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Chapter

Application of Biochar for Treating the Water Contaminated with Polar Halogenated Organic Pollutants

Barbora Kamenická, Pavel Matějíček, Tomáš Weidlich and Michael Pohořelý

Abstract

Application of biochar and ionic liquid-impregnated biochar was successfully tested for removal of nonbiodegradable polar halogenated aromatic contaminants (anti-inflammatory agents diclofenac and flufenamic acid and azo dye Mordant Blue 9) from contaminated aqueous solutions. The time dependence of removal efficiencies and adsorption isotherms were evaluated, and the effect of applied ionic liquids (quaternary ammonium salts) was considered. The determined removal efficiencies of the abovementioned contaminants based on the application of biochar or biochar combined with quaternary ammonium salts were compared with the action of commercially available active carbon and/or published results obtained by the action of additional low-cost sorbents. It was demonstrated that a more laborious two-step technique, based on the initial preparation of impregnated biochar by the action of R_4NCl with subsequent application of this modified sorbent, is much less effective than simple mixing of biochar with R_4NCl directly in the treated wastewater solution.

Keywords: drug, water treatment, sorption, diclofenac, flufenamic acid, anionic azo dye, mordant blue 9

1. Introduction

An increase number of nonbiodegradable and often biologically active organic pollutants of anthropogenic origin, such as synthetic dyes and pharmaceuticals, have been detected in the natural environment and wastewaters. The occurrence of these artificial persistent or even biocidal pollutants in aqueous effluents of sewage treatment plants represents possible health hazard not only for the living aquatic organisms but also for terrestrial animals and people [1].

The representatives of these pollutants are polar and highly mobile halogenated aromatic carboxylic (e.g., diclofenac and flufenamic acid) or sulfonic acids and their salts (e.g., Mordant Blue 9 acid dye), respectively (**Table 1**). These ionizable polar compounds (their aqueous solubility strongly depends on the pH of the aqueous solution) are broadly used as remedies or colorants.
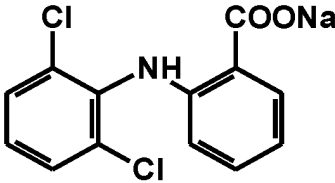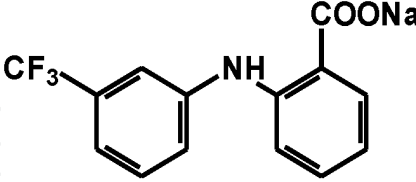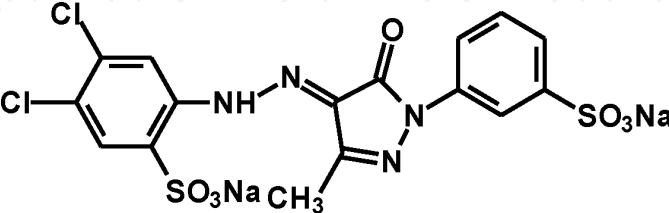
Applied contaminant (M$_r$ [g/mol])	Chemical structure
Diclofenac sodium salt (304.1)	
Flufenamic acid sodium salt (303.2)	
Mordant Blue 9 (551.28)	

Table 1.
Structures of chlorinated aromatic acid salts.

Specifically in the case of the painkiller diclofenac (DCF), studies have shown that conventional treatment processes are relatively ineffective in removing DCF from water sources and wastewater treatment plants [2]. Kasprzyk-Hordern et al. [2] observed no diclofenac removal in wastewater treatment using trickling filters and activated sludge. Rosal et al. in [3] reported only 5% of DCF removal after biological treatment of urban wastewater.

The concentration of ionizable contaminants, especially of alkaline salts of organic acids, in aqueous mother liquors from the production of these chemicals is frequently high, especially in the case of acid dyes (including Mordant Blue 9) isolated from the aqueous reaction medium by the so-called salting-out process [4]. Adsorption serves as the common and broadly used technique applicable for the treatment of water streams contaminated with these nonbiodegradable pollutants. The adsorption technique requires, however, high quantities of sorbent for effective water treatment which is accompanied by significant material costs. Therefore, carbonaceous rest, obtained by pyrolysis of waste biomass (biochar), potentially offers possible utilization in water treatment processes based on sorption as an alternative low-cost sorbent in comparison with activated carbon. For biochar, a porous structure with a sufficient specific area (above 400 m^2/g) is typical. Biochar poses polyaromatic systems substituted with some functional groups on its surface (COOH, OH, C=O) and even inorganic impurities (metal oxides) capable of engaging in **hydrogen-bonding or π-π** interactions with polar compounds.

Another notable attribute is biochar's affinity with the cationic surfactants (quaternary ammonium salts) [5].

This ability is of great interest for us due to the feasible utilization of cationic surfactants as liquid ion exchangers for chemisorption of the abovementioned chlorinated organic acid salts [6]. Ionizable halogenated contaminants produce ion pairs with only limited aqueous solubility and a good affinity with the biochar by the action of quaternary ammonium salts [7, 8].

The price of biochar is reasonably lower (around 1000 EURO/t) in comparison with active carbon (the cost of active carbon is approximately 2000 EUROs/t [9]).

Due to the abovementioned reasons, good cationic surfactant affinity of biochar seems to be very useful for uptake of ionizable contaminants using combined ion exchange (chemisorption) and the sorption mechanism.

2. Origin of the tested biochar

Gasification is a thermochemical process that converts a (waste) woody biomass into a producer gas and ash or carbonaceous residue (char). It can be used for combined heat and power production. The carbonaceous residue of the gasification process (called char) can match requirements classified as biochar [10]. The quality of both biochar and producer gas is highly dependent on the gasification technology selected, most of all, on the design and operation parameters of the gasifier.

Gasification is a complex process that can be divided into four basic stages. The first stage is drying. The second stage, taking place in the absence of oxygen and at temperatures above 250°C, is called pyrolysis. The waste woody biomass is converted into volatile matter and a carbonaceous residue (char) during the pyrolysis. The third stage is exothermic partial oxidation of the char and the volatile matter with an oxidizing agent (basically air). This exothermic process produces heat. The last (fourth) stage, called char gasification, is the sum of the endothermic reactions of char with CO_2 and/or H_2O driven by the heat from the third stage leading to the additional formation of H_2 and CO.

The space separation of these four stages in a gasifier with proper process control can be used to optimize the outputs of the gasification process. The space separation and optimization of these four stages of the gasification process are the principle of the so-called multistage gasification. One concept used for multistage gasification is a twin-fire gasifier. The gas generator at the commercial heating plant (**Figure 1**)
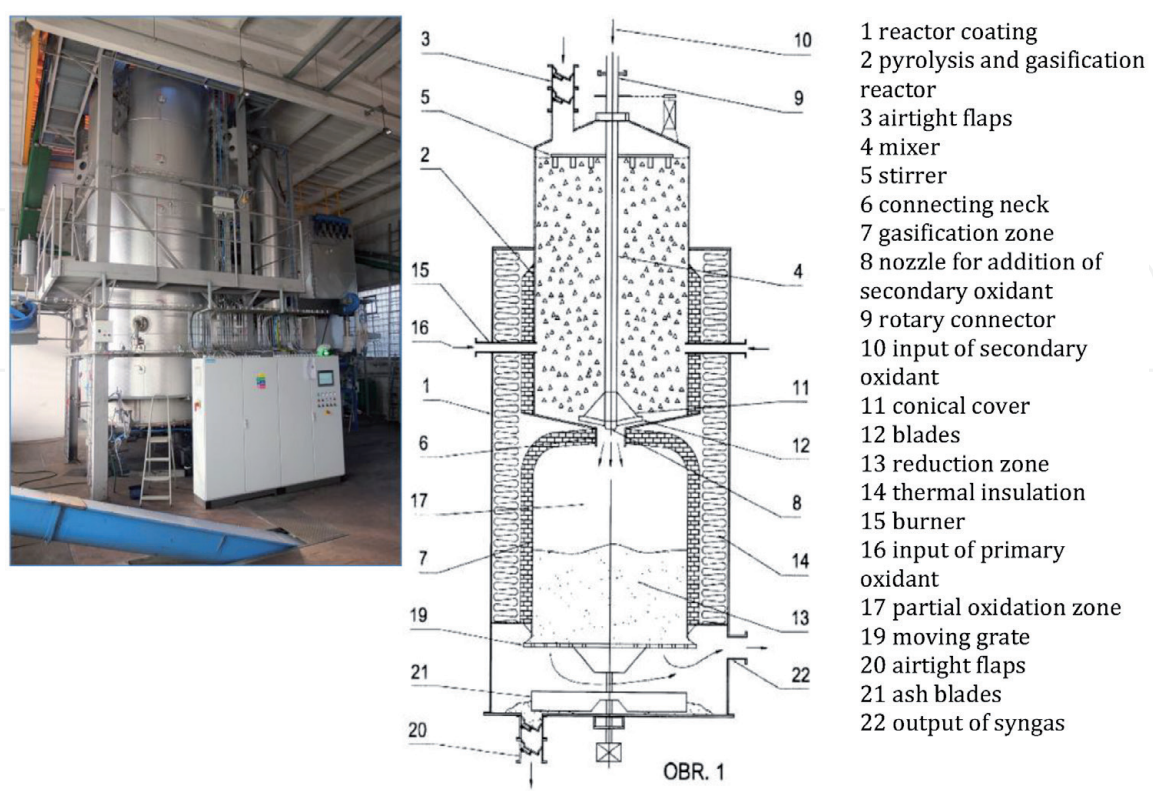

1 reactor coating
2 pyrolysis and gasification reactor
3 airtight flaps
4 mixer
5 stirrer
6 connecting neck
7 gasification zone
8 nozzle for addition of secondary oxidant
9 rotary connector
10 input of secondary oxidant
11 conical cover
12 blades
13 reduction zone
14 thermal insulation
15 burner
16 input of primary oxidant
17 partial oxidation zone
19 moving grate
20 airtight flaps
21 ash blades
22 output of syngas

Figure 1.
Commercial twin-fire Gasifier [1].

