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Comparing the adsorption of micropollutants on activated carbon from anaerobically stored, organics-depleted, and nitrified urine

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ABSTRACT

Separate collection and treatment of urine optimizes nutrient recovery and enhances micropollutant removal from municipal wastewater. One typical urine treatment train includes nutrient recovery in three biological processes: anaerobic storage, followed by aerobic organics degradation concurrently with nitrification. These are usually followed by activated carbon adsorption to remove micropollutants. However, removing micropollutants prior to nitrification would protect nitrifiers from potential inhibition by pharmaceuticals. In addition, combining simplified biological treatment with activated carbon adsorption could offer a cheap and robust process for removing micropollutants where nutrient recovery is not the first priority, as a partial loss of ammonia occurs without nitrification. In this study, we investigated whether activated carbon adsorption could also take place between the three biological treatment steps. We tested the effectiveness of micropollutant removal with activated carbon after each biological treatment step by conducting experiments with anaerobically stored urine, organics-depleted urine, and nitrified urine. The urine solutions were spiked with 19 pharmaceuticals: amisulpride, atenolol, atenolol acid, candesartan, carbamazepine, citalopram, clarithromycin, darunavir, diclofenac, emtricitabine, fexofenadine, hydrochlorothiazide, irbesartan, lidocaine, metoprolol, N_4-acetylsulfamethoxazole, sulfamethoxazole, trimethoprim, venlafaxine, and two artificial sweeteners, acesulfame and sucralose. Batch experiments were conducted with powdered activated carbon (PAC) to determine how much activated carbon achieve which degree of micropollutant removal and how organics, pH, and speciation change from ammonium to nitrate influence adsorption. Micropollutant removal was also tested in granular activated carbon (GAC) columns, which is the preferred technology for micropollutant removal from urine. The carbon usage rates (CUR) per person were lower for all urine solutions than for municipal wastewater. The results showed that organics depletion would be needed when micropollutant removal was the sole aim of urine treatment, as the degradation of easily biodegradable organics prevented clogging of GAC columns. However, CUR did hardly improve with organics-depleted urine compared to stored urine. The lowest CUR was achieved with nitrified urine. This resulted from the additional organics removal during nitrification and not the lower pH or the partial conversion of ammonium to nitrate. In addition, we showed that the relative pharmaceutical removal in all solutions was independent of the initial pharmaceutical concentration unless the background organics matrix changed considerably. We conclude that removal of micropollutants in GAC columns from organics-depleted urine can be performed without clogging, but with the drawback of a higher carbon usage compared to removal from nitrified urine.

1. Introduction

Separate collection and treatment of urine is beneficial not only for nutrient recovery but also for the targeted removal of micropollutants. About two thirds of pharmaceuticals are excreted with urine (Lienert et al., 2007). Several studies have shown that neither anaerobic storage (Gajurel et al., 2007; Jaatinen et al., 2016; Monetti et al., 2022; Özel Duygan et al., 2021; Schürmann et al., 2012) nor biological treatment (Özel Duygan et al., 2021) is sufficient to remove micropollutants from urine, because many micropollutants are not biodegradable. Hence, further treatment is needed for the production of a safe fertilizer without critical micropollutant concentrations (Larsen et al., 2021; Sohn et al.,

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Table 1

Characterization of the differently treated urine solutions collected from the urine treatment facility at Eawag, Switzerland and used in the PAC and the GAC experiments. For GAC experiments, one big tank of collected urine was used for one experiment. All measurements are before micropollutant spiking, except for *PAC 3: pH and organics,* the measurements are after spiking.

	Experiments	pH –	DOC mg L^{-1}	Cl^- mg L^{-1}	NH_4^+-N mg L^{-1}	NO_3^--N mg L^{-1}	PO_4^{3-}-P mg L^{-1}	SO_4^{2-} mg L^{-1}	Na^+ mg L^{-1}	K^+ mg L^{-1}
Stored urine	Undiluted (Udert et al., 2006)	9.1		3800					2600	2200
	PAC 2: Urine solutions	9	2670	2260	2570	<20	128	408	1230	1040
	GAC: Clogging		880	1830	2290	<20	115	360	998	912
Organics-depleted urine	*PAC 2: Urine solutions*		284	2440	3380	<20	217	644	1400	962
	PAC 3: pH and organics	8.8	190	2140	2740	<10	232	758	1150	750
	GAC: Clogging		281	1810	1940	<20	113	440	983	902
	GAC: MPs		191	1930	3110	<20	205	523	1190	775
Nitrified urine	*PAC 1: Initial conc.*		116	2330	1500	1400	209	705	1370	963
	PAC 2: Urine solutions		116	2330	1500	1400	209	705	1370	963
	PAC 3: pH and organics	6.5	108	2160	1250	1210	212	708	1240	854
	GAC: Clogging		104	1890	1230	1210	122	506	1050	963
	GAC: MPs		90	2630	1690	1570	193	705	1470	1220

2023). Larsen et al. (2021) summarized the various removal processes for micropollutants from urine, such as ozonation, nanofiltration, and advanced oxidation. Each of these comes with problems, including production of toxic by-products, fouling, loss of nutrients, and high energy demand.

The established method for removing micropollutants from nitrified urine is by granular activated carbon (GAC) filters, which do not produce toxic by-products nor remove nutrients (Köpping et al., 2020).

GAC columns have been used to ensure minimal effluent concentrations (Worch, 2021) and because GAC can be regenerated, unlike powdered activated carbon (PAC) (Crittenden et al., 2012). In practice, adsorption on activated carbon has only been applied on nitrified urine (Köpping et al., 2020), in which about 85 % of the organics had been degraded (Udert et al., 2006). Similarly, high concentrations of organic matter in wastewater have been shown to compete with micropollutants for adsorption (Gidstedt et al., 2022; Matsui et al., 2003). Consequently, in wastewater treatment, adsorption on GAC (Benstoem et al., 2017) or PAC (Boehler et al., 2012) is mainly applied after nitrification.

Urine treatment trains typically recover nutrients in three processes: anaerobic storage, followed by aerobic organics degradation concurrently with nitrification. Activated carbon adsorption to remove micropollutants usually follows these steps, but removing micropollutants prior to nitrification would protect nitrifiers from inhibition by pharmaceuticals. The sensitivity of nitrifiers towards certain micropollutants was shown for activated sludge by different studies. Especially antibiotics were reported to have EC50 values in the range of expected concentrations (Carucci et al., 2006; Dokianakis et al., 2004; Halling-Sørensen, 2001; Ortiz de García et al., 2014). Also painkillers can appear in inhibiting concentrations in wastewater (Ortiz de García et al., 2014; Park and Seungdae, 2020). In addition, combining simplified biological treatment with activated carbon adsorption could offer a cheap and robust process for removing micropollutants. However, little is known about the adsorption of micropollutants from solutions with high organic content, such as raw urine (Larsen et al., 2021), and most studies only analyzed synthetic solutions (Solanki and Boyer, 2019). Consequently, moving micropollutant removal to a more advantageous point in the urine treatment train requires better understanding of how the composition changes due to separate organics degradation and nitrification and how these changes influence the adsorption of micropollutants on activated carbon.

Anaerobically stored urine has a high organics content (Udert et al., 2006), but Heusser et al. (2023) showed that most of the easily biodegradable low molecular weight (LMW) organics in anaerobically stored urine (e.g., acetate and propionate) do not compete for adsorption. The easily biodegradable LMW organics and most other organic compounds are degraded during the separate organics degradation step. Urine nitrification decreases the organics content further and oxidizes ammonia to a mix of ammonium and nitrate, which decreases the urine pH from 9 to a minimum of 5.4 (Fumasoli et al., 2015), stabilizing the volatile ammonia. The pH change can also influence adsorption (Kah et al., 2017). In addition to the dissolved compounds, suspended solids can also influence adsorption to GAC. High concentrations of solids can cause hydraulic blockage of the filter (Benstoem et al., 2017). In urine storage tanks and in the filter, solids can be undesirably formed by biological growth or precipitation (Yan et al., 2021).

