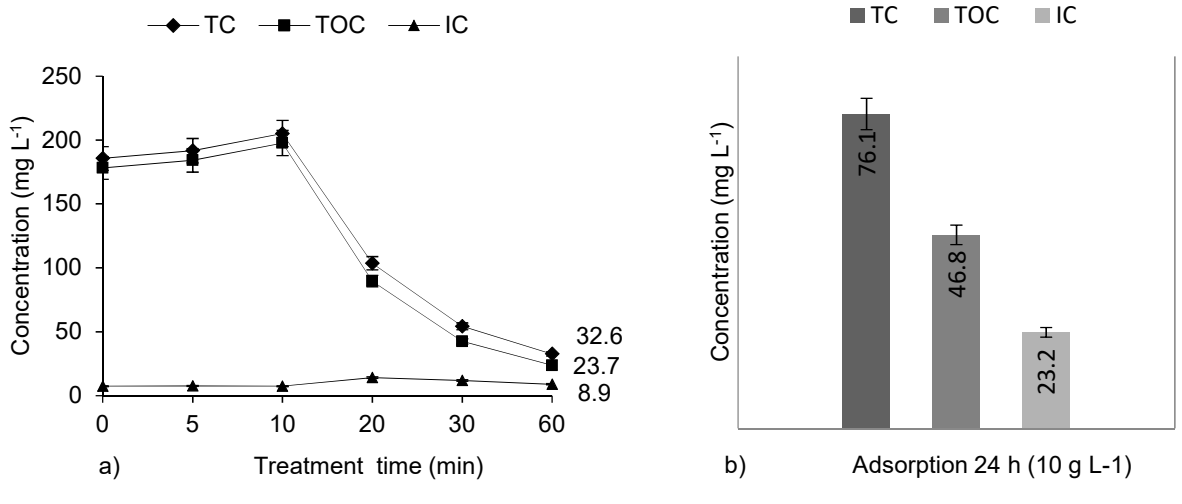



**Fig.7**. Total carbon (TC), total organic carbon (TOC), inorganic carbon (IC) concentration after (a) 60 min electrocoagulation experiment with iron electrode followed by (b) 24-hour adsorption experiment with AC load of 10 g $L^{-1}$.

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

**Table 5**

Total organic carbon (TOC) removal percent from peat solution by electrocoagulation (Al or Fe) followed by 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 |

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

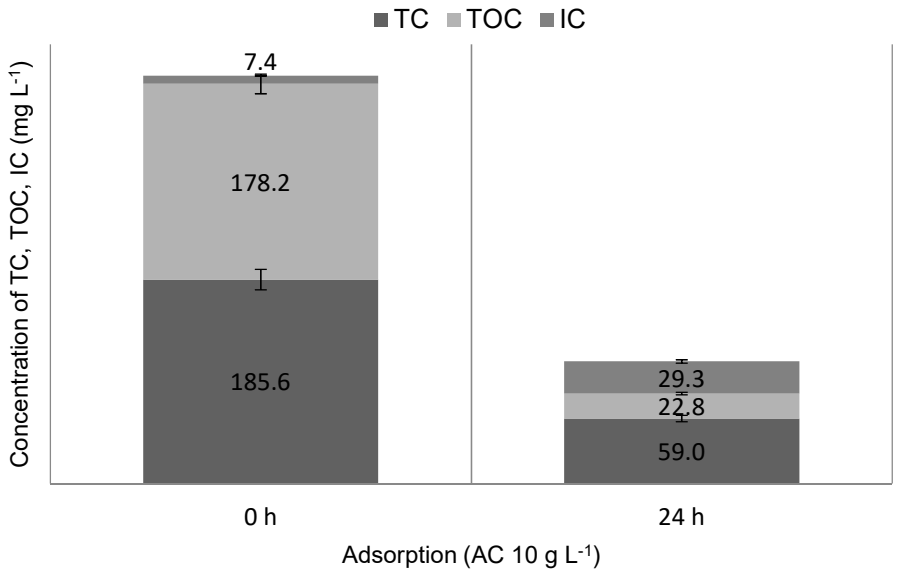



**Fig.8**. The concentration of total carbon (TC), total organic carbon (TOC) and inorganic carbon (IC) after 24-hour adsorption with activated carbon 10 g $L^{-1}$.

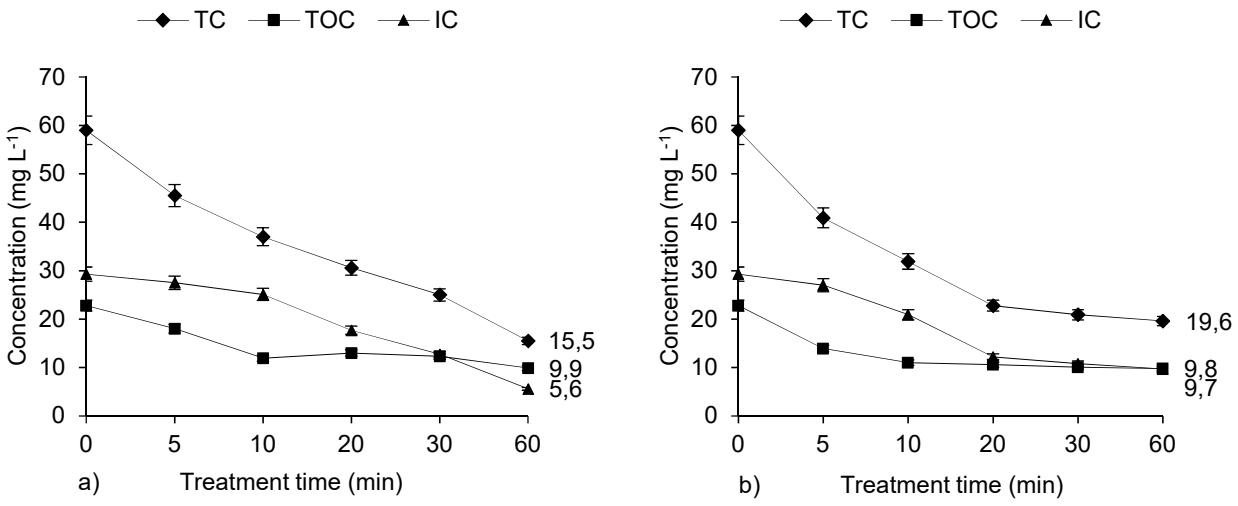



**Fig.9**. a) Electrocoagulation experiment with the aluminum electrode and b) electrocoagulation experiment with iron electrode performed after 24 h adsorption with AC 10 g $L^{-1}$.

**Table 6**

Total organic carbon (TOC) removal from peat solution by 24-hour equilibrium adsorption with 10g $L^{-1}$ of AC 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 |

## 4. Conclusions

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

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