is built on this principle [11]. This type of gasifier is composed of two autothermic stages, each with a separate air intake, creating two separate "fires," therefore "twin-fire." The first air intake used for the partial combustion of the waste biomass is directed into the upper stage of the gasifier and produces the heat necessary for "autothermal" pyrolysis. The secondary air inlet, for partial oxidation of volatile matter, is directed to the top of the lower part of the gasifier, and the temperature of its "fire" exceeds 1200°C. Partial oxidation takes place in the free space above the char bed and produces heat for char gasification at the bottom of the second stage of the gasifier, reaching a temperature of approximately 950°C. The partial oxidation stage cracks down volatile matter into gases (i.e., CO, H_2, CH_4, CO_2, and H_2O) and thereby minimalizes the tar content. In the last stage, the hot products of the partial oxidation flow through the char bed and react with it, causing a temperature drop from 950 to 750°C due to the endothermic gasifying reactions. Optimization of this step can enhance the properties of the produced solid carbonaceous residue (biochar) by increasing its specific surface and due to its "activation" by the reactions with H_2O and CO_2. Moreover, the prolonged residence time (about 1 h) of the char at a high temperature of 750°C helps to achieve the stringent requirements on the content of polycyclic aromatic hydrocarbons in the produced biochar. For safety measures (to prevent producer gas leakage), the whole gasification unit and gas

Characteristics	Value
Bulk density (g/mL)	166
Specific area, S_{BET} (m^2/g)	444
Specific total pore volume, V_{tot} (mm^3_{liq}/g)	293
Specific micropore volume, V_{micro} (mm^3_{liq}/g)	157
Specific mesopore volume, V_{meso} (m^2/g)	142
pH	11.4
Electrical conductivity, EC (μS/cm)	1450
Ash (wt. %)	9.63
Carbon content, C (wt. %)	86.8
Organic carbon content, C (wt. %)	83.8
H/C_{org} ratio	0.0890
O/C ratio	0.0205
Sulfur content, S (wt. %)	Less than 0.1
Content of combustible sulfur (mg/kg)	401
Chlorine content, Cl (mg/kg)	867
Fluorine content, F (mg/kg)	11.4
Content of P (g/kg)	0.65
Content of K (g/kg)	3.1
Content of Ca (g/kg)	15.7
Content of Mg (g/kg)	2.5
Sum PAH_{16} (mg/kg)	Less than 0.5
Water content (wt. %)	1.18

Table 2.
Characteristics of the produced biochar.

Inorganic oxide	Content of noncombustible part (wt. %)
Al_2O_3	8.89
CaO	32.6
Fe_2O_3	6.74
K_2O	6.69
MgO	5.78
MnO	1.20
Na_2O	4.49
P_2O_5	2.21
SiO_2	20.9
TiO_2	2.93
Total amount	92.5

Table 3.
Composition of noncombustible matter (ash) in the produced biochar according to XRF.

treatment line are operated at pressure slightly below atmospheric pressure (pressure difference—0.1–10 kPa) ensured by a fan (ventilator). The input material to the gasification generator is spruce wooden chips (waste biomass produced from spent packaging and pallets) with a water content max. 10 wt.%. The produced biochar (**Tables 2** and **3**) meet the European Biochar Certificate (EBC) standard of regulation (EU) 2019/1009 and the Central Institute for Supervising and Testing in Agriculture (Czech Certification Institute, the certification valid in the EU). The produced biochar can be grinded and is conveyed into a magnetic separator to eliminate any possible remaining metal particles. Lian and Xing published that increasing pyrolysis temperature above 700°C results in high aromaticity and porosity of obtained biochars structure, high carbon content, and progressive decreasing of nitrogen and oxygen content in produced biochar [12]. The described biochar produced in twin-fire gasifier is a typical high-temperature biochar with high carbon content, increased pH value, high porosity, increased ash content, and specific surface area (**Table 2**) [10]. As could be seen in **Tables 2** and **3**, elemental composition of produced highly porous biochar is mainly composed of C and very low contents of H, N, and O, with significant content of minerals. In comparison with starting wooden biomass, significant decrease in molar ratios of both H/C and O/C is observed in biochar due to the dehydration and thermolysis reactions caused by temperature above 700°C.

3. Preliminary experiments comparing sorption kinetics for removal of ionizable halogenated contaminants using biochar and quaternary ammonium chlorides in batch sorption

The above described biochar seems to be an interesting candidate for utilization in sorption processes due to the high porosity and specific surface comparable with active carbon (**Table 2**). This study is focused on the removal of ionizable organic compounds (halogenated organic acid salts) mentioned in the introduction chapter (**Table 1**). Due to the abovementioned high aqueous solubility of the studied sodium salts of chlorinated aromatic acids, the preliminary experiments were performed by the addition of high quantity (20 g/L) of the above-described

biochar to the concentrated aqueous solutions of contaminants simulating effluents from industrial production sites. These preliminary experiments indicated that the maximum efficiency of contaminant removal was obtained after more or less than 90 minutes of biochar action in batch sorption under vigorous stirring (**Figure 2**). The removal efficiency for each contaminant reached more than 40% in all cases after 1 h of action. This means that these efficiencies are quite low even using this huge quantity of biochar. These results correspond with known high polarity of tested fully ionized contaminants at pH above 8.5 and their low affinity to the low-polar surface of biochar. In contrast, however, it was published earlier that the addition of cationic surfactants to the wastewater contaminated with soluble organic acid salts can significantly improve removal efficiency due to the electrostatic attraction between negatively charged contaminant anions and positively charged cations of cationic surfactants [7, 8, 13].

Subsequently, possible enhancement of the removal efficiency of biochar caused by co-action with a cationic surfactant was tested. The sorption kinetics and removal efficiencies of the contaminant based on chlorinated carboxylic acid salts, biochar, and biochar in combined action with frequently used cationic surfactant quaternary ammonium salt (R_4NCl) benzalkonium chloride (alkylbenzyldimethylammonium chloride, $AlkBzMe_2NCl$) for removal of diclofenac sodium salt (NaDCF) and of flufenamic acid sodium salt (NaFLUFA) were compared.

The results for the removal rates of NaDCF and NaFLUFA are mentioned in **Figure 3**. As is apparent, after 30 min of action, the removal of NaDCF and NaFLUFA from aqueous solutions is completed. Whereas the application of sole biochar in quantity 20 g/L reduces the quantity of NaDCF (or NaFLUFA, respectively) with efficiency less than 45%, using a combination of cationic surfactant and biochar, the removal efficiency reaches over 65%. It should be said that the efficiency of NaDCF or NaFLUFA removal using sole cationic surfactant $AlkBzMe_2NCl$ without the addition of charcoal is much worse, below 34%. This observation could be explained by the known fact that NaDCF reacts smoothly with low-polar R_4NCl
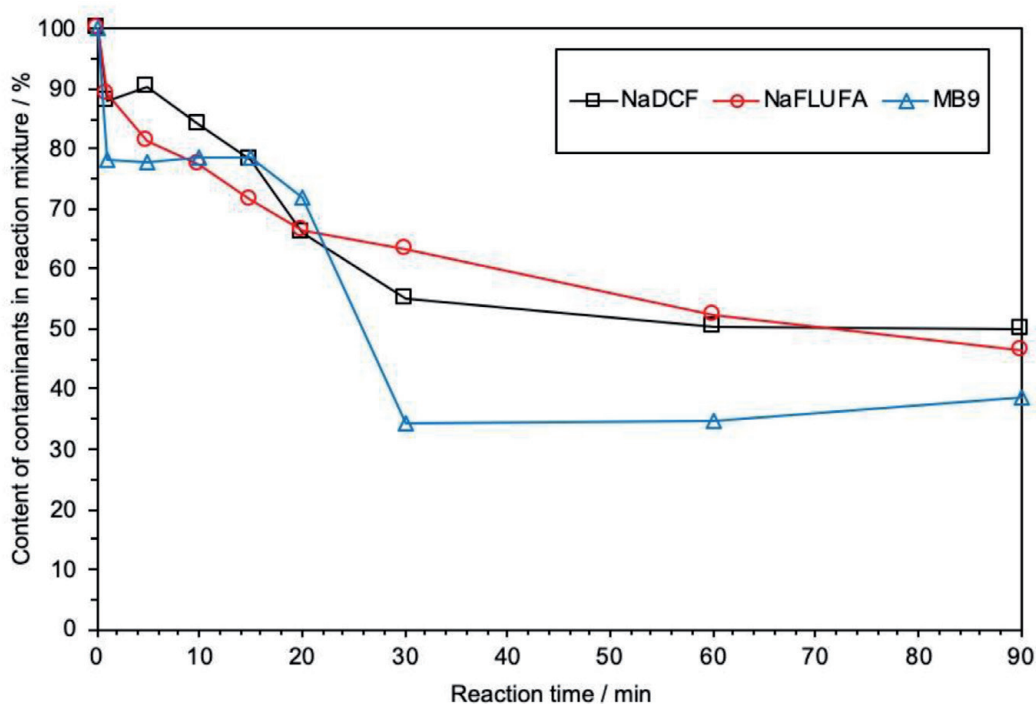