The energy- and maintenance-intensive urine nitrification process (Fumasoli et al., 2016) may not be necessary if only micropollutants need to be removed, as in direct urine application to private gardens. Treatment of urine with only organics depletion and micropollutant removal could provide an easy and robust treatment for small-scale applications when partial loss of ammonia in the fertilizer due to volatilization is not a concern. Furthermore, instead of omitting nitrification, positioning the adsorption process before the nitrification step could protect sensitive nitrifiers (Pagga et al., 2006) by adsorbing inhibitory substances (Çeçen and Aktaş, 2001). This could also reduce maintenance and increase performance, as proposed in Udert and Heusser (2023) and Heusser et al. (2024).

In this study, we tested the hypothesis that efficient micropollutant removal by adsorption to activated carbon is also possible from non-nitrified urine. We further hypothesized that the concentration of easily biodegradable organics needs to be reduced before GAC adsorption to prevent clogging of the filter. To test these hypotheses, removal of micropollutants was investigated in laboratory PAC experiments and in laboratory and pilot-scale GAC columns. The experiments with GAC also enabled us to consider operational aspects.

2. Materials and methods

2.1. Urine solutions

The urine solutions used in the experiments were collected from the urine treatment facility at Eawag, Switzerland (Fumasoli et al., 2016). Three different urine solutions, anaerobically stored urine, organics-depleted urine and nitrified urine were used for the experiments. They differed in their DOC concentration, their pH and the nitrogen species in nitrified urine. Their detailed characteristics are given in Table 1. Anaerobically stored urine was taken from the anaerobic storage tank with a hydraulic retention time (HRT) of 5 to 60 days. During anaerobic storage the organics were fermented and urea was hydrolyzed. The resulting pH was 9 in all anaerobically stored urine solutions, but the DOC concentration ranged from 880 to 2670 mg L^{-1}. Organics-depleted urine was taken after the degradation of about 70 % to 90 % of the organics in a 60 L pilot-scale membrane aerated biofilm reactor (MABR, OxyMem). The HRT in the MABR was 1 to 2 days whereas the solid retention time (SRT) was not a limiting factor as the biomass grew in a biofilm (Metcalf et al., 2014). Nitrification in the

Table 2
Characteristics of the selected micropollutants including the selection criteria. The acid dissociation constant (pK_a) and the octanol-water partition coefficient ($\log D_{OW}$) at a certain pH were calculated with ChemAxon (ChemAxon, 2022).

Name		Substance sub-group	Selection criteria	pKa		log D_{OW}		Speciation	
				acidic	basic	pH 6.5	pH 8.8	pH 6	pH 9
Acesulfame	ACS	Sweetener	a	3.02	−6	−1.49	−1.49	anion	anion
Amisulpride	AMS	Neuroleptic	a,b,c	14	8.28	−1.52	0.14	cation	neutral
Atenolol	ATE	Beta-blocker	a	3.54	9.67	−1.24	−1.29	cation	cation
Atenolol acid	ATA	Beta-blocker	d	14.1	9.67	−2.48	−0.50	zwitterion	zwitterion
Candesartan	CAN	Sartan	a,b	3.44	1.5	0.27	−0.46	anion	anion
Carbamazepine	CAR	Antiepileptic	a,b	16	−3.8	2.77	2.77	neutral	neutral
Citalopram	CIT	Anti-depressant	a,b		9.78	0.69	2.74	cation	cation
Clarithromycin	CLA	Antibiotic	a,b	12.5	9	0.78	2.82	cation	cation
Darunavir	DAR	Antiretroviral agent	a	13.6	2.39	2.82	2.82	neutral	neutral
Diclofenac	DCF	Anti-inflammatory agent	a,b	4	−2.1	1.79	0.75	anion	anion
Emtricitabine	EMT	Antiviral agent	a	14.3	1.74	−0.90	−0.90	neutral	neutral
Fexofenadine	FEX	Antihistamine	a,c	4.04	9.01	2.94	2.77	zwitterion	zwitterion/anion
Hydrochlorothiazide	HCT	Diuretic	a,b,c	9.09	−2.7	−0.58	−0.75	neutral	neutral/anion
Irbesartan	IRB	Sartan	a,b	4.29	4.08	3.42	3.33	anion	anion
Lidocaine	LID	Anesthesic	a,c	13.78	7.75	1.57	2.81	cation	neutral
Metoprolol	MET	Beta-blocker	a,b	14.1	9.67	−1.14	0.84	cation	cation
N_4-acetylsulfamethoxazole	NSMX	Antibiotic	d	5.88	0.38	0.31	−0.08	anion	anion
Sucralose	SUC	Sweetener	a	11.9	−3	−0.47	−0.47	neutral	neutral
Sulfamethoxazole	SMX	Antibiotic	a,c	6.16	1.97	0.38	−0.14	neutral	anion
Trimethoprim	TMP	Antibiotic	a	11.4	12	−1.97	−1.37	cation	cation
Venlafaxine	VEN	Anti-depressant	a,b	14.4	8.91	0.36	2.38	cation	cation

a High abundance in urine
b Swiss indicator compound
c $6<pKa<9$
d Metabolite or transformation product of another substance

MABR was inhibited by the high free ammonia concentration (Fumasoli, 2016) so that only organics but no ammonia were oxidized. The nitrified urine was taken after the nitrification step with suspended biomass, in which 50 % of the total ammonia was oxidized to nitrate, the pH was decreased from 9 to around 6.5 and the DOC content decreased further achieving 5 % to 15 % of the initial DOC content in anaerobically stored urine. The HRT in the nitrification was about 3 to 5 days. The sludge was retained in the reactor by operating it in fed batch mode (Faust et al., 2022), so that the SRT was considerably higher than the HRT (for details see S1). The urine solutions used for the different experiments were collected at different days and had different concentrations as shown in Table 1. The concentrations of chloride (Cl), sodium (Na) and potassium (K) are good indicators for dilution in the collection system because they stay inert over the treatment processes.

To differentiate the effect of pH and organics concentration on adsorption, the pH of organics-depleted and nitrified urine (see Table 1) was adapted in the experiment *PAC 2: pH and organics* (see Table 3). The pH of the organics-depleted urine was lowered to the pH of nitrified urine by adding 50 mL of a 4 mol L^{-1} HCl solution to 2 L of organics-depleted urine. The pH of nitrified urine was increased to 9 using 110 mL of a 0.4 mol L^{-1} NaOH solution.

2.2. *Micropollutant selection*

For this study, micropollutants were selected accordingly to Heusser et al. (2023) based on one or more of the following three criteria. First, the substances are often found in high abundance in urine; second, the substances are recommended by the Swiss Federal Office for the

Table 3
Overview of the experimental conditions.

Experiment	Urine solution	pH	Addition	Spiking conc.	PAC conc.	Experimental time
		–	–	μg L^{-1}	mg L^{-1}	Days / # treated empty bed volumes (for GAC)
PAC 1: Initial conc.	Nitrified urine	6.5	–	200	0, 30, 45, 67, 100, 130, 170, 220, 285, 370, 480, 630, 880, 1300, 2000, 3000	3
	Nitrified urine	6.5	–	20	0, 100, 170, 285, 480, 880	3
PAC 2: Urine solutions	Stored urine	9	–	200	0, 30, 45, 67, 100, 130, 170, 220, 285, 370, 480, 630, 880, 1300, 2000, 3000	3
	Organics-depleted urine	8.8	–	200		3
	Nitrified urine	6.5	–	200		3
PAC 3: pH and organics	Organics-depleted urine	8.8	–	200	0, 3, 10, 30, 100, 300, 1000, 3000	3
		6.5	HCl	200		3
	Nitrified urine	6.5	–	200		3
		8.8	NaOH	200		3
GAC: Clogging	Stored urine	9	–	–		12 / 678
	Organics-depleted urine	8.8	–	–		15 / 659
	Nitrified urine	6.5	–	–		15 / 636
GAC: MPs	Organics-depleted urine	8.8	–	200		56 / 995
	Nitrified urine	6.5	–	200		56 / 1134

Environment as indicator compounds to assess micropollutant removal in advanced wastewater treatment plants (FOEN, 2015); third, the substances have pK_a values between 6.5 and 9 and therefore substantially change their speciation in the pH range of interest. The final list including the reason for selection, the pK_a calculated using ChemAxon (ChemAxon, 2022), and the speciation is presented in Table 2 and consists of 19 pharmaceuticals and two artificial sweeteners. N_4-acetylsulfamethoxazole, a relevant human metabolite of sulfamethoxazole and atenolol acid, a transformation product of atenolol were added.

