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SUPPLEMENTARY MATERIAL TO

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

TIJANA MARJANOVIĆ[1]*, MINJA BOGUNOVIĆ KOLJAJA[1], JELENA PRODANOVIĆ[2], BERTA BARTA HOLLÓ[1] and IVANA IVANČEV-TUMBAS[1]

[1]University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia and [2]University of Novi Sad, Faculty of Technology Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia

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MATERIALS

Activated carbon

The activated carbon used in the experiments was NORIT SAE (according to the manufacturer's specifications, with a BET surface area of 1150 $m^2 g^{-1}$ and a particle size of D50 15 μm). The isoelectric point of the powdered activated carbon (PAC) is 9.81,[1] indicating a positive surface charge.

Natural coagulant

The natural coagulant was isolated from the seeds of the Gradištanac variety of beans (Phaseolus vulgaris) in the laboratories of the Faculty of Technology in Novi Sad.[2]

Synthetic matrix (SM)

The synthetic matrix without or with dissolved organic carbon (DOC) surrogates was prepared in laboratory-grade pure water (conductivity 16 μS) by adding individual stock solutions of $NaHCO_3$ (Centrohem, p.a. >99 %) at a concentration of 0.02 mol L^{-1}, $CaCl_2 \cdot 2H_2O$ (Centrohem, p.a. >99 %) at a concentration of 0.03 mol L^{-1}, and $MgSO_4 \cdot 7H_2O$ (Centrohem, p.a. >99 %) at a concentration of 0.02 mol L^{-1} in accordance with DIN EN 12 902:2004.[3] The measured pH value of the prepared synthetic water was 7.5.

SM was further enriched first DOC surrogates and then with aqueous solution of selected organic micropollutants (OMPs) to achieve initial concentrations of ibuprofen (IB), caffeine (CF), and diclofenac sodium salt (DCF) (Sigma Aldrich, purity ≥99 %) of 2-3 μg L^{-1}.

SM with the addition of low molecular weight DOC surrogates - mixture of L-serine, L-leucine, and resorcinol

The solutions of L-serine (Reagent Plus®, ≥99 %, Sigma Aldrich), L-leucine (Reagent grade, ≥98%, Sigma Aldrich) and resorcinol (Reagent Plus®, ≥99 %, Sigma Aldrich) were prepared by weighing 20 mg of each substance into 50 mL volumetric flasks and dissolving

* Corresponding author. E-mail: tijanam@dh.uns.ac.rs

them in laboratory-grade pure water. The equal volumes of these solutions were mixed to enrich the matrix with small molecular weight DOC surrogates to achieve total DOC concentrations of approximately 3 mg C L^{-1}.

SM with the addition of high molecular weight DOC surrogates - humic acid

The humic acid solution (HA, technical grade, Sigma Aldrich) was prepared according to the procedure[4] by weighing 0.3 g of HA and dissolving it in 250 mL of laboratory-grade pure water. The pH was adjusted to 10 by adding NaOH solution (0.1 mol L^{-1}). The solution was then mixed on a magnetic stirrer at 300 rpm for 24 hours. After mixing, it was filtered first through glass fibre filter paper (0.6 µm, MACHEREY-NAGEL, Germany), and then through cellulose nitrate filter paper (0.45 µm, Sartorius, US) to remove undissolved HA.

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)

In the case of SM with the addition of both high and low molecular weight DOC surrogates (humic acid and a mixture of L-serine, L-leucine, and resorcinol), low and high molecular weight DOC molecules were added at equal concentrations. Specifically, 1.5 mg L^{-1} of low molecular weight DOC molecules (a mixture of equal volumes of mixture of L-serine, L-leucine, and resorcinol solutions) and 1.5 mg L^{-1} of humic acid were combined to achieve a total DOC concentration of 3 mg C L^{-1}.

This solution was further used to enrich the matrix with large molecular weight DOC surrogates to achieve total DOC concentrations of approximately 3 mg C L^{-1}. The concentration of dissolved organic carbon in synthetic matrices with and without the addition of DOC surrogates was determined using a TOC analyzer (liquiTOCII, Elementar, Germany) and ranged from <0.5 to 3.5 mg C L^{-1}.