Figure 2.
Rate of removal of tested ionizable halogenated contaminants from 10 mM aqueous solutions (from 25 mM solution in case of NaDCF) using biochar in quantity 20 g/L.
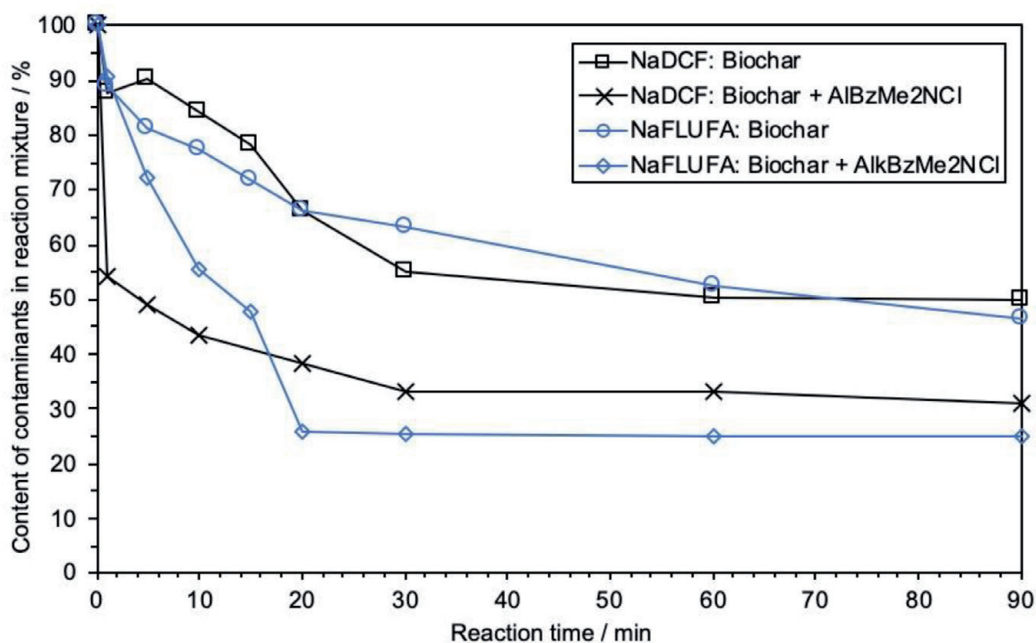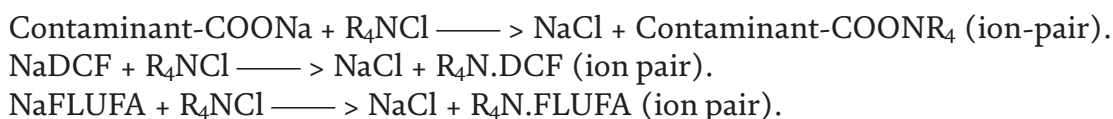
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Figure 3.
Rate of NaDCF (25 mM aq. solution) and NaFLUFA (10 mM aq. solution) removal from aqueous solutions using biochar (20 g/L) or a combination of AlkBzMe2NCl (1 g/L) with biochar (20 g/L).

by ion exchange reaction producing high molecular (and less soluble) ion pairs R_4N. DCF (R_4N.FLUFA, respectively) according to the scheme:

Contaminant-COONa + R_4NCl ——— > NaCl + Contaminant-COONR₄ (ion-pair).
NaDCF + R_4NCl ——— > NaCl + R_4N.DCF (ion pair).
NaFLUFA + R_4NCl ——— > NaCl + R_4N.FLUFA (ion pair).

Chemical structures of tested R_4NCls are depicted in **Figure 4**. The effect of cation size of different cationic surfactants R_4NCl (AlkBzMe₂NCl, hexadecyltrimethylammonium chloride (AlkMe₃NCl), and methyltrialkylammonium chloride, Aliquat 336) on removal efficiency of NaDCF and NaFLUFA is depicted in **Figures 5** and **6**. It is evident that the branched structure (quantity of long alkyl chains) of the used cationic surfactants and primarily the aqueous solubility of the produced ion pairs based on tetraalkylammonium salts R_4N^+ play an important role in the removal efficiencies of the studied contaminants. This fact could be well described by comparison of the solubility of discussed pollutants and corresponding ion pairs in water and in low-polar solvent (octan-1-ol) using distribution coefficient between these two solvents (**Figure 7**, Eq. (1)). Octan-1-ol/ water distribution ratio is the most common way of expressing the lipophilicity of a compound, and it is defined as the ratio of the concentration of a solute in a water-saturated octanolic phase to its concentration in an octanol-saturated aqueous phase. P_{ow} is defined as in Eq. (1) [14]:

$$\log P_{ow} = \frac{c_{octanol}}{c_{aqueous\ phase}} \qquad (1)$$

The observed removal efficiencies of the co-action of different R_4NCl with biochar (**Figure 5**) correspond well with the measured distribution coefficients between octan-1-ol and water of NaDCF and ion pairs R_4N.DCF produced by the ion exchange of NaDCF with R_4NCl, as could be demonstrated in **Figure 7**. The less hydrophobic quaternary cation produces less hydrophobic and more water soluble ion pair contaminant-COONR₄ (with lower value of log P_{OW},
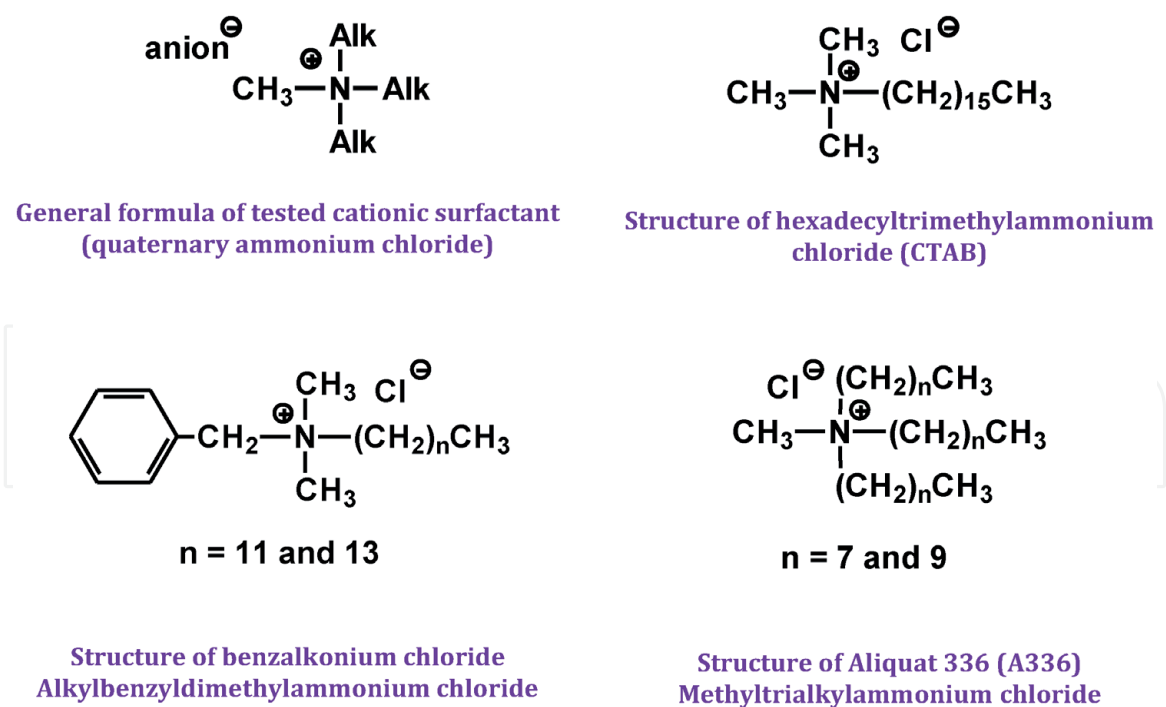
General formula of tested cationic surfactant (quaternary ammonium chloride)

Structure of hexadecyltrimethylammonium chloride (CTAB)

Structure of benzalkonium chloride Alkylbenzyldimethylammonium chloride

n = 11 and 13

Structure of Aliquat 336 (A336) Methyltrialkylammonium chloride

n = 7 and 9

Figure 4.
Chemical structures of tested cationic surfactants (quaternary ammonium chlorides, R4NCls) with different quantity of long alkyl chains (different cation size).
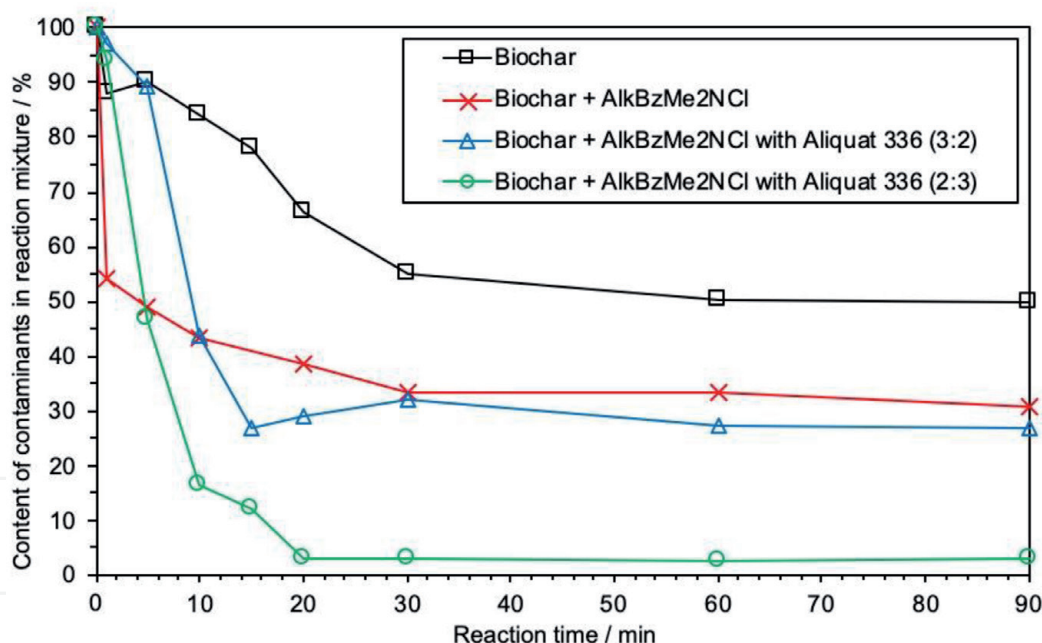
Figure 5.
Rate of NaDCF removal from 25 mM aq. Solution using biochar (20 g/L) or a combination of different R4NCls (1 g/L) and biochar (20 g/L).

Figure 5). Benzalkonium chloride (AlkBzMe$_2$NCl) which is readily soluble in water enables, for example, the worse removal of NaDCF in comparison with in-water insoluble Aliquat 336 (albeit the combination of the ion exchange with adsorption is still more effective in comparison with adsorption on sole biochar).

