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Influence of dissolved organic carbon nature on adsorption of ibuprofen, caffeine and diclofenac by powdered activated carbon from water

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Abstract: The impacts of structurally different dissolved organic carbon surrogates (DOC) on the adsorption of ibuprofen, caffeine and diclofenac (C_0 2–3 μg L^{-1}) onto powdered activated carbon (PAC) were studied. The efficiency of PAC in a synthetic matrix (SM) was tested when low or high molecular weight DOC surrogates were added. Additionally, the impact of a potential natural coagulant was investigated. Different DOC surrogates differently affected the adsorption of tested organic micropollutants (OMPs). In the first 30 min, a positive impact of all types of surrogates on the adsorption of neutral and hydrophilic caffeine was observed, while for negatively charged ibuprofen and diclofenac, the impacts varied. The low molecular weight DOC (containing amino acids and resorcinol) positively impacted the adsorption of ibuprofen, while effects were not clear for diclofenac. The high molecular weight DOC decreased the degree of adsorption for both compounds. The mass transfer calculations showed that low molecular weight DOC accelerated the transport of OMPs. High molecular weight DOC slowed reaching equilibrium (within 48 h). Thermogravimetry confirmed that the DOC coating qualitatively changes during the adsorption, which also affects the OMPs removal. The addition of a natural coagulant affected ibuprofen and diclofenac adsorption. For neutral caffeine the effects were not clear.

Keywords: dissolved organic carbon surrogates; pharmaceuticals; coagulation.

INTRODUCTION

It is well known[1] that some pharmaceuticals and their metabolites are detected in the effluents of treated wastewater at concentrations ranging from several ng L^{-1} to μg L^{-1}.[1] The efficiency of wastewater treatment is influenced by the effluent organic matter (EfOM), which has a very complex structure.[2] It is measured as the

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content of dissolved organic carbon (DOC). DOC affects the adsorption of organic micropollutants (OMPs) by blocking adsorbent pores with sufficiently large DOC molecules and/or direct binding of low molecular weight DOC to adsorption sites within the pores.[3] Various studies in pure, surface, and groundwater have demonstrated that DOC negatively impacts the adsorption efficiency of OMPs.[4–7] In the study of de Ridder *et al.*[6] the impact of DOC on pharmaceuticals adsorption (C_0 = = 2 μg L^{-1}) on granular activated carbon (GAC) treated with wastewater and surface water was investigated. It was found that the hydrophobicity of DOC originating from wastewater and the presence of smaller molecular fractions in its structure compete with micropollutants more than DOC originating from surface water. Zietzschmann *et al.*[8] also demonstrated that the size of DOC molecules in wastewater treatment plant effluents affects OMPs adsorption, with small DOC molecules causing the most significant competition effects. Guillossou *et al.*[9,10] showed that the contact time of carbon with water plays an important role and that the nature of micropollutants affects DOC influence on adsorption. They proved that a combination of ozonation and activated carbon adsorption is more effective for removing 28 different OMP from wastewater treatment plant effluents compared to adsorption alone, due to the oxidation of DOC and thus reduced absorbability and competition potential. It was observed that the presence of DOC negatively affected the removal of 12 tested OMP (atenolol, carbamazepine, erythromycin, ofloxacin, roxithromycin, trimethoprim, acetaminophen, diclofenac, ibuprofen, lorazepam, oxazepam and sulfadiazine) after 30 min of adsorption (4–60 %) in wastewater treatment plant effluent compared to ultrapure water, in which high removal (≥ 77 %) was achieved within 30 min and 72 h.[10] The positively charged and neutral substances were better removed than negatively charged ones. After 72 h, similar removal efficiency was achieved for 6 of above mentioned 12 OMPs (atenolol, carbamazepine, erythromycin, ofloxacin, roxithromycin and trimethoprim), as in ultrapure water. The difference in removal for positively charged and neutral substances between 30 min and 72 h is explained by insufficient contact time and the possibility that during the 72 h, the competition between OMP and DOC only slows down diffusion transport but does not prevent adsorption. A mechanism of DOC–OMP complex formation was proposed. They gradually adsorb onto the surface of activated carbon over time. These findings highlight the complexity of interactions between DOC and OMP during the adsorption process on activated carbon, which is important for understanding and improving the process of removing micropollutants from wastewater.[10] Anielak *et al.*[11] confirmed that for pollutants with a molecular weight higher than 230 g L^{-1}, interactions with humic substances in the solution become significant. Some studies have used different specific surrogates for DOC molecules, such as methylene blue,[12] congo red[13] and methyl orange[14] to investigate these effects. For example, in the study by Dittmar *et al.*[14] the addition of methyl orange to deionized water