The concentrations of the selected micropollutants expected in source separated urine range between 6 and 300 μg L^{-1} (Aventis Pharmaceuticals Inc., 2007; Bischel et al., 2015; Bourgin et al., 2018; Collinsworth et al., 1974; Eberhard et al., 2024, in preparation; Köpping et al., 2020; Otto et al., 2014; Roberts et al., 2000) with the exception of acesulfame (ACS), which is expected in concentrations of more than 7000 μg L^{-1} (Bourgin et al., 2018). The expected concentrations and the background concentrations of the urine solutions are shown in Table S1.

For the PAC experiments, the urine solutions were filtered using a 0.45 μm MN GF-5 filter (Macherey-Nagel) and then spiked with the micropollutant mix to a concentration of 200 μg L^{-1}. The micropollutant mix was produced using stock solutions of the individual substances of 1 g L^{-1} dissolved in ethanol or methanol. The micropollutant mix had a concentration of 100 mg L^{-1} of each substance. To reduce the effect of the solvent on the DOC, 90 % of the mix was evaporated and refilled with nanopure water. The addition of the micropollutant mix to urine increased the DOC by about 200 mg L^{-1} as shown in Table S2. However, Heusser et al. (2023) showed that ethanol does not compete for adsorption and Özel Duygan et al. (2021) did not observe any impact of high solvent concentration on adsorption of micropollutants. A spiking concentration of 200 μg L^{-1} was chosen in accordance to Heusser et al. (2023) which still allowed us to demonstrate a 95 % removal for each micropollutant. Only for the two solutions used in experiment *PAC 1: Initial conc.* the target concentrations were 20 μg L^{-1} and 200 μg L^{-1}, respectively (Table 3).

2.3. Experimental setups

Experiments with PAC were conducted to determine the removal of micropollutants in different urine solutions and experiments with GAC columns helped understanding operational considerations. The experiments are summarized in Table 3. For nitrified urine, the influence of the initial micropollutant concentration was investigated with the experiment *PAC 1: Initial conc*. The experiment *PAC 2: Urine Solutions* was used to compare the adsorption of micropollutants from stored, organics-depleted and nitrified urine. The experiment *PAC 3: pH and organics* further allowed distinguishing between the effect of organics concentration and pH on adsorption. The experiment *GAC: Clogging* was conducted to determine whether clogging occurs when feeding differently treated and unfiltered urine solutions. The experiment *GAC: MPs* assessed the application of a pilot-scale GAC column for micropollutant (MP) removal in organics-depleted urine and nitrified urine over two months.

All experiments were conducted at room temperature and the granular activated carbon Norit® GCN 830 (Cabot; particle size 0.6–2.36 mm) was used after washing it three times with nanopure water and drying it at 105 °C. Details of the GAC and the production of the PAC out of it as well as the production of the PAC solution are given in section S2 in the SI1. All urine solutions were filled in 250 mL or 500 mL Schott bottles and PAC solution was added to achieve PAC concentrations in the range of 3 to 3000 mg L^{-1} as indicated in Table 3, including a batch without PAC addition as reference. The batches were mixed in an overhead shaker for three days. Since one day equilibration is usually used for micropollutant adsorption experiments with treated municipal wastewater (Böhler, 2019; Meinel et al., 2016), it was assumed that the equilibrium between the solution and activated carbon was reached. Samples were taken before the start of the experiment and after the three days in the overhead shaker.

For the experiment *GAC: Clogging*, three columns with a diameter of 2.6 cm were filled each with 60 g GAC (see details in Table S4). Anaerobically stored urine, organics-depleted urine and nitrified urine was fed unfiltered with a peristaltic pump (ISMATEC®) at a rate of 2.6 mL min^{-1} on top of the GAC, to let it trickle down the columns. During the experiment duration of 2 weeks about 57 liters of urine were fed corresponding to more than 600 treated empty bed volumes (n_{BV}) as indicated in Table 3. Pump calibration and measurements of the water head were done all 2 to 3 days.

For the experiment *GAC: MPs*, two PVC columns with an inner diameter of 53.6 cm were used and filled each with 400 g dried GAC (see Table S4). About 1000 L organics-depleted urine and about 1000 L nitrified urine were collected, filtered with a 25 μm Whatman Grade 114 V filter (HUBERLAB), and spiked with the micropollutant mix to achieve a concentration of 200 μg L^{-1} (as shown in Table 3). The urine solutions were fed with a peristaltic pump (ISMATEC®) over two months to the bottom of the column at an average rate of 9.97 mL min^{-1} and 11.33 mL min^{-1} for organics-depleted and nitrified urine, respectively. The flowrate was interpolated linearly after weekly pump calibration to calculate n_{BV} (Table 3 and detailed data in SI2), and gave average EBCT of 79 and 70 min for organics-depleted and nitrified urine, respectively. The urine characterization is given in Table 1. Influent samples were taken at the beginning of the experiment and then in weekly intervals. Samples were taken biweekly from the effluent, sampling the overall cross section with a perforated stainless steel pipe. An aluminum foil was wrapped around the columns to prevent phototrophic activity.

2.4. Analytical methods

For all samples with micropollutants, 5 mL aliquots were frozen at −20 °C immediately after sampling for later analysis of the micropollutants. After thawing, the samples were diluted 1:100 in nanopure water and analyzed using liquid chromatography triple quadrupole mass spectrometry (LC-MS/MS, Agilent TQ6495C) after spiking internal standards and centrifugation. Limits of quantification (LOQs) ranged from 0.8 to 114 ng L^{-1} (note that LOQs in the urine were 100 times higher due to the dilution), and average recoveries from 91 to 117 %. Details are given in section S5, SI1 and in SI2. Concentrations of ACS in anaerobically stored urine and organics-depleted urine were above the calibration range and could therefore not be quantified. Tests with adjustment of pH from 9 to 7 for anaerobically stored and organics-depleted urine samples showed that the pH of the sample did not influence quantification of micropollutants significantly (see SI1, section S5).

After dilution and filtration with a 0.45 μm MN GF-5 filter (Macherey-Nagel), Ion Chromatography (881 compact IC pro, Metrohm) was used to measure sodium, ammonium, potassium, chloride, nitrate, phosphate and sulfate. DOC was measured with a total organic carbon analyzer (Shimadzu TOC-L). Size exclusion chromatography (SEC, DOC-Labor GmbH) according to the method described by Huber et al. (Huber et al., 2011) was used to quantify the organics fractions.

2.5. Calculations

Data analysis and calculations were done with the software (MATLAB, 2020).