The highest value of log P$_{ow}$ was determined for low-polar and water immiscible ion pairs produced by the action of Aliquat 336 (A336). In contrast, A336 is extremely viscous (honey-like) material and together with its low aqueous
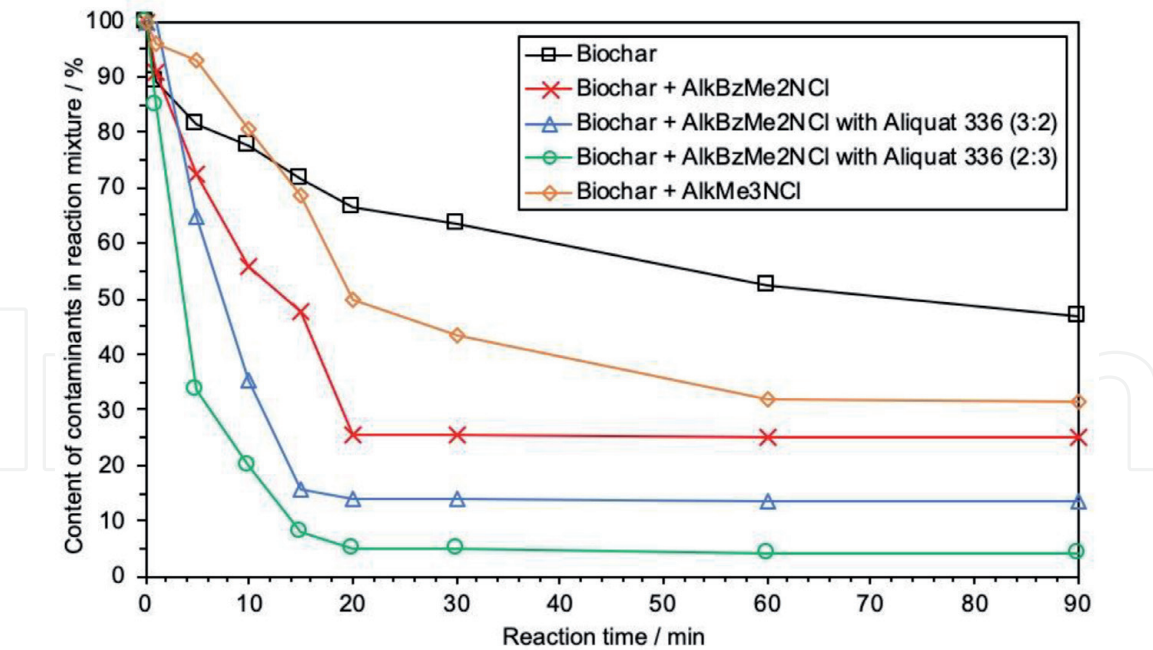
Figure 6.
Rate of NaFLUFA removal from 10 mM aqueous solution using biochar (20 g/L) or a combination of different R4NCls (1 g/L) and biochar (20 g/L).
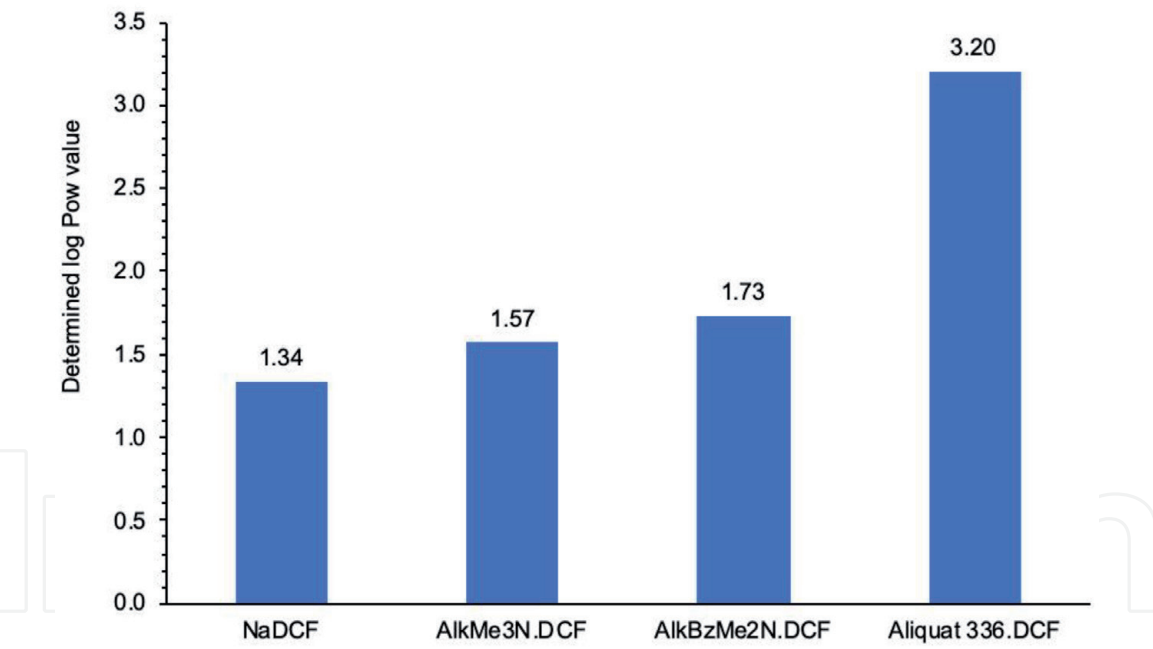

Figure 7.
Differences between the measured distribution coefficients log Pow between NaDCF and ion pairs produced by ion exchange of NaDCF with the corresponding R4NCl (R4N.DCF).

solubility is non-applicable for precise addition of appropriate quantity to treated wastewater. We tested, however, that A336 is well soluble in 50 wt.% aqueous AlkBzMe$_2$NCl solution and the obtained mixture is less viscous and enables precise addition of R$_4$NCls into the stirred aqueous solution. Due to these reasons, the mixtures of A336 and 50 wt.% aqueous AlkBzMe$_2$NCl in two different weight ratios (2/3 or 3/2) were examined (see **Figures 5** and **6**). The low solubility of ion pairs A336.DCF produced by ion exchange reaction between A336 with NaDCF enables in particular extremely effective subsequent removal from the aqueous solution by
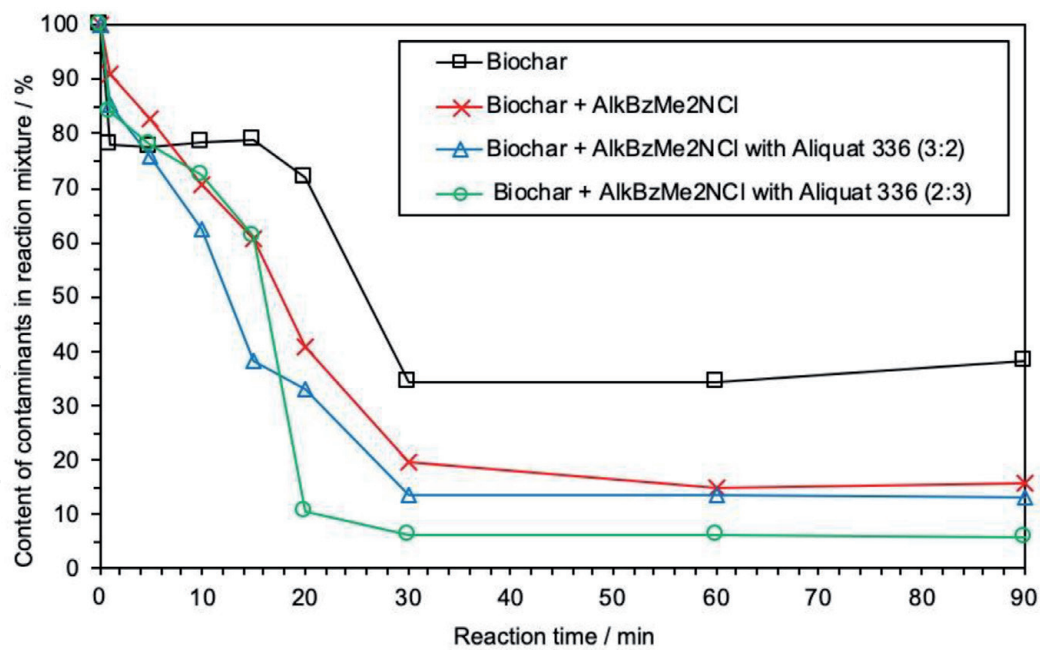
Figure 8.
Rate of mordant blue 9 removal from 10 mM aqueous solution using biochar (20 g/L) or a combination of different R4NCls (1 g/L) and biochar (20 g/L).
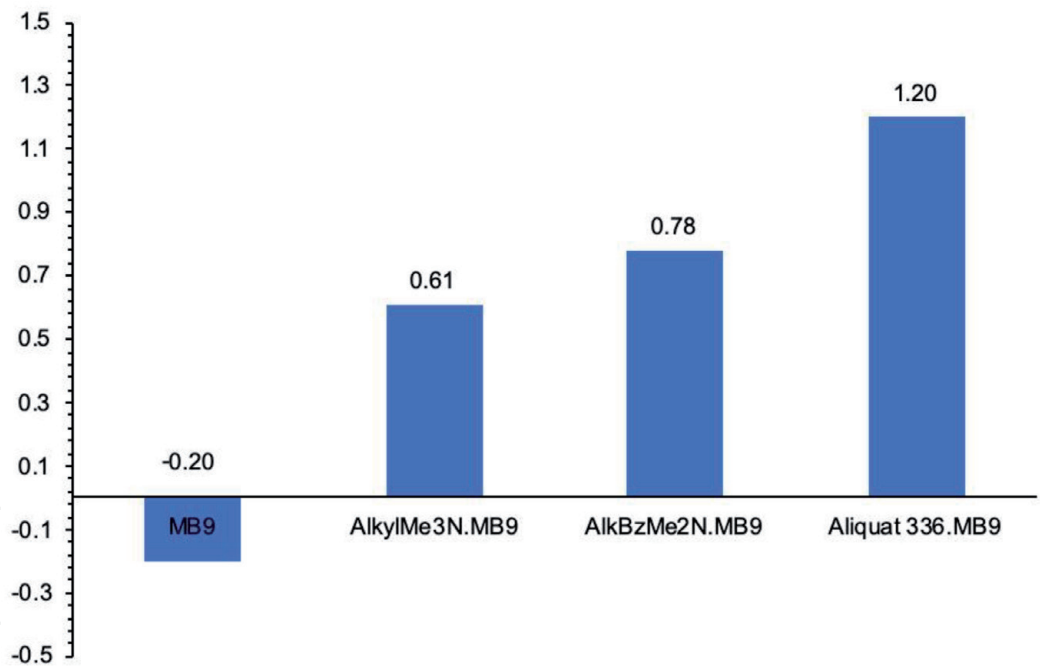

Figure 9.
Differences of measured distribution coefficients log Pow between commercial textile dye MB9 and ion pairs produced by ion exchange of MB9 with corresponding R4NCl.

the addition of biochar. The surface of biochar sorbs produced A336.DCF better than AlkBzMe2N.DCF, as could be seen in **Figure 5**.