reduced the removal efficiency of carbamazepine (C_0 = 10 μg L^{-1}; from 60 to 30 % for a contact time of 30 min and from 90 to 60 % for a contact time of 48 h) using powdered activated carbon (PAC, 10 mg L^{-1}). π–π interactions between OMPs and DOC, as well as complex formation, have also been mentioned by other authors.[15–17] The recent research[18] has shown that higher aromaticity and lower polarity both enhanced dissolved organic matter (DOM) adsorption, with aromaticity being the dominant factor for adsorption of low molecular weight DOM (<350 g L^{-1}). [18] Wang *et al.*[17] studied the impact of specific low molecular weight DOC molecules (aliphatic and aromatic compounds with hydroxyl, phenolic and carboxyl groups) on OMPs adsorption onto PAC. The study showed that unsaturated structures such as benzene rings, double and triple bonds, as well as DOC hydrophobicity, increase its competition ability, even for structures that are less adsorbable (unsaturated aliphatic compounds) or hydrophilic (polyphenols, alcohols). Besides these naturally occurring structures, the presence of amino acids in real systems is inevitable but insufficiently studied according to our findings in the literature. The amino acids contain both amino and carboxyl functional groups that engage in specific interactions with pollutants and adsorbents (hydrogen bons and electrostatic interactions). These small molecules (L-serine, L-leucine and resorcinol) are recognized in the literature as surrogates for DOC remaining in water treatment after the frequently applied coagulation process.[11] Thus, a particular goal of this work was to examine how their mixture affects the adsorption of frequently detected pharmaceuticals (ibuprofen, caffeine and diclofenac) in the presence and absence of more complex humic acid (HA). In addition to these surrogates, DOC influence was assessed also in the systems where an innovative natural coagulant, a crude extract from bean seeds, was added. It was investigated as an alternative to commercial iron and aluminum-based coagulants in water treatment[1,19,20] and it was confirmed that the addition of an optimal dose for wastewater treatment plant effluent (37.5 μL L^{-1}) does not contribute to an increase in organic carbon content measured by chemical oxygen demand, but may contribute to the removal of total DOC when applied together with the activated carbon adsorption. One closing parenthesis is missing at the end of the sentence/incorrect: In the previous studies it was found that the application of the extract, which in the solution has partially negatively and positively charged molecules, can negatively affect the adsorption of different pollutants from wastewater treatment plant effluent, when a low dose of carbon (5 mg L^{-1}) is applied (e.g. caffeine, the more hydrophobic neutral benzophenone (log D at pH 7.4: 2.96) and benzophenone-3 which also has a negative charge (log D at pH 7.4: 3.64)./correct: In the previous studies it was found that the application of the extract, which in the solution has partially negatively and positively charged molecules, can negatively affect the adsorption of different pollutants from wastewater treatment plant effluent, when a low dose of carbon (5 mg L^{-1}) is applied (e.g. caffeine, the more hydrophobic

neutral benzophenone (log D at pH 7.4: 2.96) and benzophenone-3 which also has a negative charge (log D at pH 7.4: 3.64). At a dose of 20 mg L^{-1}, such effects were absent for the mentioned three substances, as well as for neutral molecules of carbamazepine (log *D* at pH 7.4: 2.28) and triclosan (log *D* at pH 7.4: 5.13). In this study it was examined whether the addition of such a material affects the adsorption of ibuprofen, caffeine, and diclofenac in cleaner water matrices, enriched only with DOC surrogates, without other components considered as EfOM.