The removal efficiency R for the individual substances at a given PAC concentration was calculated using Eq. (1), where C is the concentration of the micropollutant after three days and C_{ref} is the concentration of the micropollutant in the reference batch without PAC addition after 3 days. For calculating the removal of all micropollutants the individual removals were averaged.

$$R = \left(1 - \frac{C}{C_{ref}}\right) * 100 \ [\%] \tag{1}$$

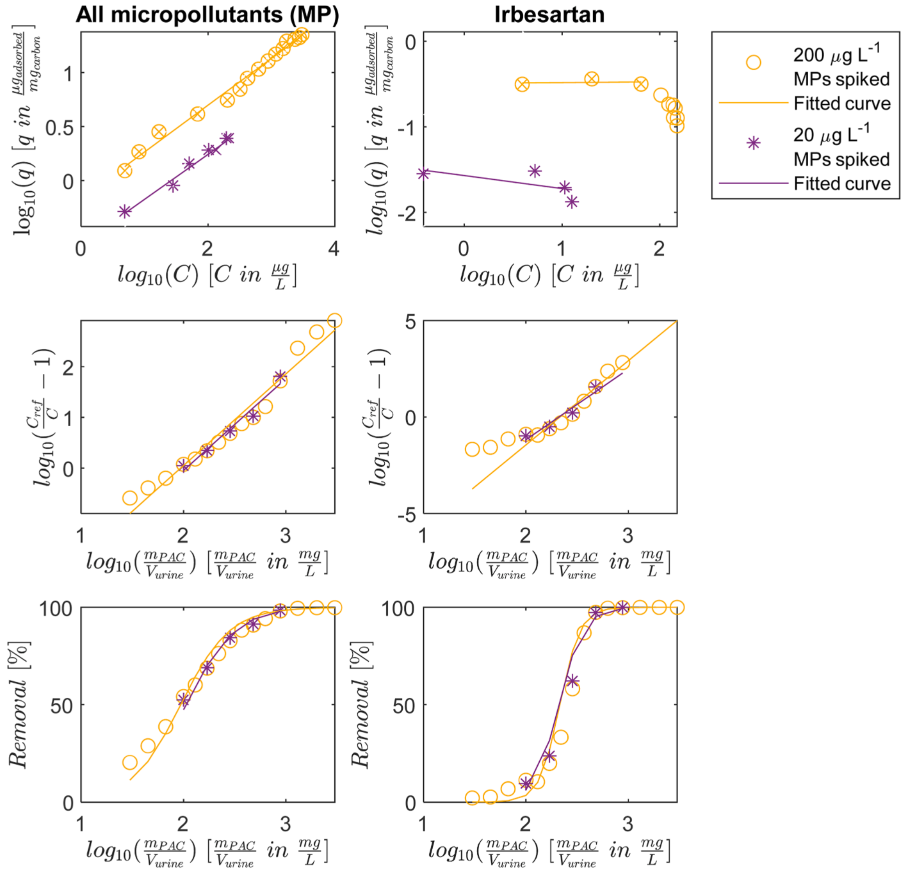

Fig. 1. Sorption in the experiment *PAC 1: initial conc.*, fitted with a Freundlich isotherm (top), the simplified equivalent background compound model (SEBCM) (middle), and removal (bottom) of all micropollutants (MPs) and irbesartan on PAC from the same nitrified urine (116 mg L^{-1} DOC), but spiked with different micropollutant concentrations. *q* is the sorbed concentration and *C* the remaining concentration in solution.

C_{ref} was used instead of the concentration at the beginning of each experiment to prevent influence of other processes than adsorption (see section S6 in the SI1 for more details).

To describe the relationship between the micropollutant loading on activated carbon and the micropollutant concentration in the liquid, Freundlich isotherms were used. In addition, the Simplified Equivalent Background Compound Model (SEBCM) was used to determine a relationship between the micropollutant removal from the liquid and the activated carbon dosage. The SEBCM does not require values for loading or concentrations in the liquid.

Freundlich isotherms were determined using linear regression of the logarithmic form of the Freundlich equation (Eq. (2)) with q [μg mg^{-1}] being the micropollutant loading of the carbon, calculated according to Eq. (3) and k the Freundlich adsorption capacity parameter [(mg g^{-1})(L mg^{-1})^n], C [μg L^{-1}] the remaining concentration of the micropollutant in the liquid and n [-] the Freundlich adsorption intensity parameter. m_{PAC} [mg] is the mass of PAC in the batch and V_{urine} [L] is the volume of urine in the batch. m_{PAC}/V_{urine} is the activated carbon dosage.

$$q = k * C^n \left[\frac{\mu g}{mg\ PAC}\right] \tag{2}$$

$$q = \frac{C_{ref} - C}{m_{PAC}/V_{urine}} \left[\frac{\mu g}{mg\ PAC}\right] \tag{3}$$

The SEBCM is based on the Ideal Adsorption Solution Theory (IAST), which can be used to consider competition between adsorbing substances. With the Equivalent Background Compound Model (EBCM) the competing organics can be summarized if they are unknown. The SEBCM further simplifies the model making the assumption that the loading of highly concentrated organics dominates over the loading of micropollutants ($q_{DOC} >> q_{MP}$) and that the exponent n in the Freundlich isotherm for both organic matter and micropollutants are approximately equal ($n_{DOC} \approx n_{MP}$), as initially proposed and validated by Qi et al. (2007). The derivation of the SEBCM and the underlying assumptions are described in detail in Worch (2021).

The parameters A and n in the SEBCM were determined using Eq. (4) (Worch, 2021), with the exclusion of data points showing less than 10 % removal to avoid numerical issues related to negative removal. Likewise, data points where removal reached 100 % were excluded to prevent division by zero in Eq. (4). When the number of data points was very low, as in the experiment *PAC 3: pH and organics*, we included the last data point with a removal below 10 % and set the first removal of 100 % to 99.9 % to ensure that an adequate number of data points was available. Fittings with high uncertainty due to low data availability are indicated in Fig. 3. In *PAC 2 urine solutions* not enough data was available for fitting CAN in organics-depleted urine.

$$\ln\left(\frac{C_{ref}}{C} - 1\right) = \frac{1}{n}\ln\left(\frac{m_{PAC}}{V_{urine}}\right) - \ln(A) \tag{4}$$

For representation, Eq. (4) was rearranged to show the removal as in Eq. (5).

$$\left(1 - \frac{C}{C_{ref}}\right) * 100 = \left(1 - \frac{A}{\left(\frac{m_{PAC}}{V_{urine}}\right)^{1/n} + A}\right) * 100\ [\%] \tag{5}$$

We used the Kolmogorov-Smirnov test to evaluate the statistical significance of differences between the fitted curves, using the *kstest2()*