Organic micropollutants (OMPs) aqueous solution preparation

The stock aqueous solution of IB, CF, and DCF (prepared from diclofenac sodium salt) in laboratory pure water was used to enrich samples with organic micropollutants in experiments. The solution was prepared by weighing the appropriate amounts of substances (around 10 mg of IB, CF, DCF) on an analytical balance, dissolving them, and transferring the solution to a 2 L volumetric flask, which was then filled with laboratory water up to the mark.

The dissolution process was enhanced by ultrasound treatment for 3 hours, after which the solution was left overnight in a refrigerator. Afterwards the solution was filtered through a cellulose nitrate membrane filter paper (0.45 µm, Sartorius, USA). In subsequent experiments, the stock aqueous solution was diluted as needed to achieve the desired initial concentration (around 2.00 µg L^{-1}). The variations in concentration (2.02–2.66 µg L^{-1}) arose due to the precision of the substance weighing. In the **TABLE S-I**, the nominal concentrations of OMPs are shown depending on the type of matrix.

TABLE S-I. Nominal concentrations of OMPs (μg L-1) in experiments

Type of matrix	Nominal concentrations of OMPs (μg/L)		
	IB	CF	DCF
SM	2.16	2.42	2.10
SRL	2.66	2.56	2.12
HA-SRL	2.16	2.02	2.02
HA	2.06	2.10	2.42

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);

EXPERIMENTAL METHODOLOGIES

The efficiency of the 30 min adsorption onto PAC

The efficiency of the adsorption process onto PAC (5 mg L^{-1}) with and without dosing of natural coagulant was conducted on the JAR apparatus FC6S VELP scientific. Simultaneous dosing of PAC and natural coagulant was tested at a contact time of 30 minutes. Experiments were performed in four types of matrices with different DOC surrogates (SM, SRL, HA-SRL, and HA). After the mixing time elapsed, the sample was filtered through a cellulose nitrate filter paper (0.45 μm, Sartorious, US) previously rinsed with 300 mL of laboratory-grade water. The first aliquot of 250 mL was discarded, and the remaining portion (250 mL) was analysed for the concentration of OMPs using gas chromatography with mass spectrometry (GC / MS). All experiments were conducted in duplicate.

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

The adsorption kinetics study was conducted using a shaker (KS 501–IKA, shaking intensity 180 rpm). In 500 mL of each matrices enriched with pharmaceuticals, PAC (5 mg L^{-1}) was added. The contact time with carbon was 15, 30, 60, 120 minutes, 24 hours, and 48 hours. The sample was filtered through a cellulose nitrate filter paper (0.45 μm, Sartorious, US) previously rinsed with 300 mL of laboratory-grade water. The first aliquot of 250 mL was discarded, and the remaining portion (250 mL) was analysed for the concentration of OMPs using GC / MS. All experiments were conducted in duplicate. Based on the experiments within the first 15-30 min, corresponding to the time frame where film diffusion is the dominant process and the kinetic curve exhibits linearity and based on the Equation 1 describing the ln c / c_0 vs. time, it was possible to compare product of multiplication of the a_m / m^2 g^{-1}, the total surface area of the adsorbent mass available in the reactor, and k_F / m min^{-1} the mass transfer coefficient through the film. The carbon mass and the reactor volume were the same in all experiments. Since the a_m / m^2 g^{-1} can be considered same in all the experiments due to the same PAC dose, the products of two numbers can be used for relative comparison.

$$ln\frac{c}{c_0} = \frac{m_A}{V_L} k_f a_m t \quad \text{(S-1)}$$

Where m_A (g) is the mass of adsorbent in the reactor, V_L (m^3) is the total volume of the reactor, a_m / m^2 g^{-1} is the total surface area of the adsorbent mass available in the reactor, and k_F / m min^{-1} is the mass transfer coefficient through the film.

Analytical method for OMPs analysis

Physicochemical characteristics of OMPs are shown in **TABLE S-II**.