EXPERIMENTAL

The influence of DOC nature on activated carbon efficiency was examined by testing the capability of PAC to remove pharmaceuticals in 30 min, in several different water matrices: without the addition of DOC surrogates – synthetic matrix (SM), and with the addition of different low and high molecular weight DOC surrogates, into SM, both separately and in combination, to achiveDOC concentrations resembling natural levels (2.5–3.5 mg L^{-1}, Table I). All details related to materials used (activated carbon, natural coagulant, water matrices, DOC surrogates, OMPs aqueous solution preparation) are provided in the Supplementary material o this paper under the stion Heading materials./correct: All details related to materials used (activated carbon, natural coagulant, water matrices, DOC surrogates, OMPs aqueous solution preparation) are provided in the Supplementary material of this paper under the section heading Materials.

TABLE I. The aqueous matrices used in the experiments

Type of matrix	Abbreviation in text	DOC mg L^{-1}
Synthetic matrix (SM)	SM	<0.5
SM with the addition of low molecular weight DOC surrogates – mixture of L-serine, L-leucine and resorcinol	SRL	2.47
SM with the addition of high molecular weight DOC surrogates – humic acid	HA	3.46
SM with the addition of both high and low molecular weight DOC surrogates (humic acid and the mixture of L-serine, L -leucine and resorcinol)	HA-SRL	2.53

Testing was performed with and without the simultaneous dosing of natural coagulant isolated from the bean seeds (dosage 37.5 μL L^{-1} selected based on its efficiency in removing organic matter from wastewater treatment plant effluent, details presented in Marjanović *et al.*[1]). The choice of the PAC contact time was based on real applications rather than reaching equilibrium. However, further tests that were 48 h long were performed to assess the kinetics of the adsorption in the different water matrices. In addition, the thermogravimetric analysis was used for the characterization of sorbents that were soaked for different times in solutions containing DOC surrogates in order to investigate the coating of DOC on the surface of PAC.

All the details related to experimental methodologies applied are provided in the Supplementary material under the section Heading methods.

RESULTS AND DISCUSSION

The efficiency of the 30-min adsorption onto PAC

In Fig. 1 the efficiency of powdered activated carbon (dose 5 mg L^{-1}, contact time 30 min) is presented separately and in combination with a natural coagulant (dose 37.5 μL L^{-1}) for the removal of ibuprofen, caffeine and diclofenac (C_0 2–3 μg L^{-1}) from a synthetic matrix, a synthetic matrix with added low molecular weight DOC surrogates, high molecular weight DOC surrogates and their combination. All experiments were performed in duplicate, and the results are presented accordingly, indicating satisfactory repeatability in the vast majority of cases. Only in the case of ibuprofen in the SM, and in the case of diclofenac in the HA-SRL matrix, was poorer reproducibility of the experiments observed.