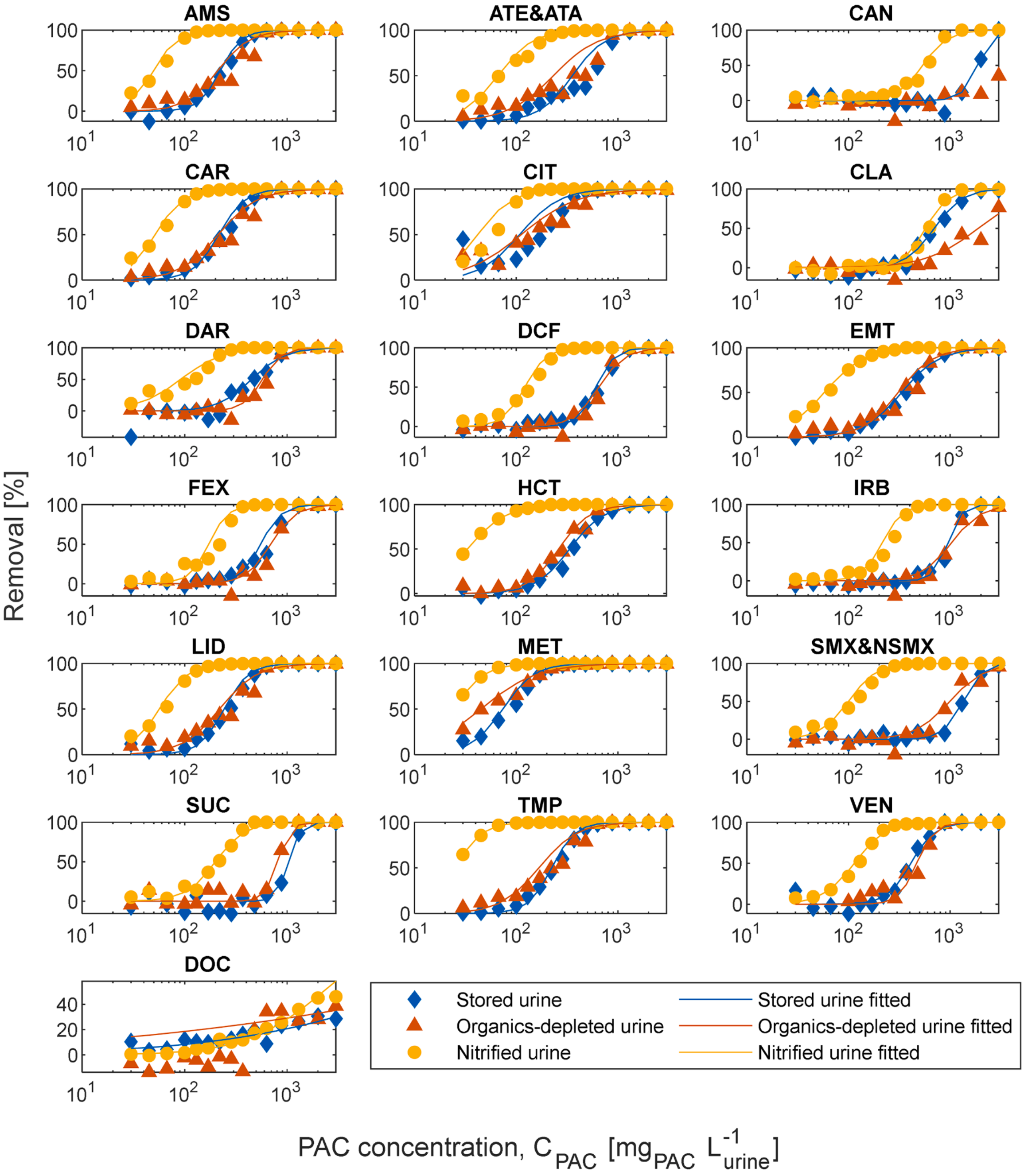

Fig. 2. Results of the experiment *PAC 2: urine solutions*: Removal of micropollutants by powdered activated carbon (PAC) from anaerobically stored, organics-depleted and nitrified urine and fitted with SEBCM (Eq. (4)) excluding the removal <10 % (parameters are shown in Table S9 to Table S11). The concentration of PAC is presented in logarithmic scale. Results from anaerobically stored and organics-depleted urine were already presented in Heusser et al. (2023).

function in MATLAB (2020). This non-parametric test is ideal for comparing distributions without making assumptions about their shape or parameters.

The carbon usage rate (CUR) indicates how much carbon is needed to remove a compound or group of compounds by a certain percentage from a given liquid volume, expressed in [mg L^{-1}]. For PAC, the term for the carbon usage rate is the same as for the dosage. Rearranging Eq. (4), the CUR for PAC was calculated according to Eq. (6).

$$\frac{m_{PAC}}{V_{urine}} = A^n \left(\frac{C_{ref}}{C} - 1\right)^n = CUR \left[\frac{mg}{L}\right] \tag{6}$$

For the CUR of GAC the time to breakthrough (t_{bk}) for the removal objective is decisive, hence, the first sampling time when the removal objective was not met anymore, as presented in Eq. (7). Q_{GAC} is the flowrate into the GAC column [L h^{-1}]. If no breakthrough occurred during the duration of the experiment, the duration time of the experiment was used as breakthrough time to evaluate the maximal CUR required, highlighted with dashed bars in Fig. 6.

$$CUR = \frac{m_{GAC}}{Q_{GAC} * t_{bk}} \tag{7}$$

To make the comparison between urine and wastewater, Köpping et al. (2020) introduced the person specific CUR (Eq. (8)). The underlying assumptions are flow rates for wastewater and urine of 350 L p^{-1} d^{-1} (Gujer, 2007) and 1.25 L p^{-1} d^{-1} (Udert et al., 2006), respectively.

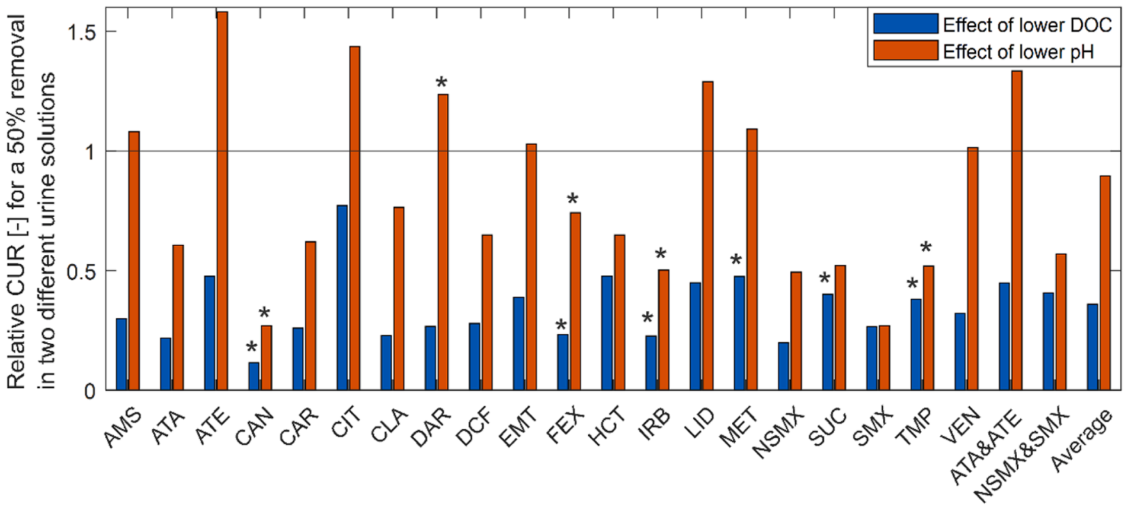

Fig. 3. Results of the experiment *PAC 3: pH and organics*: Effect of different background DOC concentration (190 mg L^{-1} in organics-depleted urine and 108 mg L^{-1} in nitrified urine) and different pH (8.8 and 6.5) on the carbon usage rate (CUR) for a 50 % removal. Blue (dark): CUR ratio for nitrified urine at pH 8.8 relative to the organics-depleted urine at pH 8.8; Red (bright): CUR ratio for organics-depleted urine at pH 6.5 relative to pH 8.8. Bars marked with an asterisk (*) are less reliable because only two points were available for the fitting for at least one of the urine solutions (see Figure S9 and S10). The relative removal as function of the activated carbon concentration is shown in Figure S11 and S12.

$$\text{person specific } CUR = \frac{CUR}{1000} * Q \left[g \cdot p^{-1} \cdot d^{-1}\right] \tag{8}$$

Q is the volumetric flow rate in L p^{-1} d^{-1}. To consider the dilution with water, we multiplied the flow rate of urine by a factor of 2, using 2.5 L p^{-1} d^{-1}. This factor was estimated based on the concentrations of the inert ions chloride, sodium and potassium (see Table 1).

3. Results and discussion

3.1. Removal with PAC does not depend on the initial micropollutant concentration

To evaluate the effect of different initial concentrations, 200 µg L^{-1} and 20 µg L^{-1} of each of the 21 micropollutants were spiked in the same nitrified urine. The measured concentrations in the solution and the calculated loadings on the PAC were fitted with Freundlich isotherms shown in Fig. 1 on top. The isotherms for the low and high initial micropollutant concentrations were significantly different, which was confirmed by the Kolmogorov-Smirnov test resulting in p values of 0.0024 and 0.0003 for all micropollutants and for the example compound IRB, respectively. Nevertheless, the calculated removal efficiencies were very similar (Fig. 1, bottom), which was also confirmed with the Kolmogorov-Smirnov test resulting in p values of 0.994 and 0.976 for all micropollutants and for IRB, respectively (Fig. 1, middle). The fitted parameters and the goodness of fit are shown in Table S9 and S10, the curves for all substances are shown in Figure S4 to S6 and the statistics are given in Table S11.