In accordance with the above described facts, the best removal efficiency of NaFLUFA was obtained using a combination of mixture of 3/2 (w/w) of A336 and 50% aq. AlkBzMe$_2$NCl. The lowest effect of AlkMe$_3$NCl on the removal of NaFLUFA corresponds, in contrast, with the least branched structure of AlkMe$_3$N$^+$ cation (**Figure 6**).

The same relationship between the structure of the used cationic surfactants and removal efficiency was observed in the case of the anionic textile dye Mordant

Blue 9 (MB9). Subsequently, the measured log P_{ow} values for MB9 and ion pairs $R_4N.MB9$ are in good agreement once again with the measured removal efficiencies (**Figures 8** and **9**).

4. A comparison of adsorption isotherms measured for removal efficiencies of diclofenac or flufenamic acid sodium salts using active carbon, biochar, and biochar in co-action with RNX

The abovementioned differences in removal capacity of active carbons, biochar, modified biochar, and biochar in co-action of RNCls possessing quaternary cations with different bulkiness are illustrated in **Figure 10** for removal of NaDCF. The tested sorbents (active carbons or biochar) were used in quantity 10 g/L (with appropriate co-action of 1 g/L of $R_4NCl(s)$).

Figure 10 illustrates that the sorption capacity (q) showed the following behavior: PAC > [Biochar + AlkBzMe$_2$NCl with Aliquat 336 (2:3)] > [Biochar + AlkBzMe$_2$NCl with Aliquat 336 (3:2)] > [Biochar + AlkBzMe$_2$NCl] > GAC > Biochar > [Modified biochar AlkBzMe$_2$NCl].

The worst removal capacity poses modified biocharAlkBzMe$_2$NCl prepared by mixing biochar with aqueous AlkBzMe$_2$NCl solution, subsequent washing with water, and drying [15] (for more details see Experimental section) probably due to the low concentration of AlkBzMe$_2$N-cations immobilized on surface of prepared modified biochar. **Figure 10** compared the effect of the addition of highly hydrophobic A336 added in different quantities to the hydrophilic 50% aq. AlkBzMe$_2$NCl on the sorption capacity of biochar/ R_4NCl mixture (which means sorption capacity of in situ-prepared biochar modified with added R_4NCls). In agreement with the abovementioned effect of different R_4NCls, using a higher quantity of A336 enables an increase of sorption capacity of biochar after the addition of R_4NCls. In addition, the comparison of the effectiveness of traditional charcoal (granulated
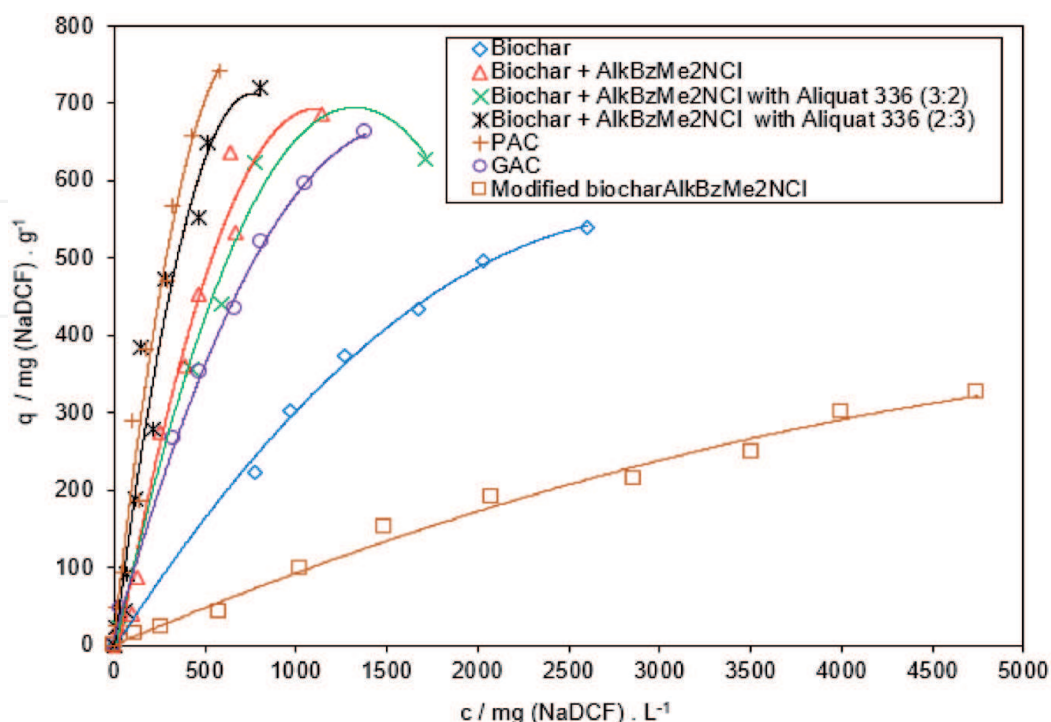

Figure 10.
The dependence of sorption capacity of powdered (PAC) and granulated (GAC) active carbons, biochar, modified biochar and biochar in co-action with R4NCls on the equilibrium concentration of the NaDCF solution.

Hydraffin CC8x30 GAC and powdered PAC Silcarbon CW20) and tested biochar and biochar with the co-action of the most effective mixture of cationic surfactants AlkBzMe$_2$NCl with A336 is depicted in **Figure 10** using initial NaDCF concentration 0.25–8 g /L. It is evident that the combination of the aqueous surfactants mixture 50% aq. AlkBzMe$_2$NCl and A336 in weight ratio 2/3 (used in quantity 1 g/L) with biochar (10 g/L) exhibits a similar sorption capacity as powdered active carbon Silcarbon CW20 (10 g/L) and a higher sorption capacity than granulated active carbon Hydraffin CC8x30 (10 g/L).

Similarly, studying removal efficiencies of NaFLUFA (initial concentration 0.25–7 g FLUFA/L) using active carbons (10 g/L), biochar (10 g/L), modified biochar (10 g/L), and biochar (10 g/L) with co-action of R$_4$NCls (1 g/L), we observed that the activity of these sorbents was similar to the abovementioned removal of NaDCF (**Figure 11**). The sorption capacity has the rank order PAC mixture Aliquat 336 in 50% aq., AlkBzMe$_2$NCl 3/2 with biochar mixture Aliquat 336 in 50% aq., and AlkBzMe$_2$NCl 2/3 with biochar mixture of AlkBzMe$_2$NCl with biochar AlkBzMe$_2$NCl biochar. This similarity with NaDCF removal is not surprising; the chemical structures of both NaDCF and NaFLUFA are very similar (see **Table 1**). On the other hand, the sorption experiments using NaDCF and NaFLUFA were performed at different pH due to the low aqueous solubility of FLUFA at pH bellow 10. High removal efficiencies of A336/AlkBzMe$_2$NCl mixtures with biochar even at high pH values are in agreement with our observation and the observation of Kosaiyakanon that the effect of pH is not crucial using separation method based on the formation of ion pairs [7, 8, 15].

Sorption capacity q (mg/g) was calculated according to the following Eq. (2) [15]:

$$q = \frac{(c_0 - c) \cdot V}{m} \qquad (2)$$

where c_0 is the initial concentration (mg/L), c is the equilibrium concentration (mg/L), m is the mass of biochar (g), and V is the volume of treated model wastewater (L).
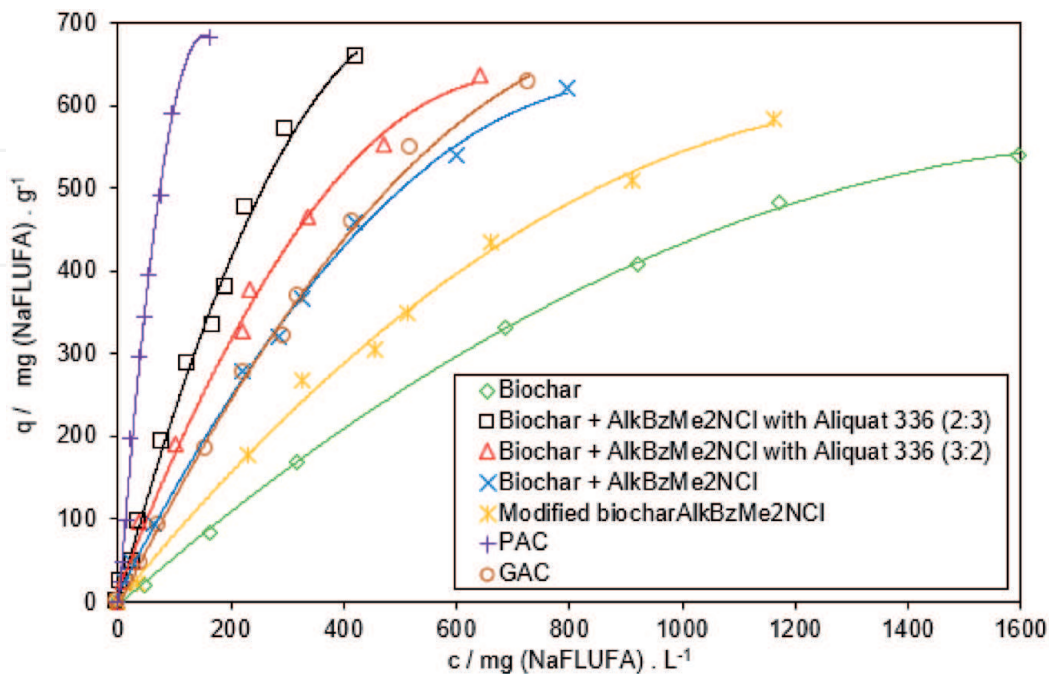

Figure 11.
The dependence of sorption capacity of biochar, in-situ modified biochar two types of active carbons (powdered (PAC) Silcarbon CW20 and granulated (GAC) Hydraffin CC8x30 on the equilibrium concentration of the NaFLUFA solution).