TABLE S-II. Physicochemical characteristics of the selected organic micropollutants

Organic Micropollutants	Molecular weight (g mol^{-1})[a]	pKa[b]	log D[c] (pH 7.4)	Charge[d]
Ibuprofen	206.3	4.91	0.45	Negative
Caffeine	194.2	14.0	0.28	Neutral
Diclofenac	296.1	4.15	1.37	Negative

Source: a[5]; b, c, d[6]

For the preparation of samples for OMPs analysis, solid-phase extraction (60 mg, Oasis® HLB, Waters) and derivatization using N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA, Synthesis grade, Sigma-Aldrich) were applied. In a sample aliquot (250 mL), the pH value is first adjusted (pH=2) using concentrated HCl (p.a >37 %, Centrohem). Then, a solution of the internal standard mecoprop (PESTANAL®, analytical 99.6 % (HPLC), Sigma-Aldrich) in methanol was added so that the final concentration in the water sample is 2 μg L^{-1}. After that, the solid-phase extraction (60 mg, Oasis® HLB, Waters) was performed by conditioning the cartridge using 3x0.5mL dichloromethane (for HPLC, ≥99.8 %, Sigma-Aldrich), 3x0.5mL methanol (for Pesticide Residue Analysis, Chromasolv™, Honeywell), and 3x0.5 mL acidified laboratory-grade water, sequentially. After passing the sample (3 mL / min), the cartridge was dried under vacuum for 1 hour and eluted using 3x1 mL dichloromethane. The obtained eluate was evaporated to dryness under a stream of nitrogen and reconstituted in 0.5 mL toluene (99.85 %, for pesticide residue analysis, Thermo Scientific™). Prior to transferring the reconstituted eluate to the vial, 5 μL of a methanol solution of the internal standard phenanthrene-d10 (c= 100 μg mL^{-1}; analytical standard, Supelco) was added and evaporated to dryness. Then, the derivatization follows by adding 100 μL of N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA; Synthesis grade, Sigma-Aldrich) and heated up to 60 °C for 1 hour.[7] Gas chromatography-mass spectrometry (GC / MS) is used for separation, detection, and quantification. A capillary column DB-5 MS (30 m × 0.25 mm × 0.25 μm, Agilent, USA) was used, with helium as the carrier gas at a constant flow rate of 1 mL min^{-1}. A 2 μL sample was injected in spitless mode (Purge flow 15 mL min^{-1} at 0.75 min) at an injector temperature of 250 °C. The analysis is performed in SIM mode (selected ion monitoring), tracking ions for quantification (TABLE SII). In all synthetic matrices, the initial concentrations of substances and concentrations after the applied processes were determined using a standard calibration method with internal standards. Separate calibrations were used for each type of matrix. In the synthetic matrix and synthetic matrix with the addition of high molecular weight DOC surrogates, internal validation of the analytical method for OMP analysis was performed (linearity, method and instrument repeatability, analytical method bias, extraction efficiency, method detection limit (MDL), and practical quantitation limit (PQL).

The method detection limit is calculated according to Equation S2:

$$MDL = SD \bullet t(n-1) \quad \text{(S-2)}$$

Where:

SD - standard deviation of the measured concentrations of ibuprofen, caffeine, and diclofenac; t(n-1) - Student's coefficient for a 95 % confidence level, for (n-1) degrees of freedom, where n represents the number of repetitions for determining the MDL (Student's coefficient for a 95 % confidence level for four measurements, n-1= 3 is 3.182)

The practical quantification limit is calculated according to Equation S3:

$$PQL = 3 \bullet MDL \quad \text{(S-3)}$$

Where:

SD - standard deviation of the measured concentrations of ibuprofen, caffeine, and diclofenac.

Method repeatability is determined in a synthetic matrix without added DOC and a synthetic matrix with added HA as the relative standard deviation of three measurements of different extracts.

Instrument repeatability is determined as the relative standard deviation of three measurements in the same extract.

Analytical method bias is determined in a synthetic matrix without added surrogate DOC and a synthetic matrix with added HA. It is expressed as the ratio of the measured concentration to the expected concentration for measurement in triplicate.

Extraction efficiency is based on the ratio of the signal intensity for substances in the sample undergoing solid-phase extraction and in the sample representing the matrix extract spiked with substances after the solid-phase extraction. In both cases, the signal intensity for substances is normalized by the peak area of the internal standard (mecoprop, c=2 μg L^{-1}) added to the matrix extract. Both types of measurements were performed in triplicate and the RSD of the measurements was calculated.