The data in Fig. 1 show that the removal of micropollutants was independent of the initial concentration. Freundlich isotherms would be independent of initial micropollutant concentration without the presence of competing background organics. However, Freundlich isotherm parameters are different, when the initial concentrations of micropollutants differ because the background organics affect the micropollutant load (q) more at lower initial micropollutant concentrations (Crittenden et al., 2012). The SEBCM parameters however, did not change. This is due to the much higher concentrations of background organics compared to the micropollutant concentrations. Similar effects have been reported for water with considerably lower organic contents and lower micropollutant concentrations, i.e. for drinking water (Newcombe et al., 2002a), lake water (Gillogly et al., 1998), groundwater (Knappe et al., 1998) and wastewater (Zietzschmann et al., 2016). From an operational point of view, this finding is highly relevant because micropollutants often occur as shock-loads. For instance, the usage of a pharmaceutical by one patient can result in high concentrations in a urine collection tank with few users connected. Even if the concentrations suddenly increase, the removal efficiency is unlikely to decrease, if the concentration of the background organics does not change considerably. In the equation for SEBCM (Eq. (4)), a change of the background organics would affect parameter A.

3.2. Removal of micropollutants is higher in nitrified urine compared to anaerobically stored urine and organics-depleted urine

Removal of micropollutants with PAC in anaerobically stored urine and organics-depleted urine was very similar despite the strong difference in the initial organics concentration of 2670 mg L^{-1} and 284 mg L^{-1}, respectively (from experiment *PAC 2: urine solutions*, see Fig. 2). The fitted removal with SEBCM shown in Fig. 2 (with the linear fit shown in Figure S8 with the goodness of fit in Tables S12 to S14) confirms the finding. The very small effect of the organics is due to the fact that mainly non-adsorbing LMW organics were removed during organics-depletion as shown by Heusser et al. (2023). However, in nitrified urine with only about 60 % less organics (116 mg L^{-1}) and a lower pH (pH 6.5 instead of 9), micropollutant adsorption on PAC was substantially higher than for the other two urine solutions for all micropollutants. CAN and CLA were the least adsorbing substances in all urine solutions but in nitrified urine complete removal was possible with PAC concentrations of 2000 mg L^{-1}. It should be noted that the results of the chemical analysis of CLA was rather uncertain compared to all other compounds, which is shown by the higher analytical uncertainty (see discussion in S5, SI1) and low comparability to the results from *PAC 3: pH and organics* (see Figure S12). Generally, better removal in nitrified urine was most pronounced for weakly adsorbing substances such as CAN, CLA, DCF and SUC (Figs. 2 and 6). Wang et al. (2021) also found that weakly adsorbing substances experience more competition with organics. The much better sorption in nitrified urine compared to organics-depleted urine can be caused by different parameters: by the lower DOC, by different matrix constituents, or by the lower pH after nitrification. This will be discussed in more detail in the following chapters.

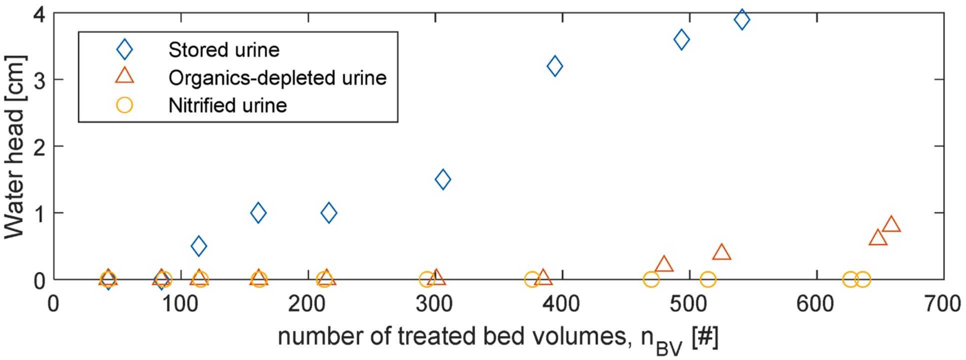

Fig. 4. Pressure increase measured as water head over the GAC in the filter. Anaerobically stored, organics-depleted and nitrified urine was fed unfiltered on top of the GAC and infiltrated gravimetrically.

3.3. Micropollutant adsorption in nitrified urine is more efficient due to further degradation of organics

By using organics-depleted urine and nitrified urine with adjusted pH values in experiment *PAC 3: pH and organics*, we could determine whether the lower pH value or the lower content of organics in nitrified urine was the reason for the better adsorption. The amount of PAC (mg/L), also called carbon usage rate (CUR), needed for a 50 % removal of each substance was taken from the SEBCM fit (Figure S11 and S12). In the two experiments with pH 8.8 (where the pH of nitrified urine was adjusted), the CUR for a 50 % removal was lower in nitrified urine than in organics-depleted urine for all micropollutants (blue (dark) columns in Fig. 3 and the values in SI2). This shows that the further DOC removal and not the pH decrease was the main factor leading to a lower CUR in nitrified urine. The underlying micropollutant removal curves of the individual urine solutions at different pH and DOC concentrations are shown in Figure S11 and S12. In the nitrification step, the organics concentration was reduced by about 50 % compared to the organics-depleted urine (Table 1). These organics competed for adsorption, as opposed to the special case of the easily biodegradable organics which were removed in organics-depleted urine. In a previous study, we could show that the easily biodegradable LMW organics, such as acetate and propionate, which make up for most of the easily biodegradable organics in anaerobically stored urine, hardly compete with micropollutants for adsorption (Heusser et al., 2023). However, the remaining LMW organics in organics-depleted urine competed with the micropollutants for sorption. In the nitrification, the LMW organics were degraded by 70 % (see Table S17), resulting in lower competition. The same was shown in publications for different waters where the fraction of LMW organics was found to be the main competitor for adsorption of micropollutants (Newcombe et al., 2002b; Velten et al., 2011; Zietzschmann et al., 2014). Size exclusion chromatograms showed that in nitrified urine about 90 % of the LMW organics are removed by adsorption, while only about 60 % of the DOC was removed. Details on the chromatograms can be found in section S8. Apart from the lower CUR, a further advantage of nitrification is that it can already degrade more micropollutants than the organics degradation alone. An example is the artificial sweetener ACS. In the samples taken of the urine treatment chain, ACS was always present in anaerobically stored and organics-depleted urine at concentrations greater than 2000 μg L^{-1} on all days of measurement and below the LOQ in nitrified urine (Table S1), thus, ACS was degraded during nitrification, as has been also shown during wastewater treatment (Achermann et al., 2018; Bourgin et al., 2018). It can be expected that microbial communities are different in nitrified urine and in organics-depleted urine, leading to a better biodegradation in nitrification, as has been shown for wastewater (Clara et al., 2005; Ternes and Joss, 2007).

3.4. The effect of pH on micropollutant adsorption is substance specific

By adjusting the pH in the organics-depleted urine from 8.8 to 6.5, the pH effect on single micropollutant removal could be determined. The results of our experiment (red (bright) columns in Fig. 3) show that the pH effect on adsorption was substance-specific. Most micropollutants showed a lower CUR for a 50 % removal at the lower pH, a few substances showed a higher CUR and a few micropollutants were hardly affected. The change in pH affects the properties of the activated carbon such as its surface charge (Moreno-Castilla, 2004) as well as the properties of the micropollutants such as the speciation and therewith the tendency for electrostatic interactions (De Ridder et al., 2010; Kah et al., 2017). The point of zero charge of the carbon is 8.6, therefore, lowering the pH of the solution from 8.8 to 6.5 generally decreased the CUR of negatively charged micropollutants and increased the CUR of positively micropollutants as the carbon surface became positively charged. One of the strongest effect of lowering the pH from 8.8 to 6.5 was observed for CIT, needing 1.4 times more carbon to be removed from urine at pH 6.5. CIT has the highest pK_a (Table 2) and is positively charged at both pH, but lowering the pH increased the CUR because the carbon became more positively charged. This holds true for most positively charged micropollutants (see Figure S14). CAN, on the other side, needed about four times less carbon when removed from urine with a lower pH. CAN is negatively charged at both pH and has the lowest pK_a (Table 2). Lowering the pH decreased the CUR for all negatively charged micropollutants (see Figure S15). Most micropollutants that are neutral or zwitterions were unaffected by the pH change (Figure S16 and S17). From this analysis it can be concluded that the lower pH in nitrified urine showed an effect on the CUR of individual micropollutants but was not the reason for the overall lower CUR of nitrified urine compared to organics-depleted urine. Apart from the concentration of organics and the pH, also the speciation of nitrogen changes during nitrification. As already shown by Köpping et al. (2020), nitrate and ammonium did not adsorb on activated carbon. Therefore, these two compounds did not contribute to the difference in adsorption in organics-depleted urine and nitrified urine, shown for our experiments in Figure S18 to S20.