Langmuir and Freundlich isotherm models were fitted to the data. The Langmuir model describes monolayer adsorption on a homogenous surface. The Freundlich model describes multilayer adsorption on a heterogeneous surface. The Freundlich and Langmuir models are expressed in Eqs. (3) and (4), respectively:

$$q = k_F c^{1/n} \tag{3}$$

$$\frac{q}{q_{max}} = \frac{k_L c}{1 + k_L c} \tag{4}$$

Here, q is the amount of adsorbed contaminant on the adsorbent at equilibrium (mg/g), q_{max} is the maximum adsorption of contaminant on the adsorbent (mg/g), c is the residual contaminant concentration at equilibrium (mg/L), k_L is the Langmuir constant related to the energy of adsorption (L/mg), k_F is the Freundlich constant indicating the adsorption capacity, and n is the Freundlich exponent accounting for the adsorption intensity or the energetic heterogeneity of the adsorbing surface [15].

The correlation coefficients suggest that the Freundlich model fits the data better than the Langmuir model (**Tables 4** and **5**). This can be an indication that NaDCF and NaFLUFA and/or ion pairs R_4N.DCF (R_4N. FLUFA, respectively) were adsorbed in multilayers into the active sites of the biochar surface.

The maximum contaminant sorption capacities (q_{cont}) of the biochar, both tested active carbons, and biochar with co-action of R_4NCls at final pH of 8.7 were determined according to the Freundlich model (calculated for maximum applied concentration of contaminant using Eq. (3)). The differences in the action of sole biochar and biochar modified by different cationic surfactant(s) could be summarized by the ratio of increasing sorption capacity q_{cont}/q_{cont}^* [6] (**Table 6**).

For the tested active carbons, the q_{cont} values obtained by the same method were 661.6 mg NaDCF/g for granulated active carbon Hydraffin CC 8x30 and 742.3 mg NaDCF/g for powdered active carbon Silcarbon CW20.

Interestingly, in all the cases, modified biochar prepared independently (ex situ) by impregnation of biochar with aqueous solution of R_4NCls exhibited lower activity than the sequential addition of biochar and cationic surfactant(s) to the aqueous

	Freundlich			Langmuir		
Sorbent	k_F (mg/g (L/mg)$^{1/n}$)	n	R^2	q_{max} (mg/g)	k_L (L/mg)	R^2
PAC	2.14	1.03	0.954	833.3	0.0075	0.862
GAC	1.85	1.16	0.949	714.2	0.0034	0.811
Biochar	0.98	1.23	0.996	555.6	$6.6\ 10^{-4}$	0.886
Modified biocharAlkBzMe$_2$NCl	1.95	0.73	0.975	400.0	$5.3\ 10^{-4}$	0.714
Biochar + AlkBzMe$_2$NCl	1.25	1.01	0.978	1250.0	0.0012	0.865
Biochar +2/3 A336/ 50% aq. AlkBzMe$_2$NCl	1.22	0.93	0.986	1428.6	$5.7\ 10^{-4}$	0.418
Biochar +3/2 A336/ 50% aq. AlkBzMe$_2$NCl	1.12	0.99	0.983	1111.1	0.0022	0.577

Table 4.
Identified parameters in Langmuir and Freundlich isotherm models for NaDCF (used in initial concentration range 0.25–8 g/L) adsorbed by sorbents.

Sorbent	Freundlich			Langmuir		
	k_F (mg/g) $(L/mg)^{1/n}$	n	R^2	q_{max} (mg/g)	k_L (L/mg)	R^2
PAC	2.06	0.77	0.949	1000.0	0.010	0.702
GAC	1.13	1.01	0.997	833.3	0.0029	0.634
Biochar	0.85	1.11	0.987	666.7	0.0018	0.766
Modified biocharAlkBzMe$_2$NCl	0.95	1.07	0.996	714.3	0.0023	0.728
Biochar + AlkBzMe$_2$NCl	1.62	1.07	0.982	833.3	0.0027	0.770
Biochar +2/3 A336/ 50% aq. AlkBzMe$_2$NCl	1.88	1.04	0.968	909.1	0.0032	0.748
Biochar +3/2 A336/ 50% aq. AlkBzMe$_2$NCl	1.84	0.97	0.969	909.1	0.0044	0.635

Table 5.
Identified parameters in Langmuir and Freundlich isotherm models for NaFLUFA (used in initial concentration range 0.25–7 g/L) adsorbed by sorbents.

Contaminant	Sorbent	q_{cont} (mg/g)	Ratio of increasing capacity (q_{cont}/q_{cont}^*)
NaDCF	Biochar	539.5*	—
	Modified biocharAlkBzMe$_2$NCl	325.8	0.604
	Biochar + AlkBzMe$_2$NCl	682.2	1.264
	Biochar+2/3 A336/50% aq. AlkBzMe$_2$NCl	628.5	1.165
	Biochar +3/2 A336/50% aq. AlkBzMe$_2$NCl	719.9	1.334
NaFLUFA	Biochar	540.3*	—
	Modified biocharAlkBzMe$_2$NCl	514.6	0.952
	Biochar + AlkBzMe$_2$NCl	620.4	1.148
	biochar+2/3 A336/50% aq. AlkBzMe$_2$NCl	635.9	1.177
	biochar +3/2 A336/50% aq. AlkBzMe$_2$NCl	657.8	1.217

*Value of sorption capacity defined as q_{cont}^*

Table 6.
A comparison of surface modification technique on increasing sorption capacity of chlorinated aromatic carboxylic acid sodium salts.

solution contaminated with NaDCF (**Figure 10**). This could be explained by the possible parallel action of:

1. Rapid ion exchange reaction between the added R$_4$NCl and NaDCF accompanied by coagulation of the produced ion pairs R$_4$N.DCF (this reaction was proved by isolation of mentioned R$_4$N.DCF ion pairs by extraction and by subsequent NMR analysis)

2. The effect of polyvalent metal cations from inorganic components of biochar on additional precipitation of insoluble DCF salts (with composition M^{+n}.(DCF)$_n$) [12] (M^{+n} = Ca^{II}, Mg^{II}, Al^{III}, Fe^{III}, etc., see the content of minerals in

biochar in **Tables 2** and **3**) (effect of the well-known insolubility of DCF salts with the mentioned polyvalent metal cations)

3. The effect of negative charge-assisted H-bonds which were published as the main mechanism for sorption of ionizable organic compounds at alkaline pH area (pH above zero point of charge of biochar [12, 16, 17])

4. Subsequently the high affinity of biochar to the produced ion pair $R_4N.DCF$ [15] (caused by decreasing of polarity of produced $R_4N.DCF$ ion pairs in comparison of NaDCF with subsequent increasing of their affinity to surface of tested biochar, as we were observed)

The abovementioned results demonstrated that using a two-step procedure to enhance the biochar's adsorption capacity using $AlkBzMe_2NCl$ as a modification agent is not effective and is more laborious in comparison with the addition of a sole biochar.

5. A comparison of adsorption isotherms measured for removal efficiencies of textile dye mordant blue 9 using active carbons, biochar, and biochar in co-action with R4NX

In order to test the removal potential of active carbons (10 g/L), biochar (10 g/L), and biochar (10 g/L) with co-action of R_4NCls (1 g/L), broad concentrations (0.25–5.5 g/L) of MB9 in model aqueous solutions were chosen for the performed experiments, similar to the tested drugs. It is well-known that anionic dyes are efficiently removable from wastewater using adsorption on charcoal at low pH due to the suppression of their ionization. As the pH of the mixture increases,
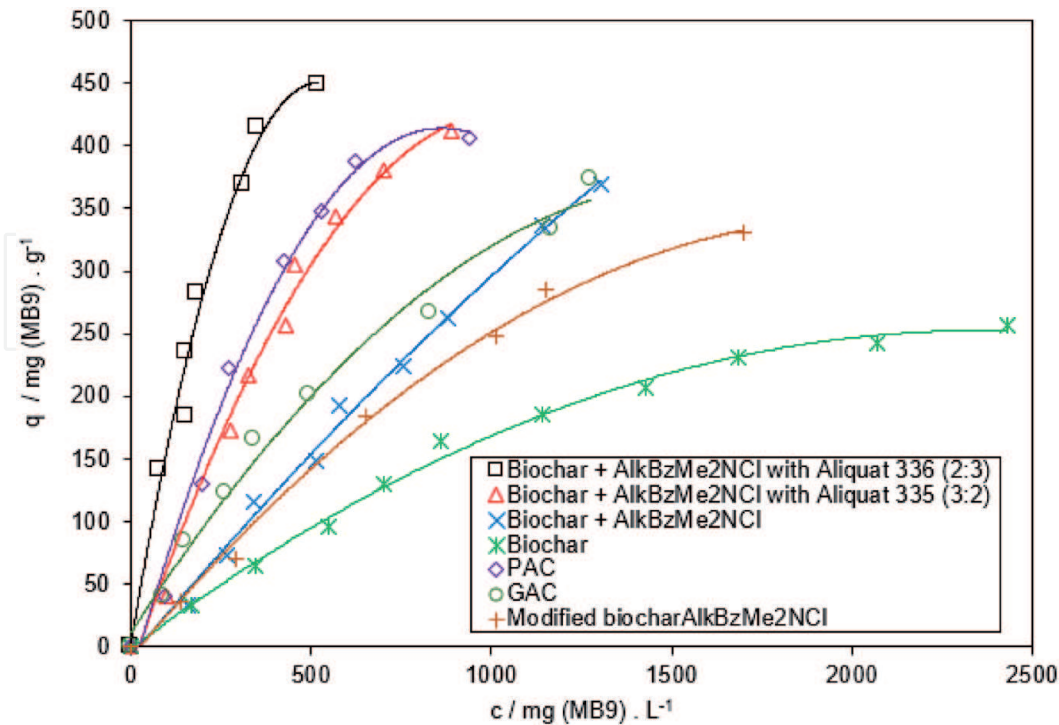

Figure 12.
The dependence of sorption capacity of powdered (PAC) and granulated (GAC) active carbons, biochar, modified biochar and biochar in co-action with R4NCls on the equilibrium concentration of the MB9 solution.