The method validation is presented in Table SIII. It is important to note that correction of the results is not performed in the cases where matrix influence was noticed (for example, in some samples containing HA, higher bias was observed) since it is considered constant for the initial solution and solution after adsorption experiments. All the samples for one batch of experiments were analysed in one sequence at once in order to avoid the possible interference of changes in matrix influence during the both sample preparation and sample analysis by GC / MS.

Removal efficiency

The removal efficiency (%) of the selected OMPs in all experiments was calculated using Equation (S4):

$$\text{Removal efficiency, \%} = C_0\text{-}C_e/C_0 \cdot 100 \qquad \text{(S-4)}$$

where C_0 is the initial concentration of OMPs in matrix before the treatment and C_e is the concentration of compounds after sample treatments.

“no removal achieved”- the calculated removals were lower than method bias and not taken into consideration

TABLE S-III. Method validation

Type of matrix	OMP[a]	**Target ion**, ion	MDL[b] (µg L^{-1}) n=4	PQL[c] (µg L^{-1}) n=4	Method repeatability n=3		Instrument repeatability n=3		Bias n=2		Extraction efficiency (E)	
					Conc. level µg L^{-1}	RSD %	Conc. level µg L^{-1}	RSD %	Conc level µg L^{-1}	RSD %	Conc. level µg L^{-1}	RSD %
Synthetic Matrix (SM)	IB	**160,** 263,117	0.019	0.056	0.20	14.3	0.20	1.44	0.20	14	0.20	106 (3.0)
					2.00	10.0	2.00	0.95	2.00	4.6	2.00	101 (4.0)
	CF	**194**,109, 82	0.037	0.111	0.20	7.75	0.20	5.67	0.20	20	0.20	94.6 (2.0)
					2.00	12.5	2.00	2.28	2.00	4.5	2.00	94.1 (7.0)
	DCF	**214**, 242, 367	0,028	0.084	0.20	7.11	0.20	6.14	0.20	21	0.20	93.1 (6.0)
					2.00	13.5	2.00	4.75	2.00	1.1	2.00	19.2 (13)
SM with the addition of large molecular weight DOC surrogates - humic acid (HA)	IB	160, 263,117	0.008	0.023	0.20	8.6	0.20	0.32	0.20	7.2	0.20	107(5.0)
					2.00	12	2.00	1.5	1.5	10	2.00	96.2 (6.0)
	CF	194,109, 82	0.003	0.008	0.20	11	0.20	0.54	0.20	4.2	0.20	81.3(12)
					2.00	8.0	2.00	5.0	1.5	1.9	2.00	83.5 (9.0)
	DCF	**214**, 242, 367	0.005	0.016	0.20	14	0.20	4.1	0.20	40	0.20	32.1 (12)
					2.00	15	2.00	0.99	1.5	7.0	2.00	15.9 (6.0)

TABLE S-IV. The removal efficiency (%) of ibuprofen, caffeine, and diclofenac in kinetic experiments at a PAC dose of 5 mg L^{-1}

	Type of matrix	**Ibuprofen**				**Caffeine**				**Diclofenac**			
		SM	SRL	HA	HA-SRL	SM	SRL	HA	HA-SRL	SM	SRL	HA	HA-SRL
Time	15min	59	86	77	26	30	81	98	41	84	90	45	**26**
	15min D*	69	87	57	32	72	82	85	49	85	90	**20**	**20**
	30 min	**5.0**	93	-11	50	48	80	69	71	87	93	**-9.0**	**30**
	30 min D*	28	82	-15	48	50	78	70	74	83	90	**27**	48
	1h	56	94	-3,0	**	75	81	78	71	34	94	31	33
	1h D*	37	96	8.0	**	75	83	90	74	51	>95	70	30
	2h	84	94	**	83	85	79	82	>97	93	>95	35	64
	2h D*	84	93	45	>92	87	79	95	>97	92	>95	73	61
	24h	84	>97	79	>92	88	85	>98	>97	92	>95	80	90
	24h D*	84	>97	74	-	89	84	>98	-	92	>95	83	-
	48h	86	>97	89	>92	91	84	>98	>97	92	>95	76	88
	48h D*	85	>97	88	-	89	85	>98	-	92	>95	85	-

*Experiment duplicate; ** Analysis failed; - No experiment duplicate; 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); Note: The bolded values in the table fall outside the analytical method bias and cannot be considered relevant.