It has been shown that without the addition of surrogates, 30 min adsorption on PAC in SM in one case did not achieved significant removal for ibuprofen while in duplicate experiment it was 28 %. The values for caffeine and diclofenac were more consistent – 48 and 50 % for caffeine and 83 and 87 % of diclofenac. A relevant positive effect of DOC on the adsorption was observed for ibuprofen a hydrophilic and negatively charged molecule, in matrices containing DOC exclusively of low molecular weight (removal increased up to 90 %, analytical method bias 4.6–14 %, Supplementary material, Table S-III) and in combination with HA (up to 40–60 % removal, analytical method bias 7.2–10 %, Table S-III). Considering the analytical method bias (Table S-III), HA alone reduced the ibuprofen adsorption, likely due to the lack of specific interactions with small molecules (*e.g.*, hydrogen bonds and complex formation with amino acids) and competition of negatively charged molecules during adsorption on positively charged carbon (the isoelectric point of the PAC is 9.81).[21] For hydrophilic, but neutral caffeine, all types of surrogates positively influenced the removal efficiency. The reason for the absence of commonly observed DOC competition effects, confirmed in the literature, may be the unimpeded sorption of caffeine on DOC coatings. For negatively charged diclofenac, expected negative effects on adsorption were observed in matrices containing HA, probably due to competition with negative HA molecules, while the positive effects of the SRL matrix could not be observed. The reason for this is unknown. Based on log *D* at relevant pH 7.4, diclofenac is less hydrophilic than ibuprofen (Supplementary material, Table S-I).[22] However, some literature data show that there are no large differences between log *D* values when other software is used for the calculations.[23,10] In any case, diclofenac is a larger molecule with two aromatic rings, containing nitrogen and chlorine which are both capable of electron withdrawal, while ibuprofen has only one aromatic ring and has no other heteroatoms than oxygen. Relevant positive effects in terms of improved adsorption with the addition of a natural coagulant were also observed only for ibuprofen, both in the absence of DOC surrogates and in the presence of HA