Contaminant	Sorbent	q_{cont} (mg/g)	Ratio of increasing capacity (q_{cont}/q_{cont}^*)
MB9	Biochar	257.1[*]	—
	Modified biocharAlkBzMe$_2$NCl	329.9	1.283
	Biochar + AlkBzMe$_2$NCl	369.6	1.437
	biochar+2/3 A336/50% aq. AlkBzMe$_2$NCl	411.2	1.599
	biochar +3/2 A336/50% aq. AlkBzMe$_2$NCl	448.2	1.743

Value of sorption capacity defined as q_{cont}^*

Table 7.
A comparison of surface modification technique on increasing sorption capacity of MB9.

Sorbent	Freundlich			Langmuir		
	k_F (mg/g) (L/mg)$^{1/n}$	n	R^2	q_{max} (mg/g)	k_L (L/mg)	R^2
PAC	0.91	1.08	0.984	500.0	0.0042	0.772
GAC	1.03	1.17	0.995	526.3	0.0015	0.611
Biochar	0.96	1.36	0.995	384.6	$8.2 \; 10^{-4}$	0.739
Modified biocharAlkBzMe$_2$NCl	0.90	1.24	0.995	357.1	0.0032	0.611
Biochar + AlkBzMe$_2$NCl	0.85	1.20	0.986	476.2	0.0014	0.550
Biochar +2/3 A336/ 50% aq. AlkBzMe$_2$NCl	0.88	1.09	0.985	500.0	0.0035	0.742
Biochar +3/2 A336/ 50% aq. AlkBzMe$_2$NCl	1.19	0.99	0.985	555.6	0.0058	0.768

Table 8.
Identified parameters in Langmuir and Freundlich isotherm models for MB9 (used in initial concentration range 0.5–5.5 g/L) adsorbed by sorbents.

the formation of negatively charged MB9 anions increases due to the ionization. The surface site of charcoal does not favor the adsorption of dye anions due to the electrostatic repulsion [18].

It has been observed, however, by Kosyiyakanon et al. that the addition of R_4NCls to the biochar enables the high efficiency of acid dyes removal even in a broad pH area from 3 to 9 [15].

This fact could be explained by the formation of low-soluble high-molecular ion pairs (dye-SO_3NR_4) by the ion exchange reaction between the added R_4NCl and -SO_3Na groups bound in the structure of dye according to the scheme:

$$\text{dye-}SO_3Na + R_4NCl \longrightarrow NaCl + \text{dye-}SO_3NR_4 \text{ (ion-pair)}.$$

As could be seen in **Figure 12**, biochar is the worst sorbent; however, using R_4NCls selected similarly to abovementioned separation of chlorinated aromatic carboxylic acids sodium salts, the sorption capacity rises efficiently.

As the sorption capacities for the removal of chlorinated aromatic sulfonic acid sodium salt MB9 were (biochar +3/2 A336/50% aq.

AlkBzMe2NCl) > PAC ~ (biochar+2/3 A336/50% aq.AlkBzMe2NCl) > GAC ~ (biochar + AlkBzMe2NCl) > (modified biocharAlkBzMe2NCl) > biochar, this indicated that the combined action of the sorted R_4NCls mixture and biochar could specifically increase the sorption capacity for the used biochar above the adsorption capacity of commercial powdered active carbon Silcarbon CW20 (**Figure 12** and **Table** 7).

Langmuir and Freundlich isotherm models were fitted to the data. Similarly, the correlation coefficients suggest that the Freundlich model fits the data better than the Langmuir model (**Table 8**). This indicates that MB9 and/or ion pairs R_4N.MB9 were adsorbed in multilayers into the active sites of the biochar surface.

In case of the tested acid dye, the sorption capacity of the ex situ-prepared modified BiocharAlkBzMe$_2$NCl is closer to the sorption capacity of in situ-mixed R_4NCls with biochar (**Figure 12**). The observed higher sorption capacity of modified biocharAlkBzMe$_2$NCl in comparison with biochar agrees with the published results by Mi et al. [13] and Kosaiyakanon [15]. This observation is in good agreement with hard and soft acids and bases (HSAB) theory [19]. According to the HSAB principle, cations of hard bases (AlkBzMe$_2$N$^+$) prefer to bond to anions of hard acids (dye-SO$_3^-$). Probably due to this reason, the observed removal efficiency of used modified biocharAlkBzMe$_2$NCl is higher in case of MB9 removal than in the application for removal of anions of soft carboxylic acids DCF and FLUFA.

6. Conclusions

Biochar obtained as a by-product in the gasification process of waste biomass was verified as a suitable sorbent for the removal of the three tested highly mobile, ionizable, and nonbiodegradable chlorinated aromatic acid sodium salts NaDCF, NaFLUFA, and MB9 from model wastewater solutions in a broad range of concentrations. For increasing biochar's removal efficiency, biochar was intentionally mixed with selected cationic surfactants to produce an in situ-modified sorbent designed for the effective removal of the abovementioned negatively charged pollutants even from alkaline aqueous solutions. The higher efficiency obtained using biochar mixed in situ with selected R_4NCls in model wastewater could be explained by the multilayer adsorption of ion pairs (contaminant-COONR$_4$ or contaminant-SO$_3$NR$_4$, respectively) on the heterogeneous biochar surface described by Freundlich isotherms.

We demonstrated that a more laborious two-step technique, based on the initial preparation of impregnated biochar by the action of R_4NCl with subsequent application of this modified sorbent, is much less effective than simple mixing of biochar with R_4NCl directly in the treated wastewater solution. According to the performed experiments, cationic surfactants based on tetraalkylammonium chloride R_4NXs carrying highly branched R_4N$^+$ cations were verified as very effective for the uptake of NaDCF, NaFLUFA, and MB9 from aqueous solutions by the co-action of biochar. The most effective R_4NX for the removal of these contaminants was verified Aliquat 336, which is, however, highly viscous and nonmiscible with water. Its dilution with an organic solvent is prohibited due to environmental reasons. From a practical point of view, we successfully tried and chose the application of the mixture containing three parts of A336 dissolved in two parts of 50 wt.% aqueous AlkBzMe$_2$NCl, having acceptable removal efficiency for the studied contaminants and enabling the simple and precise addition of the most effective A336 cationic surfactant together with the tested biochar for effective wastewater treatment. This technique based on joint addition of selected R_4NCls together with biochar enables attainment of removal

efficiency comparable with commercial active carbons containing at least twice higher specific area as biochar. These obtained results agree with the information by Xi et al. [20] which observed that the surface area of the used sorbent by the co-action of R_4NX does not play a major role in sorption of anionic contaminants.

7. Experimental details

Additional used chemicals (benzalkonium chloride 50 wt.% aqueous solution (AlkBzMe$_2$NCl), Aliquat 336 (A336), hexadecyltrimethylammonium chloride (AlkMe$_3$NCl), diclofenac sodium salt (NaDCF, 98%+, Mr = 303.21), flufenamic acid (FLUFA, 98% + Mr = 281.23), Mordant Blue 9 (MB9, purity, 50% Mr = 551.28), and octan-1-ol, etc.) were purchased from Sigma-Aldrich, Czech Republic.

Powdered active carbon (PAC) Silcarbon CW20 (specific area 1300 m^2/g) was obtained from Brenntag Co. Granular active carbon (GAC) Hydraffin CC8x30 (specific area 1000 m^2/g) was purchased from Donau Carbon GmbH & Co.

Demineralized water was used for the preparation of the used aqueous solutions.

7.1 Preparation of used stock solutions

25 mM aqueous diclofenac stock solution was obtained by a dissolution of 8.0 g of NaDCF in 1 liter of water; the pH of the stock solution was 8.7. Aqueous 10 mM stock sol. of NaFLUFA was obtained by a dissolution of 2.81 g of flufenamic acid in 12 mM aqueous NaOH (pH = 10.3). Aqueous 25 mM stock sol. of NaFLUFA was obtained by a dissolution of 7 g of flufenamic acid in 30 mM aqueous NaOH (pH = 10.3). Aqueous 10 mM solution of MB9 was obtained by a dissolution of 11.0 g of MB9 (50% purity) in 1 liter of water (pH = 8.2).

7.2 Preparation of the mixtures of A336 with aqueous 50% AlkBzMe$_2$NCl

Solution 3/2 A336/50% aq. AlkBzMe2NCl.
30 g of Aliquat 336 was dissolved in 20 g (21 mL) of 50 wt. % aqueous AlkBzMe$_2$NCl under stirring.
Solution 2/3 A336/50% aq. AlkBzMe2NCl.
20 g of Aliquat 336 was dissolved in 30 g (32 mL) of 50 wt. % aqueous AlkBzMe$_2$NCl under stirring.

7.3 Preparation of ex situ modified biochar

Modified biocharAlkBzMe$_2$NCl was prepared by impregnation of biochar (20 g) using 5 wt.% aqueous AlkBzMe$_2$NCl (100 mL) under vigorous stirring at 500 rpm overnight, subsequent filtration, filter cake washing with 400 mL of water, and drying of washed filter cake at 105°C to a constant weight.

7.4 Applied analyses

A Hach DR2800 (Austria) VIS spectrophotometer was employed for the absorbance measurements using 1 cm glass cuvettes. The concentrations of MB9 and R_4N.MB9 were determined by measuring at the maximum absorbance (A_{max}) [7, 8].