TG characterization of native and sorbents coated with various types of DOC surrogates

In order to investigate the coating of DOC on the surface of PAC, thermogravimetric (TG) characterization of the native sorbent (soaked in synthetic matrix, SM) and the sorbents coated with various types of DOC surrogates (after 30 minutes and 24 hours soaking in solution) was performed.

2.5 mg of PAC was added to 500 mL of each matrix and agitated using a shaker (KS 501–IKA, at 180 rpm). After the agitation period, the sorbent was separated by filtration through pre-washed cellulose nitrate filter paper (0.45 μm, Sartorious, US) using 300 mL of laboratory-grade water. The residual PAC cake on the filter paper was further analyzed. Thermal data were collected using TA Instruments SDT Q600 thermal analyzer. The decomposition was followed from room temperature to 600 °C at a 10 °C min^{-1} heating rate in the argon carrier gas (flow rate 50 cm^3 min^{-1}). Sample holder/reference: alumina crucible/empty alumina crucible. Sample mass 1.5–3 mg. The sample of native PAC without coating after drying is stable in the temperature range of measurement, and no weight loss was observed.

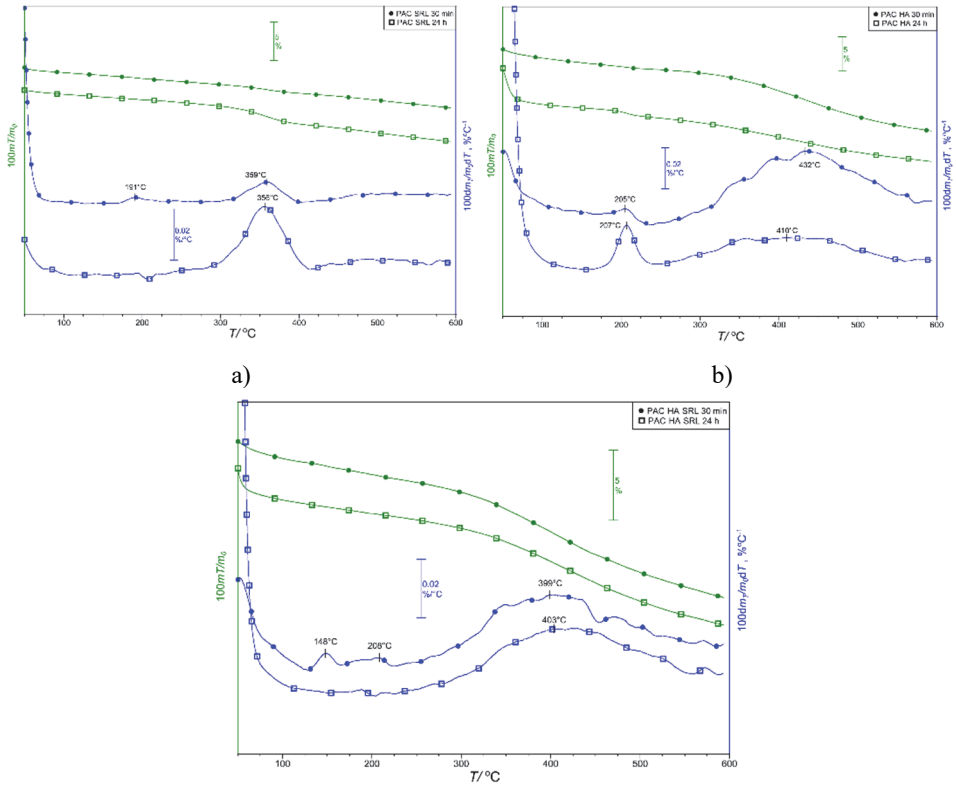

Fig. S-1. TG and DTG curves of PAC coated with a) SRL DOC surrogate, b) HA and c) HA-SRL.

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