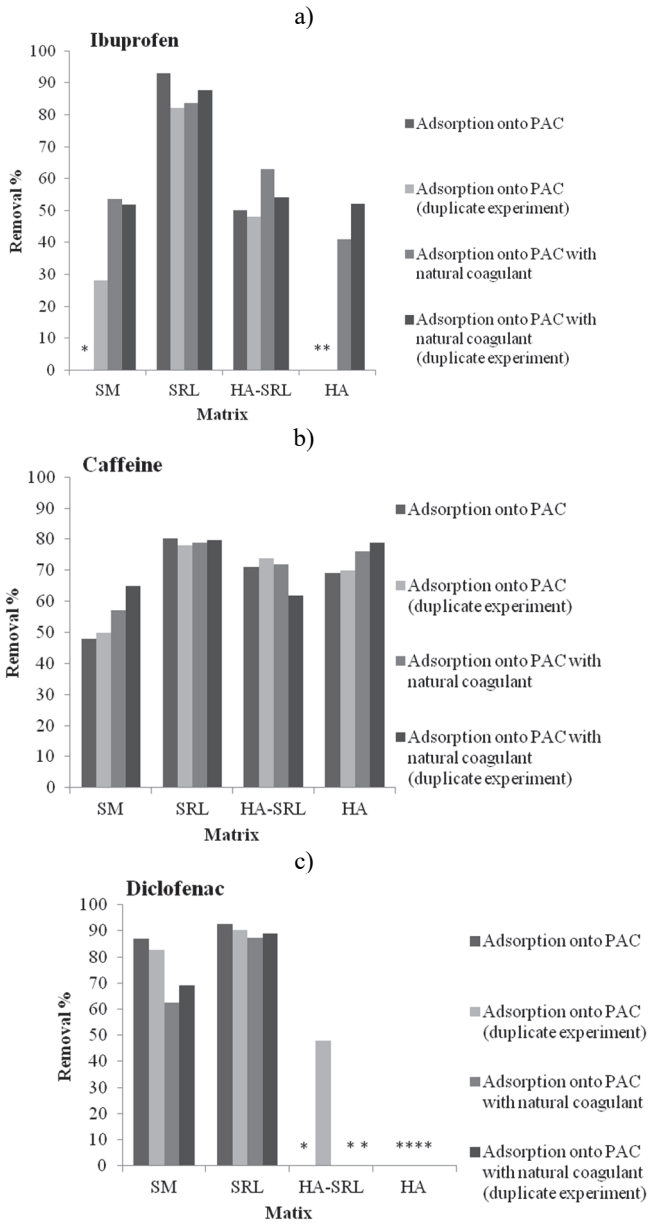

Fig. 1. Results of the study on the efficiency of PAC (dose 5 mg L^{-1}) in combination with a natural coagulant (dose 37.5 µL L^{-1}) for the removal of: a) ibuprofen, b) caffeine and c) diclofenac, C_0 2–3 µg L^{-1}, contact time 30 min; * – no removal achieved; SM – synthetic matrix, SRL – synthetic matrix with added low molecular weight DOC surrogates (a mixture of L-serine, L-leucine and resorcinol), HA-SRL – synthetic matrix with the addition of the aforementioned low molecular weight DOC mixture and humic acid, HA – synthetic matrix with added high molecular weight DOC surrogates (humic acid).

alone (Fig. 1a). In the case of diclofenac (Fig. 1c), the addition of the coagulant to the matrix without surrogates had the opposite effect, reducing the adsorption, likely due to the possibility of preventing the large diclofenac molecule from reaching the adsorption sites due to competition with small molecules of the SRL matrix.

In cases of matrices containing HA, observed differences were of the order of analytical method bias (7–40%) and cannot be considered relevant. It can be concluded that the structure of the negatively charged molecules and the size of the DOC surrogates affect the degree of pollutant removal, and that the natural coagulant induces the same type of effect as HA in the given system. Some of the obtained results are opposite to most frequently reported result in literature that DOC decrease the removal of OMPs due to competition effects. It should be noted that in comparison to literature, very low concentrations of OMPs are used in this study as well as the low PAC dose. As mentioned before, the possible specific interactions between the selected pollutants and the chosen DOC surrogates, might be the reason for this. Table II summarizes the results of the impact of the natural coagulant on the adsorption of ibuprofen, caffeine, and diclofenac in matrices with different types of DOC surrogates.

TABLE II. The impact of a natural coagulant on the adsorption of ibuprofen, caffeine and diclofenac in matrices with different types of dissolved organic carbon (DOC) surrogates (only differences higher than analytical method bias taken into account); +: positive impact; –: negative impact; *: no impact; SM – synthetic matrix, SRL – synthetic matrix with added low molecular weight DOC surrogates (a mixture of L-serine, L-leucine and resorcinol), HA-LSRL – synthetic matrix with the addition of the aforementioned low molecular weight DOC mixture and humic acid, HA – synthetic matrix with added high molecular weight DOC surrogates (humic acid)

Type of matrix	Ibuprofen	Caffeine	Diclofenac
SM	+	*	–
SRL	*	*	*
HA-SRL	*	*	–
HA	+	*	*

The previous work with wastewater treatment plants effluent[1] and same carbon dose, showed mainly negative effects of the natural coagulant addition on the removal of caffeine and the more hydrophobic neutral benzophenone and negatively charged benzophenone-3. In the cleaner water matrices used in this work, no negative effects for caffeine were observed (Fig. 1c). However, similar to the previous case, negative effects were observed for diclofenac in the SM and HA-SRL matrices. Conversely, for ibuprofen, a positive effect was observed, but it was significant only when there were no small molecule DOC surrogates in the matrix. Prodanović[24] demonstrated that the isoelectric point (pI) of the raw bean extract is 3.61. This means that most macromolecules in the raw bean extract are

negatively charged at the pH at which the experiments were conducted (pH around 7.5). However, the electrostatic interactions with negative OMPs are possible due to the partially positive charge of peptide bonds and the probable formation of hydrogen bonds, which can also be influenced by the size of the molecules (ibuprofen is smaller than diclofenac, Table S-I). A similar mechanism could be proposed for the observed effects of DOC surrogates on adsorption due to the presence of positively charged amino groups in the DOC surrogates. Such interactions most probably can form complexes that may be more easily adsorbed onto activated carbon, provided that the interactions between the carbon surface and other parts of the molecule in the formed complex are favourable (*e.g.*, electrostatic, van der Waals interactions, hydrogen bonds and π–π interactions). This confirms the earlier hypotheses about the complexity of the pollutant and the DOC interactions in the adsorption process, which require deeper investigation to potentially utilize their existence for the improvement of water treatment process performance.[10,15–17]