Concentration of NaDCF and NaFLUFA was determined by voltammetric determination at carbon paste electrode in situ modified by AlkMe$_3$NCl cetyltrimethylammonium bromide (CTAB) [21]. Electrochemical measurements were carried

out using an AUTOLAB analyzer (model PGSTAT-128 N; Autolab/Metrohm, the Netherlands/Switzerland), coupled with the three-electrode cell incorporating the working carbon paste electrode (CPE), containing the hand- homogenized carbon paste containing 0.5 g graphite powder (product "CR-5"; Maziva, Czech Republic) and 0.3 mL paraffin oil (Uvasol® grade; Merck, USA). This paste mixture was then manually filled into a piston-driven electrode body. The remaining electrodes were a Ag/AgCl/3.5 M KCl reference and a platinum auxiliary electrode (both from Metrohm).

It was confirmed that the anodic oxidation of NaDCF at the CPE gives rise to a well-developed signal with a peak potential of about +0.6 V vs. Ag/AgCl/3.5 M KCl (further denoted as "ref.") and anodic oxidation of NaFLUFA at the CPE gives rise to a well-developed signal with a peak potential of about +0.78 V vs. ref. Almost identical responses for measurements with differential pulse and square-wave voltammetry (DPV and SWV, respectively) have indicated that the reaction of interest is not kinetically controlled and hence suitable for (electro)analytical purposes. Therefore, measurements of all water samples were performed using DPV. It was also found that the most favorable response could be obtained in neutral media, whereas more alkaline solutions had already caused a decrease of the first peak and the total disappearance of the second one. Thus, pH 7.0 was definitely set as optimal; therefore, phosphate buffer (PBS) at pH 7.0 was used for all measurements.

Because the respective measurements had not sensitive response, electrochemical measurements were extended to the effect of a modifier on a possible enhancement of the response. Such a modification is very simple as it can be realized in situ; i.e., by adding a small amount of surfactant directly to the sample analyzed. This can be exemplarily illustrated in **Figure 13**, portraying the effect of CTAB that had
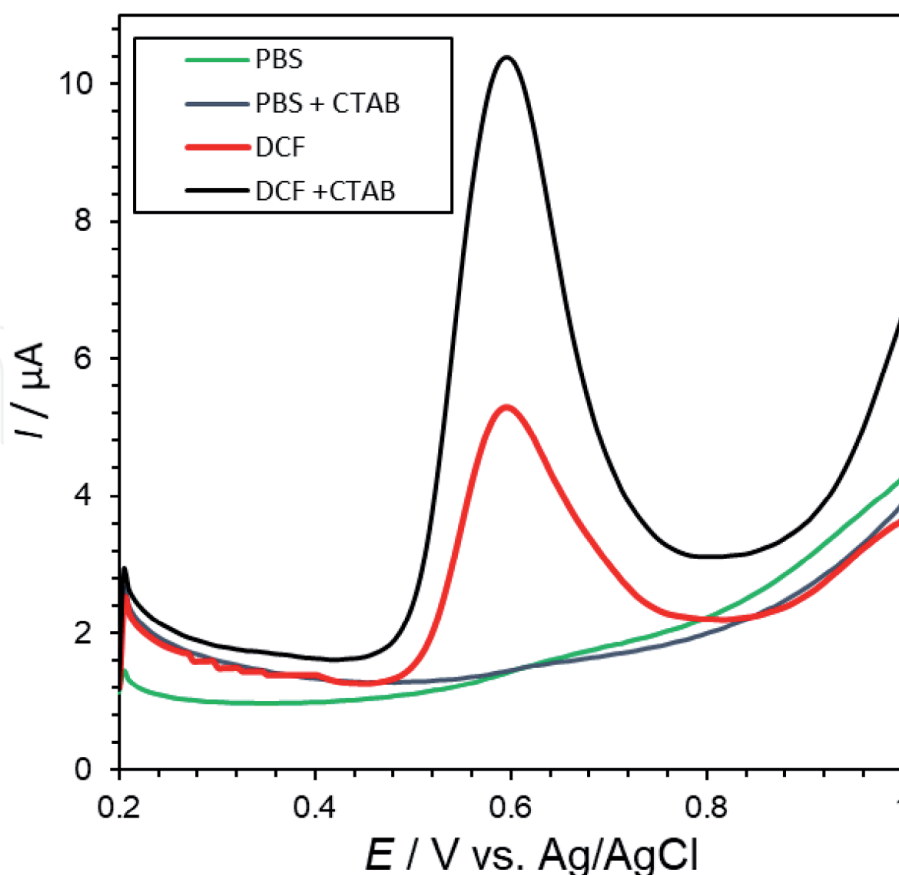

Figure 13.
The main oxidation peak of NaDCF and the effect of the presence of cetyltrimethylammonium bromide (CTAB) surfactant in the solution and phosphate buffer baseline (PBS) [19].
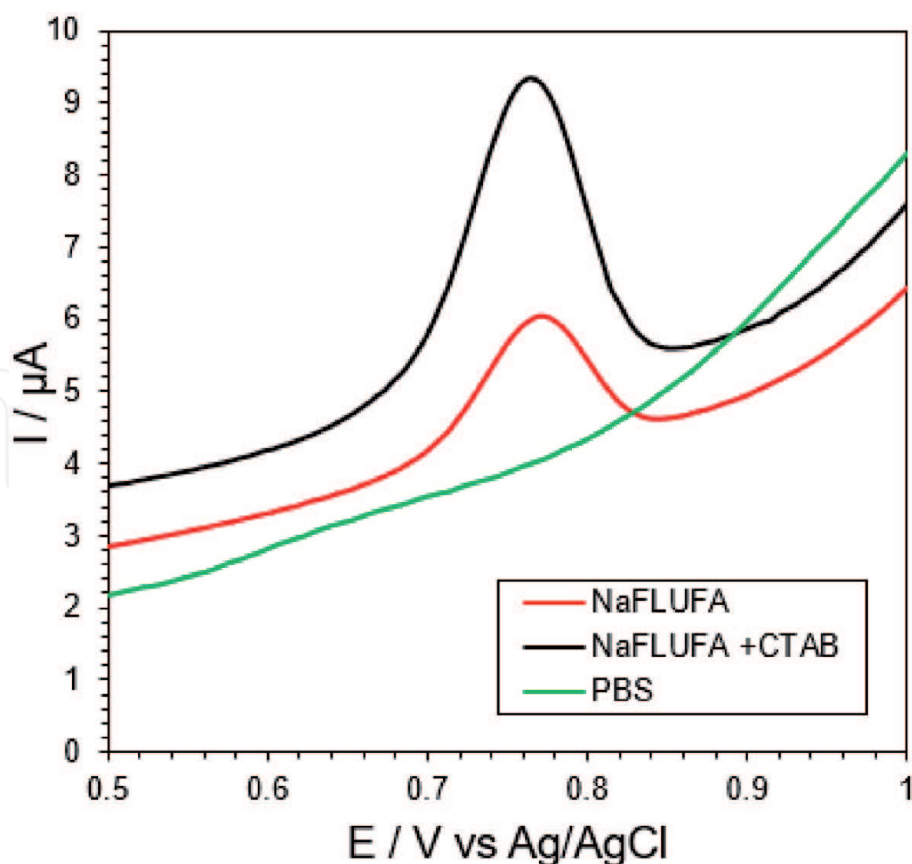
Figure 14.
The main oxidation peak of NaFLUFA and the effect of the presence of cetyltrimethylammonium bromide (CTAB) surfactant in the solution and phosphate buffer baseline (PBS).

been found the most effective for this function among all the surfactants tested. The observed benefit of CTAB was attributed to the (pre)treatment of CPE by means of "erosion effect." The same modifier effect was observed for NaFLUFA, as could be seen in **Figure 14**.

Typical experimental and instrumental conditions of NaDCF and NaFLUFA voltammetric determination (DPV) had included the following parameters: supporting electrolyte 0.1 M PBS + 0.1 mM CTAB, potential scan from +0.2 to 1.2 V vs. ref., and scan rate of 50 mV/s.

7.5 Sorption experiments

Sorption experiments were carried out in a magnetically, at 400 rpm, stirred 250 mL round-bottomed flasks at 25°C using Starfish equipment installed on an electromagnetic stirrer Heidolph-Hei-Standart with a temperature sensor Pt1000. The appropriate quantity of biochar was added to 100 mL of synthetic wastewater (possibly after the addition of $R_4NCl(s)$). In performed kinetic experiments (**Figures 2**, **3**, **5**, **6**, and **8**), the initial concentration of NaDCF in synthetic wastewater was 25 mM (8 g NaDCF/L and pH = 8.7), the concentration of FLUFA in synthetic wastewater was 10 mM NaFLUFA in 12 mM NaOH (2.81 g FLUFA/L and pH = 10.3), and the concentration of MB9 was 10 mM (5.5 g MB9/L). In a subsequent comparative study for the construction of adsorption isotherms (**Figures 10–12**), the concentrations of contaminants in starting aqueous solutions were 0.25–8 g NaDCF /L, 0.25–7 g -FLUFA/L, and 0.5–5 g MB9/L (for additional information see the text and Figures and Tables in the previous chapters). Stirred suspensions were immediately filtered and analyzed after an appropriate time period.

Experiments dealing with log P_{OW} determination were performed using the same apparatus. An aqueous solution containing 1 mmol of studied contaminant was introduced to the round-bottomed flask (in case of studying log P_{OW} of ion pairs, 1 mmol of R_4NCl per mmol of -COONa or -SO$_3$Na group bound in contaminant was added subsequently); the total volume of aqueous phase was adjusted to 100 mL with water saturated with octan-1-ol, and the mixture was fulfilled using 100 mL of octan-1-ol. The prepared two-phase mixture was agitated at 400 rpm overnight, and the immiscible phases were separated in a separatory funnel, and a concentration of the tested chlorinated aromatic acid sodium salt or their ion pair with R_4N^+ in the aqueous phase was analyzed using VIS spectroscopy in the case of MB9 and $R_4N.MB9$. In the case of NaDCF or $R_4N.DCF$, the concentration in the aqueous phase was analyzed using voltammetric determination.

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