3.5. Upstream organics removal does not improve adsorption on GAC but has operational advantages

The finding that anaerobically stored urine and organics-depleted urine have the same removal efficiencies with PAC does not mean that both solutions will perform equally well in applications with GAC. In the experiment *GAC: Clogging*, the three urine solutions were dosed to lab-scale GAC columns without previous filtration to elucidate the risk of head loss due to clogging. In the column fed with anaerobically stored urine, urine accumulation above the column was observed after 100 treated empty bed volumes (n_{BV}). Urine accumulation increased strongly during the remaining experiment (Fig. 4). The column fed with

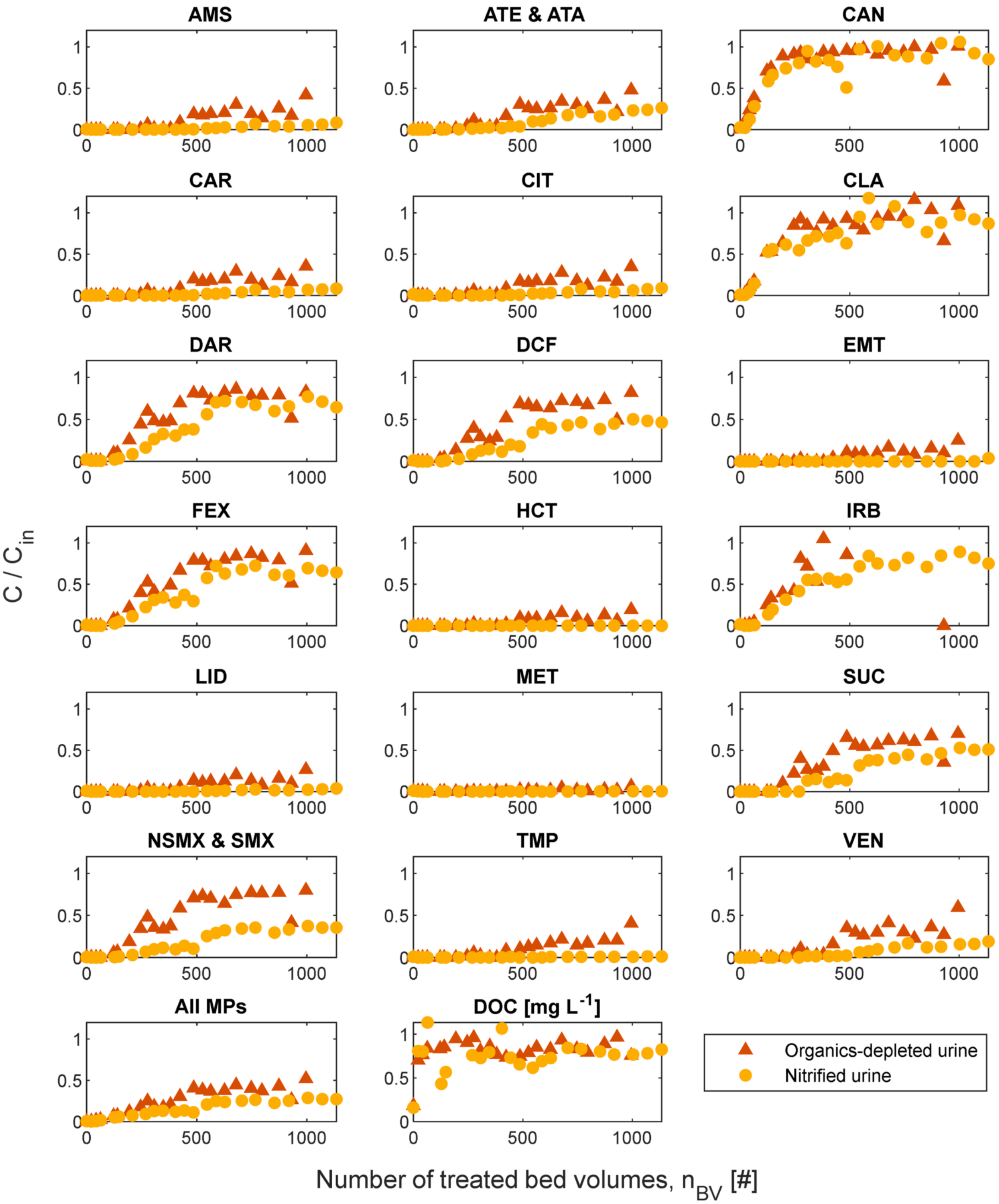

Fig. 5. Results of the experiment *GAC: MPs*: Breakthrough curves of the micropollutants and the DOC in GAC columns operated over 1000 treated bed volumes for organics-depleted urine (DOC: 191 mg L^{-1}, pH 8.8) and nitrified urine (DOC: 90 mg L^{-1}, pH 6.5), both at an EBCT of 70 min.

organics-depleted urine started a urine accumulation much later, i.e. after 480 n$_{BV}$, hence, the upstream organics removal was able to postpone clogging and therewith the time until a backwashing would be needed by almost a factor of five compared to anaerobically stored urine. The GAC column fed with nitrified urine showed no accumulation during the whole duration of the experiment of 640 n$_{BV}$. In Köpping et al. (2020) no backwashing was needed until 1040 n$_{BV}$ with nitrified urine filtered with a 50 μm filter. The fast increase of the water head in the column fed with anaerobically stored urine was most probably due to enhanced bacterial growth in the presence of easily biodegradable organics (Simpson, 2008).

It can be concluded that for robust micropollutant removal in a GAC column without the need for frequent backwashing, at least aerobic degradation of the easily biodegradable organics is necessary. Operation without backwashing is aimed for as it provides an easier setup. To postpone the clogging of the filter, a simple cloth filter could be installed before the GAC column to retain particulate organics, which can cause clogging as e.g. during wastewater treatment (Frank et al., 2015).

3.6. GAC is suitable for micropollutant adsorption from organics-depleted and nitrified urine

The operation of GAC columns fed with filtered organics-depleted and nitrified urine, spiked with micropollutants and operated over