Adsorption kinetics of ibuprofen, caffeine and diclofenac under different water matrices

The removal efficiencies of ibuprofen, caffeine and diclofenac in kinetic experiments at a PAC dose of 5 mg L^{-1} are presented in Table S-III. It was found that different DOC surrogates affect the rate of establishing adsorption equilibrium differently. In some cases, desorption and adsorption occurred over 48 h. For all three OMPs equilibrium was established after 2 h in the synthetic matrix (SM). The addition of small DOC molecules (SRL) did not affect the time needed to reach it. However, the addition of HA extended the time required to establish equilibrium for all three substances to 24–48 h. In the synthetic matrix, with added high molecular weight DOC, adsorption equilibrium is established only after 24 h or, in the case of ibuprofen, even later. In the synthetic matrix with added DOC surrogates of both small and large molecules, the concentration of ibuprofen (one of the two experiment duplicates) and caffeine (both experiment duplicates) is already below the practical quantitation limit of the method after 2 h of contact, while for diclofenac, the adsorption equilibrium is established later, after 24 h.

Table III shows products of film mass transfer coefficients (k_F / m min^{-1}) of ibuprofen, caffeine and diclofenac and total surface area of the adsorbent mass available in the reactor (a_m / m^2 g^{-1}). Based on the experiments within the first 15–30 min (depending on whether linearity is obtained in the initial part of the curve) and based on Eq. (S-1) in the Supplementary Material, describing the ln (C/C_0 *vs*. time, it was possible to compare the product of the multiplication of the a_m and k_F.

The carbon mass and the reactor volume were the same in all experiments. Since the a_m can be considered the same in all experiments due to the same PAC dose, the products of two numbers can be used for the relative comparison in

different water matrices. It is important to note that the contact times (0, 15 and 30 min) used for this purpose were relatively long, but this approach was the only possible having in mind the time needed for the manipulation of a larger sample volume (500 mL), which was necessary at the chosen concentration level.

TABLE III. Product of the total surface area of the adsorbent mass available in the reactor (a_m / m^2 g^{-1}) and mass transfer coefficient (k_F / m min^{-1}) through the film for ibuprofen, caffeine and diclofenac

Type of matrix	Ibuprofen		Caffeine		Diclofenac	
	t / min	r^2	t / min	r^2	t / min	r^2
SM	0; 15	0.9530	0; 15; 30	0.9969	0; 15	0.9986
	0.014		0.004		0.025	
SRL	0; 15;	0.9988	0; 15;	0.9998	0; 15;	0.9999
	0.027		0.022		0.031	
HA	0; 15;	1.0000	0; 30;	1.0000	0; 15;	1.0000
	0.006		0.008		0.005	
HA-SRL	0; 15; 30;	0.9845	0; 15; 30;	0.9839	0; 15; 30;	0.8051
	0.005		0.008		0.003	

The differences in mass transfer coefficients between the tested pharmaceuticals are most pronounced in the synthetic matrix where there are no interacting DOC surrogates. The largest molecule, diclofenac, which is negatively charged exhibits the fastest transport through the film. Conversely, caffeine transports most slowly toward positively charged carbon particles. The calculations showed an acceleration in the SRL matrix, whereas slowdown was observed in matrices containing HA for negatively charged compounds in comparison to SM. In the presence of small DOC molecules, all have 1.2–5 times higher mass transfer coefficients through the film. The given fact is particularly pronounced for ibuprofen and caffeine, contrary to the results reported by Zeitzschmann *et al.*[8] where small DOC molecules caused the greatest competitive effects. According to Wang *et al.*[25] low molecular weight molecules do not universally compete with organic micropollutant adsorption onto activated carbon. The competitive impact varied significantly depending on the absorbability of the specific OMPs (caffeine, carbamazepine, sulfamethoxazole). It was reported that poorly adsorbable DOC even can contribute to adsorption of OMPs due to their complexation. Further investigation of Wang *et al.*[18] showed that aromatic DOM did not significantly compete with OMPs (caffeine, sulfamethoxazole and carbamazepine) since the highly aromatic and polar fraction of DOM exhibited lower adsorption competitiveness than the less aromatic and less polar fraction.[18] This confirms that in addition to the DOC size, the type of DOC molecule affects competition. It is hypothesized that DOC molecules such as small amino acids containing amino groups can facilitate additional interactions between OMPs and DOC in solution, thereby accelerating transport through the film to the particle surface. Ibuprofen and diclofenac

(negatively charged ions, Table S-I) can engage in electrostatic interactions with the carbon itself (applied PAC isoelectric point 9.8, indicating positive charge at pH 7.5),[21] whereas transport of the neutral molecule caffeine accelerates up to five times likely due to different interactions such as SRL–carbon and SRL–caffeine. Conversely, the addition of large DOC molecules (HA) slows down ibuprofen and diclofenac transport 2–5 times compared to the synthetic matrix, while caffeine transport still can speed up 2 times. Similar effects were observed when small DOC molecules were present in the matrix along with large molecules (HA-SRL). Overall, these interactions affect the time to establish adsorption equilibrium, which is achieved after 48 h, consistent with the findings of Guillossou *et al.*[10]

Thermogravimetric (TG) characterization of native sorbent and sorbent coated with various types of DOC surrogates

The results of TG measurements are presented in Supplementary material, Fig. S-1a, b and c. TG and derivative thermogravimetric (DTG) curves are shown for carbons that were exposed to different types of DOC surrogates for short-term (30 min) and long-term (24 h). The freshly filtered model matrices at first lose water up to ~100 °C. Since the water content of the samples highly depends on the temperature, relative humidity and time between filtering and thermal measurement, only the properties after water evaporation above 100 °C are analysed here. The sample of native PAC without coating showed no change in weight and therefore was omitted from further discussion. The PAC exposed to model matrix with low molecular weight DOC (PAC-SRL), analysed after 30-min contact, loses 1.2 and 1.3 % of the weight in two low-intensity steps through a wide temperature range with DTG maxima at 191 and 359 °C, respectively (Fig. S-1a). Differently, the same mixture after 24 h contact shows only one weight loss step of 3.3 % with DTG maximum at 356 °C (Fig. S-1a). This weight decrease is also detected in a wide range. The difference in between the two materials indicates that the sorbent surface changes during 24 h. The higher weight loss in only one step suggests that a coat of higher amount of low molecular weight DOCs is formed on the surface of PAC after longer contact.

Fig. S-1b shows the results for the PAC exposed to the model matrix with high molecular weight DOC (PAC-HA), after 30 min and 24 h. After 30 min contact weight loss happens in two steps, like in the previous case. In the first one 0.8 % with DTG maximum at 207 °C, and in the second step 8.6 % with DTG maximum at 432 °C. After 24 h contact in the first step lost a higher amount of weight (1.3 %) and in the second one, a somewhat lower weight (5.8 %) than after 30 min contact. The overall weight loss tendency of this sample suggests that up to ~400 °C the contact time between the PAC and HA does not affect the thermal properties of the sample. Above this temperature, the lower weight loss in the sample after

24 h may be the consequence of the change in interactions between the PAC and the HA during 24 h in comparison to 30 min contact time.