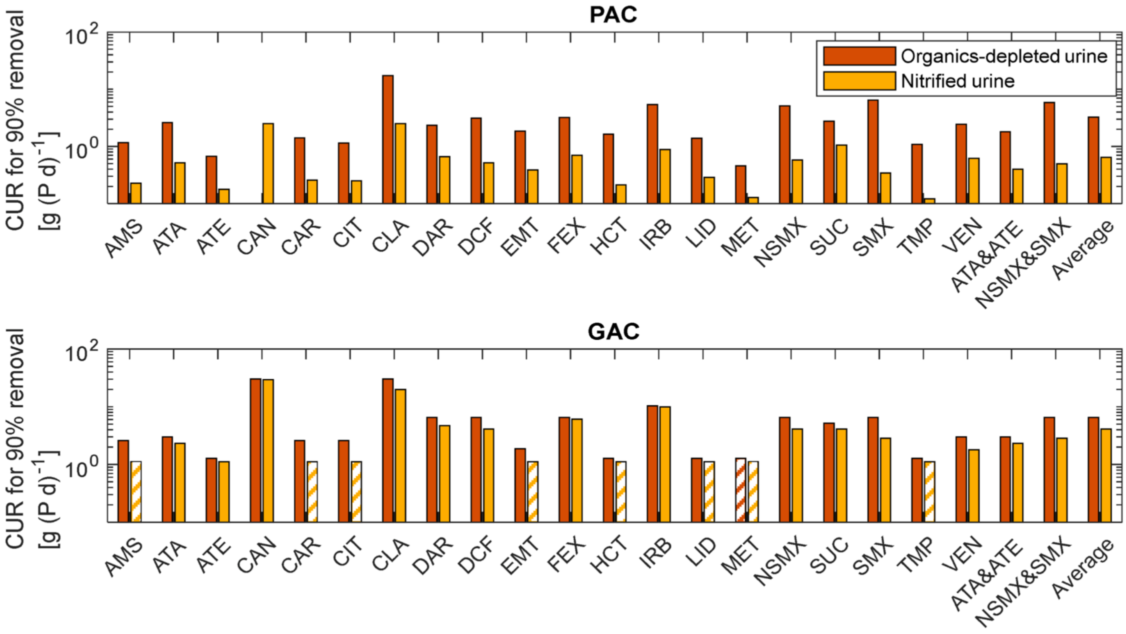

Fig. 6. Carbon usage rate (CUR) for a 90 % removal for *PAC 2: urine solutions* and *GAC: MPs* from organics-depleted urine and nitrified urine. For CAN in organics-depleted urine with PAC, not enough data was available. For the GAC, the micropollutants presented in dashed bars have a CUR < the presented value, as during two month GAC operation the removal never fell below the 90 % removal objective. A boxplot of all micropollutants in different urine solutions compared to wastewater effluent is shown in Figure S24.

approximately 1000 n_{BV} showed that all spiked micropollutants were adsorbed in the GAC column in both urine solutions (Fig. 5). Removal was calculated relative to the influent concentration at each point in time (Figure S21) as for a few substances (CLA, EMT, FEX, HCT, IRB, NSMX&SMX and TMP) some removal in the influent tank was observed (see Figure S22 for the effluent concentrations and Figure S23 for the breakthrough curves relative to the initial concentration). The earliest breakthrough was observed in both urine solutions for CAN (42 n_{BV} and 43 n_{BV}) and CLA (42 n_{BV} and 64 n_{BV}) (Fig. 5), which were also the weakest adsorbing substances in the PAC experiments (Fig. 2). During the two month, no breakthrough was observed in organics-depleted urine (995 n_{BV}) for MET and no breakthrough was observed in nitrified urine (1134 n_{BV}) for AMS, CAR, CIT, EMT, HCT, LID, MET and TMP. The columns did not face blockage due to clogging during the two months, however, the pumps, feeding the columns at the bottom, were calibrated and adapted to keep the flow constant, increasing the pressure over time.

3.7. Nitrified urine has the lowest carbon usage rate with PAC and GAC

For a comparison of the activated carbon demand in organics-depleted urine and nitrified urine, the CUR for a 90 % removal per person was calculated (see Eq. (8)). The removal objective for micropollutants in Swiss wastewater treatment is 80 % (Bourgin et al., 2018; Confederation, 2016), but for fertilizer production a more stringent objective (90 %) was chosen. For the different urine solutions, the CUR shown in Fig. 6 confirmed the finding that organics-depleted urine required more carbon than nitrified urine for all micropollutants when treated with PAC or GAC. Figure S25 further confirmed that the CUR for anaerobically stored and organics-depleted urine were similar in *PAC 2: urine solutions*.

In the experiment *PAC 2: urine solutions* the CUR for organics-depleted urine was 3 to 19 times higher than the CUR for nitrified urine. The CURs for organics-depleted urine in the experiment *PAC 3: pH and organics,* shown in Figure S26, were lower than in the experiment *PAC 2: urine solutions* because the organics concentration was lower (Table 1). Hence, the performance of the organics degradation affects the subsequent CUR, and as more organics are removed, the CUR for organics-depleted urine becomes more similar to the CUR of nitrified urine. The CURs for nitrified urine were similar in *PAC 2* and *PAC 3* as shown in Figure S26, the two solutions had similar organics concentrations with 116 mg L^{-1} and 108 mg L^{-1}. Özel Duygan et al. (2021) performed PAC experiments with nitrified urine with 62 to 100 mg L^{-1} DOC and found CURs in the same range as our experiments despite using a different PAC as shown in Figure S27.

The data collected with the GAC columns show the same conclusion, that organics-depleted urine requires overall more carbon, but the difference is substantially smaller than for PAC (Fig. 6). In the GAC experiments, the inflow was filtered with 25 µm instead of 0.45 µm as in the PAC experiments. This might have affected the micropollutant removal as colloids might have sorbed and competed with sorption. In general, the flow regime, GAC particle size and other column specific factors might have influenced the micropollutant removal, highlighting the importance of design. Furthermore, biodegradation in the GAC filters might be different in the two urine solutions. The results of Köpping et al. (2020) for adsorption of 11 micropollutants in nitrified urine with 103 mg L^{-1} DOC on the same GAC material but different particle sizes fed top down showed the same order of micropollutant breakthroughs. However, they observed better adsorption for weakly-adsorbing substances such as CAN and CLA and worse adsorption for well adsorbing substances such as HCT and MET compared to our results for which the reason is unclear. All the CURs are shown in Table S18.

It has been shown before that less carbon is required per person to remove micropollutants from nitrified urine compared to biologically treated municipal wastewater with PAC (Özel Duygan et al., 2021) and GAC (Köpping et al., 2020). The CUR for 90 % removal from nitrified wastewater with GAC in Joss et al. (2024, in preperation), compiled by Köpping et al. (2020), ranges from 6 g $(p\ d)^{-1}$ for HCT and MET to 147 g $(p\ d)^{-1}$ for CAN, and the CUR for nitrified urine with GAC was 2 (CLA) to 18 (SMX) times lower. The CUR for organics-depleted urine with GAC was 4 to 9 times lower for all substances except CLA, which had a similar CUR as wastewater (Table S18). The greatest difference in CUR we observed for DCF, with a 9 times higher CUR in nitrified wastewater compared to organics-depleted urine. The results are shown as boxplots for all micropollutants in Figure S24 and visualize nicely that adsorption of micropollutants from all urine solutions clearly requires less carbon per person than adsorption from wastewater effluent.

4. Conclusions

- The carbon usage rate for removing micropollutants is similar for anaerobically stored urine and organics-depleted urine, but considerably lower for nitrified urine.
- Nitrification of urine improves the adsorption of micropollutants on activated carbon due to the degradation of LMW organics, which compete with micropollutants for adsorption.
- The lower pH value after nitrification causes a higher adsorption of some micropollutants, but the main reason for better micropollutant removal is the reduced competition by LMW organics.
- Treating anaerobically stored urine directly in a GAC column, without pre-filtration or regular backwashing, causes quick filter clogging. Biological degradation of the easily biodegradable organics can mitigate clogging.
- The removal of micropollutants from a certain urine matrix is independent of the initial micropollutant concentration, because competition is determined by the high concentration of background organics.
- The carbon usage rate per person and day for all urine solutions is lower than for biologically treated municipal wastewater, showing that urine treatment at the source is an economic solution.
- For micropollutant removal from source-separated urine, the maintenance and energy intensive nitrification can be omitted, but with the drawback of a higher carbon usage. Only degradation of easily biodegradable organics is needed to prevent rapid GAC filter clogging.

CRediT authorship contribution statement

Aurea Heusser: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Writing – original draft, Writing – review & editing. **Anne Dax:** Data curation, Methodology, Validation, Writing – review & editing. **Christa S. McArdell:** Conceptualization, Methodology, Supervision, Validation, Writing – review & editing. **Kai M. Udert:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Kai M. Udert reports a relationship with VunaNexus that includes: board membership and travel reimbursement. Aurea Heusser and Kai M. Udert have a patent pending to Eawag. The patent includes the separate removal of organics from source-separated urine but is only marginally relevant for the publication. The other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data are provided in the supplementary information.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2024.121615.

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