In the model matrix with both types of DOC (PAC-HA-SRL) the weight loss steps were distinguished only in the sample after 30 min contact their DTG maxima are at 148, 208 and 399 °C (Fig. S-1c). In the first two steps, the overall weight loss is 1.1 %, and in the third 7.8 %. After 24 h contact, only one step can be distinguished with DTG maximum at 403 °C and weight loss of 7.1 % (Fig. S-1c). In this matrix, the missing DTG peak at 207 °C, which is detected on the DTG curve of PAC-HA for 24 h, and the different shape of the DTG peak at 403 °C compared to PAC-HA and PAC-SRL suggest some intermolecular interactions between HA and SRL. This confirms the very complex dynamic nature of DOC––PAC interactions which may also affect the adsorption of pharmaceuticals during different contact times in addition to PAC interaction with pharmaceuticals and DOC interactions with pharmaceuticals in solution.

CONCLUSION

This study highlights the role of dissolved organic carbon in the removal of organic micropollutants and its complex interactions with the micropollutants and the adsorbents. The results show that the presence of DOC enhanced the initial adsorption of caffeine independently of molecular weight of DOC surrogates. In contrast, the ibuprofen adsorption increased only in low molecular weight DOC matrices while the adsorption of diclofenac was not affected by this kind of matrix. The high molecular weight DOC (*e.g.*, humic acid) reduced the adsorption of negatively charged compounds (ibuprofen and diclofenac), suggesting competitive interactions. It has been demonstrated that the lower molecular weight DOC surrogates enhance the adsorption rates, whereas higher molecular weight ones slow the process. The natural coagulant affects the adsorption of only negatively charged compounds, but in different ways for different compounds. The thermogravimetric analysis revealed that DOC coatings on powdered activated carbon (PAC) evolved over time, providing the opportunity for altering interactions with pollutants and affecting adsorption efficiency.

Having in mind the observed effects of DOC quality on adsorption of OMPs, the next interesting topic for the research can be the evaluation of PAC's reuse across multiple cycles in water matrices containing DOC of different characteristics. This should include the aspects of harvesting the PAC after the adsorption stage in water treatment train and its preparation (conditioning) for the reuse not only in water treatment but also in other environmental applications (*e.g.*, soil amendments).

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/13067, or from the corresponding author on request.

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И З В О Д

УТИЦАЈ ПРИРОДЕ РАСТВОРЕНОГ ОРГАНСКОГ УГЉЕНИКА НА АДСОРПЦИЈУ ИБУПРОФЕНА, КОФЕИНА И ДИКЛОФЕНАКА ПРИМЕНОМ АКТИВНОГ УГЉА У ПРАХУ ИЗ ВОДЕ

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У овом раду је испитан утицај структурно различитих сурогата растворене органске материје (DOC) на адсорпцију ибупрофена, кофеина и диклофенака (C_0 2–3 μg L^{-1}) применом активног угља у праху (PAC). Испитана је ефикасност PAC у синтетичком матриксу (SM) са додатком сурогата DOC мале или велике молекулске масе. Такође, истраживан је и утицај додатка природног коагуланта. Сурогати DOC су различито утицали на адсорпцију различитих органских микрополутаната (OMP). У првих 30 min примећен је позитиван утицај свих врста сурогата на адсорпцију неутралног и хидрофилног кофеина, док је за негативно наелектрисани ибупрофен и диклофенак утицај варирао. Матрикс са сурогатима DOC мале молекулске масе (који садржи аминокиселине и резорцинол) позитивно је утицао на адсорпцију ибупрофена, док за диклофенак ефекти нису били јасни. Сурогати DOC велике молекулске масе умањили адсорпцију за оба једињења. Апроксимација брзине транспорта OMP кроз филм указује да DOC мале молекулске масе убрзава транспорт ибупрофена, кофеина и диклофенака у односу на синтетички матрикс. Сурогати DOC велике молекулске масе узроковали су споријe достизање равнотеже (у року од 48 h). Термогравиметрија је потврдила да се DOC превлака на PAC квалитативно мења током адсорпције што такође утиче на уклањање OMP. Додавање природног коагуланта утицало је на адсорпцију ибупрофена и диклофенака. За неутрални кофеин, ефекти нису били јасни.

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